

LIBRARY

Michigan State University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
NOV 02 2002	_____	_____
SEP 25 2002 192	_____	_____
MAY 28 2009	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

MSU is An Affirmative Action/Equal Opportunity Institution

ct:ctrc/datedue.pm3-p.1

CONTR
US

in p

De

**CONTROLLED SYNTHESIS OF DIAMOND FILMS
USING A MICROWAVE DISCHARGE
(NON-EQUILIBRIUM PLASMA)**

By

Saeid Khatami

Volume 1

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Electrical Engineering

1997

CON

The M.S.
experimentally c
tion. The many c
were divided into
dependent interna
 $X = f(U)$ and $Y =$
displaying the outp
growth parameter
consisting of linear
multi-dimensional
particularly film m
substrate temperat
deposition time (t)
films with high str

ABSTRACT

CONTROLLED SYNTHESIS OF DIAMOND FILMS USING A MICROWAVE DISCHARGE (NON-EQUILIBRIUM PLASMA)

By

Saeid Khatami

The M.S.U. designed microwave plasma diamond thin film reactor was experimentally characterized in the non-equilibrium discharge pressure regime of 20 - 80 torr. The many different experimental variables associated with the microwave reactor were divided into three groups: (i) independently controllable input variables (U), (ii) dependent internal variables X , and (3) output variables $Y = [Y_1, Y_2]$, where in general $X = f(U)$ and $Y = g(U, X)$. Deposition maps were constructed from the empirical data displaying the output film properties Y_1 consisting of morphology as expressed by the growth parameter α and structural quality, and reactor performance variables Y_2 consisting of linear growth rate, carbon conversion efficiency, and specific yield vs. the multi-dimensional experimental input variable space. It is shown that the output variables, particularly film morphology as described by α , are not only functions of CH_4/H_2 and substrate temperature (T_s) but are also sensitive functions of the total gas flow rate (f_t), deposition time (t), and reactor geometry (U_2). Typically twin free well-faceted {100} films with high structural quality ($FWHM \cong 7 \text{ cm}^{-1}$) were deposited in intermediate

substrate temper

-20°C, and low

broader methane

regimes (i.e., T_s =

a two-step grow

initial deposition

occurred when

morphology). The

deposit diamond

substrate temperature, $T_s = 700 - 850\text{ }^{\circ}\text{C}$, methane concentration range of $\text{CH}_4/\text{H}_2 = 1.0\%$ - 2.0% , and low flow rates. High quality films with $\{111\}$ facets were grown typically in a broader methane concentration and flow rate ranges but mostly at higher temperature regimes (i.e., $T_s = 900 - 1000\text{ }^{\circ}\text{C}$). Film morphology varied with deposition time. Through a two-step growth process which included varying the methane concentration after an initial deposition period, the original film morphology was preserved. High growth rates occurred when $\alpha \cong 3$ which corresponds to octahedron crystal habit with $\{111\}$ morphology). The experimental results achieved in this dissertation have enabled us to deposit diamond films with desired pre-determined characteristics.

Copyright by
SAEID KHATAMI
1997

The author
and support thro
Dr. Timothy Gro
serving on my co
for their valuable

This research
Fund and the NSF

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Jes Asmussen, Jr. for his guidance, encouragement, and support throughout this research. Special thanks is extended to Dr. Donnie Reinhard, Dr. Timothy Grotjohn, Dr. Brage Golding, Dr. John Mcgrath, and Dr. Eldon Case for serving on my committee. The author also wishes to thank K. P. Kuo and Jorg Mossbrucker for their valuable assistance and discussions.

This research was supported in part by the State of Michigan Research Excellence Fund and the NSF MRSEC/Center for Sensor Materials.

List of Tables.....

List of Figures.....

1.1 Diamond.....

1.2 A brief history.....

1.3 A generic block.....

1.4 Motivation.....

1.5 Objectives of the.....

1.6 Dissertation outline.....

2.1 Introduction.....

2.2 Microwave plasma.....

2.3 Bell-jar microwave.....

2.4 Microwave jet reactor.....

2.5 Hot filament reactor.....

2.6 Microwave cavity.....

2.6.1 Basic design.....

2.6.2 Approximate.....

electromagnetic.....

2.7 Examples of various.....

2.8 A common feature.....

Literature.....

3.1 Introduction.....

3.2 Textures and morphology.....

3.3 Reactor output variables.....

3.3.1 Film production.....

3.3.1.1 Nitrogen.....

3.3.1.2 Hydrogen.....

3.3.1.3 Silicon.....

3.3.2 Reactor.....

TABLE OF CONTENTS

List of Tables.....	xii
---------------------	-----

List of Figures	xiv
-----------------------	-----

CHAPTER 1

Introduction

1.1 Diamond.....	1
1.2 A brief history of CVD diamond synthesis.....	3
1.3 A generic block diagram representation of diamond deposition reactors.....	13
1.4 Motivation.....	17
1.5 Objectives of the research	18
1.6 Dissertation outline	19

CHAPTER 2

A Review of Deposition Reactors

2.1 Introduction.....	21
2.2 Microwave plasma tubular reactor	22
2.3 Bell-jar microwave reactor.....	23
2.4 Microwave jet reactor	26
2.5 Hot filament reactor (HFCVD)	26
2.6 Microwave cavity plasma reactor (MCPR).....	29
2.6.1 Basic description of the reactor.....	29
2.6.2 Approximate determination of the empty cavity electromagnetic modes.....	33
2.7 Examples of various reactors' film characteristics	39
2.8 A common feature among various diamond CVD reactors.....	39

CHAPTER 3

Literature Review on Film Properties vs. Deposition Conditions

3.1 Introduction.....	46
3.2 Textures and morphologies of CVD diamond films	46
3.3 Reactor output variables $Y = [Y_1, Y_2]$ vs. deposition conditions	50
3.3.1 Film properties (Y_1) vs. deposition conditions	50
3.3.1.1 Morphology.....	50
3.3.1.2 Film morphology vs. deposition condition	50
3.3.1.3 Structural quality vs. deposition condition	61
3.3.2 Reactor performance (Y_2) vs. deposition conditions.....	63

3.3.2.1	0
3.3.3	Conclusions
3.4	Structural defects
3.4.1	Dislocations
3.4.2	Stacking faults
3.4.3	Intrinsic defects
3.4.4	Twinning
3.4.5	Dislocations
3.5	Surface reconstruction
3.5.1	Periodic structures
3.5.2	F-like structures
3.5.3	The origin of surface reconstruction
3.5.4	Growth of surface reconstruction

Experimental Section

4.1	Introduction
4.2	Experimental system
	deposition machine
4.2.1	Vacuum chamber
4.2.2	Microcomputer control system
4.2.3	Computer control system
4.2.4	Microcomputer control system
4.2.5	Repeatability
4.3	Experimental procedure
4.3.1	Substrate preparation
4.3.2	Reaction conditions
4.3.3	Quenching
4.4	Experimental results
4.5	Measurement and analysis
4.5.1	Surface morphology
4.5.2	Average surface roughness
4.5.3	Structural analysis
4.5.3.1	Structure analysis
4.5.4	Film thickness
4.5.5	Carbon content
4.5.6	Gas permeability
4.5.7	Substrate adhesion

References

5.1	Introduction
5.2	Film deposition

3.3.2.1 Growth rate vs. deposition condition	63
3.3.3 Concluding remarks	65
3.4 Structural defects	68
3.4.1 Dislocations.....	69
3.4.2 Stacking faults in an f.c.c. lattice	73
3.4.3 Intrinsic and extrinsic stacking faults in an f.c.c. lattice	82
3.4.4 Twinning in an f.c.c. lattice	82
3.4.5 Dislocations, stacking faults, and twinning in diamond structure	86
3.5 Surface reconstruction in CVD crystals.....	88
3.5.1 Periodic bond chain theory and surface reconstruction in crystals.....	88
3.5.2 F-like behavior due to surface reconstruction	92
3.5.3 The orientation of growth steps on reconstructed {001} faces	95
3.5.4 Growth steps and reconstruction on {111} planes	97

CHAPTER 4

Experimental System, Experimental Procedures, Experimental Parameter Space and Measurement Methodologies

4.1 Introduction	104
4.2 Experimental system: Michigan State University microwave plasma deposition machine	104
4.2.1 Vacuum pump and the gas flow control system.....	106
4.2.2 Microwave power supply and microwave waveguide/transmission system	108
4.2.3 Computer controller	108
4.2.4 Microwave cavity plasma reactor (MCPR) general operational performance	109
4.2.5 Repeatability of the diamond CVD experiments	115
4.3 Experimental procedures	118
4.3.1 Substrate seeding and seeding density	118
4.3.2 Reactor start-up and shut-down procedures.....	119
4.3.3 Quartz dome cleaning	120
4.4 Experimental parameter space	120
4.5 Measurement Methodologies.....	121
4.5.1 Surface morphology analysis.....	121
4.5.2 Average grain size.....	122
4.5.3 Structural quality analysis.....	123
4.5.3.1 The Raman effect.....	123
4.5.4 Film linear growth rate.....	127
4.5.5 Carbon conversion efficiency.....	127
4.5.6 Gas residence time.....	128
4.5.7 Substrate temperature.....	128

CHAPTER 5

Reactor Field Map: 5" Quartz Dome/3" Substrate Reactor

5.1 Introduction.....	130
5.2 Film deposition vs. input and internal variables for a fixed deposition time	

of eight hours ...

5.2.1 Film p

5.2.1.1

5.2.1.2

5.2.2 React

5.2.2.1

5.2.2.2

5.3 Effect of depos

5.3.1 Film p

5.3.1.1

5.3.1.2

5.3.2 Reacto

5.3.2.1

5.3.2.2

5.4 Summary of the
deposition time

5.4.1 Film p

5.4.1.1

5.4.1.2

5.4.2 Reacto

5.4.2.1

5.4.2.2

of eight hours	140
5.2.1 Film properties (Y_1) vs. various input variables	140
5.2.1.1 Morphology and grain size	140
5.2.1.1.1 Total gas flow rate, $f_t = 400$ sccm	140
5.2.1.1.2 Total gas flow rate, $f_t = 200$ sccm	157
5.2.1.1.3 Total gas flow rate, $f_t = 100$ sccm	170
5.2.1.1.4 Total gas flow rate, $f_t = 60$ sccm	175
5.2.1.1.5 Total gas flow rate, $f_t = 30$ sccm	190
5.2.1.2 Structural quality.....	196
5.2.1.2.1 Total gas flow rate, $f_t = 400$ sccm	196
5.2.1.2.2 Total gas flow rate, $f_t = 200$ sccm	210
5.2.1.2.3 Total gas flow rate, $f_t = 100$ sccm	218
5.2.1.2.4 Total gas flow rate, $f_t = 60$ sccm	219
5.2.1.2.5 Total gas flow rate, $f_t = 30$ sccm	228
5.2.2 Reactor performance (Y_2) vs. various input variables	229
5.2.2.1 Linear growth rate	229
5.2.2.1.1 Total gas flow rate, $f_t = 400$ sccm	229
5.2.2.1.2 Total gas flow rate, $f_t = 200$ sccm	231
5.2.2.1.3 Total gas flow rate, $f_t = 100$ sccm	231
5.2.2.1.4 Total gas flow rate, $f_t = 60$ sccm	234
5.2.2.1.5 Total gas flow rate, $f_t = 30$ sccm	234
5.2.2.2 Carbon conversion efficiency	237
5.2.2.2.1 Total gas flow rate, $f_t = 400$ sccm	237
5.2.2.2.2 Total gas flow rate, $f_t = 200$ sccm	239
5.2.2.2.3 Total gas flow rate, $f_t = 100$ sccm	239
5.2.2.2.4 Total gas flow rate, $f_t = 60$ sccm	242
5.2.2.2.5 Total gas flow rate, $f_t = 30$ sccm.....	242
5.3 Effect of deposition time on output variables (Y).....	246
5.3.1 Film properties (Y_1) vs. deposition time	246
5.3.1.1 Film morphology	246
5.3.1.2 Structural quality.....	256
5.3.2 Reactor performance (Y_2) vs. deposition time	266
5.3.2.1 Linear growth rate	266
5.3.2.2 Carbon conversion efficiency	266
5.4 Summary of the effect of total gas flow rate on output variables for a fixed deposition time of eight hours.....	269
5.4.1 Film properties (Y_1) vs. total gas flow rate	269
5.4.1.1 Film morphology	269
5.4.1.2 Structural quality.....	276
5.4.2 Reactor performance (Y_2) vs. total gas flow rate.....	276
5.4.2.1 Linear growth rate	276
5.4.2.2 Carbon conversion efficiency	276

5.5 Relationship be

5.5.1 Relat

5.5.1

5.5.2 Relat

variab

5.5.2

5.5.2

5.6 Discussion.....

5.6.1 Outpu

(fixed

5.6.1

5.6.1.2

5.6.2 Outpu

5.6.2

5.6.2

5.6.3 Outpu

5.6.3

5.6.3

5.7 Summary.....

Reactor

6.1 Introduction.....

6.2 Film deposition

6.2.1 Film

5.5 Relationship between output variables	281
5.5.1 Relationships between film properties ($Y_{1i} \leftrightarrow Y_{1j}$)	281
5.5.1.1 Relationship between film morphology and structural quality	281
5.5.2 Relationship between film properties and reactor performance variables ($Y_1 \leftrightarrow Y_2$)	282
5.5.2.1 Relationship between film morphology (Y_1) and linear growth rate (Y_2)	282
5.5.2.2 Relationship between film morphology (Y_1) and carbon conversion efficiency (Y_2)	282
5.6 Discussion	283
5.6.1 Output variables (Y) vs. gas chemistry and substrate temperature (fixed flow rate)	283
5.6.1.1 Diamond film properties (Y_1) vs. gas chemistry and substrate temperature	283
5.6.1.1.1 Morphology vs. substrate temperature and CH_4/H_2	283
5.6.1.1.2 Structural quality of the diamond films	284
5.6.1.1.2.1 Structural quality vs. CH_4/H_2	284
5.6.1.1.2.2 Structural quality vs. T_s	285
5.6.1.2 Reactor performance (Y_2) vs. gas chemistry and substrate temperature	286
5.6.1.2.1 Linear growth rate vs. CH_4/H_2	286
5.6.1.2.2 Linear growth rate vs. substrate temperature, T_s	286
5.6.2 Output variables (Y) vs. deposition time (fixed flow rate)	287
5.6.2.1 Diamond film properties (Y_1) vs. deposition time	287
5.6.2.1.1 Film morphology vs. deposition time	287
5.6.2.1.2 Structural quality vs. deposition time	290
5.6.2.2 Reactor performance (Y_2) vs. deposition time (fixed flow rate)	290
5.6.2.2.1 Linear growth rate vs. deposition time	290
5.6.3 Output variables (Y) vs. total gas flow rate	290
5.6.3.1 Film properties (Y_1) vs. total gas flow rate	290
5.6.3.1.1 Film morphology vs. total gas flow rate	290
5.6.3.1.2 Structural quality vs. total gas flow rate	292
5.6.3.2 Reactor performance (Y_2) vs. total gas flow rate	292
5.6.3.2.1 Linear growth rate vs. total gas flow rate	292
5.6.3.2.2 Carbon conversion efficiency vs. total gas flow rate	292
5.7 Summary	293

CHAPTER 6

Reactor Field Map: 4" Quartz Dome/2" Substrate Reactor Geometry Configuration

6.1 Introduction	298
6.2 Film deposition vs. input and internal Variables	311
6.2.1 Film properties (Y_1) vs. various input variables	311

6.2.1

6.2.1

6.2.2 React

6.2.2

6.2.2

6.3 Summary of the

6.3.1 Film p

6.3.1.

6.3.1.

6.3.2 React

6.3.2

6.3.2

6.4 Comparison be

5" quartz dome

geometries.....

6.4.1 Diarr

6.4.1.

6.4.1.

6.4.2 React

6.4.2

6.4.2

6.4.2

6.5 Discussion.....

6.6 Summary.....

7.1 Introduction.....

7.2 CO₂-H₂ Film de

time of eight ho

7.2.1 Film p

6.2.1.1 Morphology and grain size	311
6.2.1.1.1 Total gas flow rate, $f_t = 400$ sccm	311
6.2.1.1.2 Total gas flow rate, $f_t = 200$ sccm	326
6.2.1.1.3 Total gas flow rate, $f_t = 60$ sccm	336
6.2.1.2 Structural quality.....	351
6.2.1.2.1 Total gas flow rate, $f_t = 400$ sccm	351
6.2.1.2.2 Total gas flow rate, $f_t = 200$ sccm	358
6.2.1.2.3 Total gas flow rate, $f_t = 60$ sccm	365
6.2.2 Reactor performance (Y_2) vs. various input variables	371
6.2.2.1 Linear growth rate.....	371
6.2.2.1.1 Total gas flow rate, $f_t = 400$ sccm	371
6.2.2.1.2 Total gas flow rate, $f_t = 200$ sccm	371
6.2.2.1.3 Total gas flow rate, $f_t = 60$ sccm	373
6.2.2.2 Carbon conversion efficiency.....	376
6.2.2.2.1 Total gas flow rate, $f_t = 400$ sccm	376
6.2.2.2.2 Total gas flow rate, $f_t = 200$ sccm	376
6.2.2.2.3 Total gas flow rate, $f_t = 60$ sccm	379
6.3 Summary of the effect of total gas flow rate on output variables	379
6.3.1 Film properties (Y_1) vs. total gas flow rate.....	379
6.3.1.1 Film morphology	379
6.3.1.2 Structural quality.....	380
6.3.2 Reactor performance (Y_2) vs. total gas flow rate.....	387
6.3.2.1 Linear growth rate.....	387
6.3.2.2 Carbon conversion efficiency.....	388
6.4 Comparison between the output variables ($Y = [Y_1, Y_2]$) of the 5"quartz dome/3" substrate and the 4" quartz dome/2" substrate reactor geometries.....	389
6.4.1 Diamond film properties (Y_1).....	389
6.4.1.1 Film morphology	389
6.4.1.2 Structural quality.....	395
6.4.2 Reactor performance (Y_2).....	396
6.4.2.1 Linear growth rate, d.....	396
6.4.2.2 Carbon conversion efficiency.....	397
6.4.2.3 Specific yield (KW-hr/g).....	397
6.5 Discussion.....	403
6.6 Summary	403

CHAPTER 7

Diamond CVD with Carbon Monoxide

7.1 Introduction.....	408
7.2 CO-H ₂ Film deposition vs. input and internal variables for a fixed deposition time of eight hours	418
7.2.1 Film properties (Y_1) vs. CO/H ₂ and pressure	418

7.2.1
7.2.1
7.2.2 React
7.2.2
7.2.2
7.3 Discussion ...
7.3.1 Outp
7.3.1

7.3.1

Microwave P
8.1 Introduction
8.2 Experimental ...
8.2.1 Diarn
8.2.2 Diarn
8.3 Results and disc
8.3.1 Diarn
8.3.2 Film p

9.1 Summary of th
9.2 Recommendati

REFERENCES

7.2.1.1 Morphology and grain size	418
7.2.1.2 Structural quality	423
7.2.2 Reactor performance (Y_2) vs. CO/H ₂ and pressure	428
7.2.2.1 Linear growth rate	428
7.2.2.2 Carbon conversion efficiency	428
7.3 Discussion	431
7.3.1 Output variables (Y) vs. CO/H ₂ chemistry and pressure	431
7.3.1.1 Diamond film properties (Y_1) vs. CO/H ₂ and pressure	431
7.3.1.1.1 Morphology vs. CO/H ₂ and pressure	431
7.3.1.1.2 Structural quality vs. CO/H ₂ and pressure	431
7.3.1.2 Reactor performance (Y_2) vs. CO/H ₂ and pressure	432
7.3.1.2.1 Growth rate vs. CO/H ₂ and pressure	432

CHAPTER 8

Microwave Plasma Assisted CVD of Diamond Films on Tungsten Substrates

8.1 Introduction	433
8.2 Experimental	435
8.2.1 Diamond deposition on tungsten	435
8.2.2 Diamond film patterning using plasma etch	440
8.3 Results and discussion	449
8.3.1 Diamond deposition on tungsten	449
8.3.2 Film patterning using plasma etch	457

CHAPTER 9

Summary

9.1 Summary of the experimental measurements	460
9.2 Recommendations for future research	470

REFERENCES	471
------------------	-----

Table 1.1 Some

Table 2.1 A s

Table 5.1 Rea

Table 5.2 Max
for

Table 6.1 Rea

Table 6.2 A co
film

Table 6.3 A co
con

Table 6.4 Max
for t

Table 7.1 Rea

Table 8.1 Som

Table 8.2 A co
and
CH₂

Table 9.1 Max
film
dorm

Table 9.2 A co
con

Table 9.3 Rang

LIST OF TABLES

Table 1.1	Some properties of natural and (CVD) diamond	2
Table 2.1	A summary of film characteristics of various reactors	42
Table 5.1	Reactor input/internal/output variables studied in this chapter.....	133
Table 5.2	Maximum growth rate and the corresponding deposition conditions for the total gas flow rate experimentally investigated in Chapter 5.....	296
Table 6.1	Reactor input/internal/output variables studied in this chapter.....	303
Table 6.2	A comparison of the structural qualities (FWHM) of the diamond films synthesized by the two reactor configurations	395
Table 6.3	A comparison of the specific yields associated with the two reactor configurations.....	402
Table 6.4	Maximum growth rate and the corresponding deposition conditions for the total gas flow rate experimentally investigated in Chapter 6.....	406
Table 7.1	Reactor input/internal/output variables for CO-H ₂ diamond film	410
Table 8.1	Some properties of diamond, silicon and tungsten	435
Table 8.2	A comparison of properties of diamond films deposited on silicon and tungsten substrates. Deposition condition: $f_t = 400$ sccm, CH ₄ / H ₂ = 1.50%, and T _s ~ 850°C	451
Table 9.1	Maximum growth rate and the corresponding deposition conditions, film characteristics Y ₁ , and reactor performance Y ₂ for the 5" quartz dome/3" substrate reactor configuration	461
Table 9.2	A comparison of the specific yields associated with the two reactor configurations.....	468
Table 9.3	Ranges and ratios of the normalized performance variables associated	

with the two reactor geometries	469
---------------------------------------	-----

Figure 1.1 Gra

Figure 1.2 Dia

Figure 1.3 Pha

Figure 1.4 Carh
corre

Figure 1.5 Gen
reac

Figure 1.6 Sch
diam

Figure 1.7 A g

Figure 2.1 Sch

Figure 2.2 Sch

Figure 2.3 Sch

Figure 2.4 Sch

Figure 2.5 MC

Figure 2.6 Flo

Figure 2.7 An

Figure 2.8 Mo

Figure 2.9 Fie

Figure 2.10 Line
vs. g

LIST OF FIGURES

Figure 1.1	Graphite lattice structure.	4
Figure 1.2	Diamond lattice structure.	4
Figure 1.3	Phase diagram of carbon [3].	5
Figure 1.4	Carbon phase diagram with temperature and pressure ranges corresponding to various diamond synthesis processes ([3], [10]).	7
Figure 1.5	Generalized schematic of the chemical processes in a CVD diamond reactor ([1], [13]).	11
Figure 1.6	Schematic of the major elements of gas phase reactions in CVD diamond ([3], [12]).	12
Figure 1.7	A generic block diagram for deposition reactors.	16
Figure 2.1	Schematic drawing of a tube-style microwave plasma CVD reactor [1].	24
Figure 2.2	Schematic drawing of microwave Bell-Jar reactor ([1], [14]).	25
Figure 2.3	Schematic drawing of microwave jet reactor ([14], [15]).	27
Figure 2.4	Schematic drawing of a Hot filament CVD reactor ([1], [14]).	30
Figure 2.5	MCPR-3 reactor under forced flow configuration.	32
Figure 2.6	Flow pattern regulator (4) with substrate (11) [14].	34
Figure 2.7	An empty circular cavity of length L_s and radius a	35
Figure 2.8	Mode diagram of an ideal 7 inch cavity [14].	40
Figure 2.9	Field patterns of discharge loaded TM_{011} and TM_{013} modes [14].	41
Figure 2.10	Linear growth rate (um/hr) for different diamond CVD methods vs. gas temperature in their activation zones [25].	43

Figure 2.11 At
Back

Figure 3.1 The

Figure 3.2 Var

(11)

Figure 3.3 The
temp

Figure 3.4 Gro
and

Figure 3.5 Mor

Figure 3.6 Sche
by Y

Figure 3.7 Cry

Figure 3.8 FWH
by Y

Figure 3.9 The d
ASte

Figure 3.10 Summ
reacto

Figure 3.11 Edge

Figure 3.12 (a) an

Figure 3.13 (a) A

Figure 3.14 (a) A

Figure 3.15 F.c.c.

Figure 3.16 Appea

Figure 3.17 Layer

Figure 3.18 Stack

Figure 2.11	Atomic C-H-O diamond deposition phase diagram developed by Bachmann [25].	45
Figure 3.1	The van der Drift competitive growth model [28].	47
Figure 3.2	Various crystal habits and their corresponding $\alpha = V_{100} / V_{111}$ values ([10], [31], [32]).	49
Figure 3.3	The field map of morphology vs. methane concentration and substrate temperature by Zhu and Stoner [34].	52
Figure 3.4	Growth parameter as a function of: (a) $\text{CH}_4/\text{H}_2\%$ with $T_s = 800^\circ\text{C}$, and (b) substrate temperature, T_s with $\text{CH}_4/\text{H}_2\% = 2.0\%$ [31].	53
Figure 3.5	Morphology vs. CH_4/H_2 field map developed by Kobashi [38].	55
Figure 3.6	Schematic drawing of the microwave plasma CVD system utilized by Yoon-Kee and colleagues [44].	60
Figure 3.7	Crystal habit vs. crystallization temperature [8].	61
Figure 3.8	FWHM vs. substrate temperature and methane concentration obtained by Yoon-Kee [70].	63
Figure 3.9	The deposition rate vs. (a) $\text{CH}_4/\text{H}_2\%$ and (b) substrate temperature for AStex bell jar MPCVD reactor examined by Liou [46].	65
Figure 3.10	Summary of morphology vs. deposition conditions for various reactors/experiments.	67
Figure 3.11	Edge dislocation in a crystallite lattice [58].	74
Figure 3.12	(a) and (b). Screw dislocation in a crystallite lattice [58].	74
Figure 3.13	(a) A real crystal and (b) a perfect reference crystal [57].	75
Figure 3.14	(a) A perfect reference crystal and (b) a real crystal [57].	76
Figure 3.15	F.c.c. unit cell (a) atomic site model, and (b) hard-sphere model [58].	77
Figure 3.16	Appearance of (111), (100), and (110) crystal plane [55].	78
Figure 3.17	Layer displacement in {111} planes [56].	79
Figure 3.18	Stacking of close-packed atomic layers [55].	80

Figure 3.19 (c)

Figure 3.20 F

Figure 3.21 S

Figure 3.22 (a)

Figure 3.23 T
(c)

Figure 3.24 St

Figure 3.25 D
in

Figure 3.26 (a)
PB
ex

Figure 3.27 Pro
a co
In

Figure 3.28 Pro
dian

Figure 3.29 An
dang
Thi

Figure 3.30 A (2
dang
of 18)

Figure 3.31 Sche
(111)

Figure 3.32 Differ
atoms
differ
90 deg
<100>

Figure 3.33 Top v
rows r

Figure 3.19	(a) Hexagonal close-packed and (b) face centered cubic [55].	80
Figure 3.20	Partial dislocation in an f.c.c. lattice [59].	81
Figure 3.21	Separation of two partial dislocations [59].	81
Figure 3.22	(a) an intrinsic and (b) an extrinsic stacking fault [57].	84
Figure 3.23	Twin formation (solid lines) from an un-distorted single crystal (dashed lines) [57].	84
Figure 3.24	Stacking sequence of twin [61].	85
Figure 3.25	Diamond cubic lattice structure normal to (110). O represents atoms in the plane of the paper and + represents atoms in the plane below [57].	87
Figure 3.26	(a) Formation mechanism of a flat face. Each circle represents a PBC seen end on. (b) Formation mechanism of an S face. No bond exists between adjacent PBC's (between A and B) [71].	90
Figure 3.27	Projection of diamond structure along [110]. Each circle represents a carbon atom. Adjacent PBC's are bonded in slice d_{111} , not in d_{220} . In the layer d_{004} no PBC occurs [71].	91
Figure 3.28	Projection of {001} face along $\langle 110 \rangle$ showing the unit slices for the diamond (0.25d) and the zinc blende structure (0.5d) [50].	91
Figure 3.29	An unreconstructed {001} surface with (a) no growth island: 120 dangling bonds and (b) with growth island: 120 dangling bonds. Thickness of island = 0.5d [50].	94
Figure 3.30	A (2 x 1) reconstructed {001} surface with (a) no growth island: 60 dangling bonds and (b) with growth island: 68 dangling bonds. Thickness of island = 0.5d [50].	95
Figure 3.31	Schematic structure of hydrogen-chemisorbed diamond surfaces: (a) (111): H, (b) (111): CH ₃ , and (c) (100): H ₂ [38].	96
Figure 3.32	Difference in energy (i.e., number of dangling bonds and number of atoms included in nucleus) of unit thickness (0.5d) growth islands of different orientations, (a) Edges parallel to $\langle 110 \rangle$: 50 atoms in nucleus, 90 dangling bonds over the whole surface area, (b) Edges parallel to $\langle 100 \rangle$: 30 atoms in nucleus, 100 dangling bonds [50].	98
Figure 3.33	Top view of (a) the (2 x 1) reconstructed {100} planes; (2 x 1) dimer rows normal to $\langle 110 \rangle$ are rearranged, (b) the alternate (2 x 1) dimer	

re
th
d
Figure 3.34 T
ad
d.
st
re
on

Figure 3.35 M

Figure 4.1 Va
ma

Figure 4.2 Va
plas

Figure 4.3 Mic

Figure 4.4 Com

Figure 4.5 Rea
For

Figure 4.6 Press
rates

Figure 4.7 SEM
CH₄

Figure 4.8 SEM
CH₄/

Figure 4.9 A bas

Figure 4.10 A typ
and tra

Figure 4.11 A fit

Figure 4.12 A sim

Figure 5.1 Micro
descri

rows perpendicular to the previous ones. A $\langle 110 \rangle$ step indicated by the dashed lines is formed. Open circles represent atoms with dangling bonds. Large filled circles represent upper terrace atoms [51]. .99

Figure 3.34	Top view of (a) the unreconstructed $\{111\}$ planes. Each $[112]$ step atom has two dangling bonds, whereas $[112]$ step atom has one dangling bond, (b) the $[112]$ step reconstructed $\{111\}$ planes. $[112]$ step atoms have one additional bond. Closed circles and open circles represent atoms with one bond directed downwards and atoms with one bond directed upwards, respectively [51].102
Figure 3.35	Morphology of diamond as expected from the PBC theory [73].103
Figure 4.1	Various components of the M.S.U. microwave plasma deposition machine.105
Figure 4.2	Vacuum pump and the gas flow system of the M.S.U microwave plasma deposition machine.107
Figure 4.3	Microwave power supply and waveguide circuit [14].110
Figure 4.4	Computer monitor program flow chart for the MCPR [14].111
Figure 4.5	Reactor operating field map under thermally floating configuration For 5" quartz dome/3" substrate reactor configuration.113
Figure 4.6	Pressure-substrate temperature relationship for various total gas flow rates and CH_4/H_2 chemistry under thermally floating configuration.114
Figure 4.7	SEM pictures of samples deposited at $f_t = 400$ sccm, $T_s = 1000^\circ\text{C}$, and $\text{CH}_4/\text{H}_2 = 0.60\%$ deposited approximately three years apart.116
Figure 4.8	SEM pictures of samples deposited at $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, and $\text{CH}_4/\text{H}_2 = 1.50\%$ deposited one week apart.117
Figure 4.9	A basic schematic of an SEM [74].122
Figure 4.10	A typical Raman spectrum with a diamond peak with different leading and trailing points.126
Figure 4.11	A fit for FWHM measurement for a typical Raman spectrum.126
Figure 4.12	A simplified substrate temperature measurement setup.129
Figure 5.1	Microwave cavity plasma reactor block diagram for the experiments described in this chapter. The dashed curve encircles the T_s , p , and P_t

Figure 5.2

Figure 5.3

Figure 5.4

Figure 5.5

Figure 5.6

Figure 5.7

Figure 5.8

Figure 5.9

Figure 5.10

Figure 5.11

Figure 5.12

Figure 5.13

Figure 5.14

Figure 5.15

Figure 5.16

Plot of
fixed

	variables indicating that this triad of variables can be considered as a single input variable for this investigation.....	132
Figure 5.2	Locations of various methane gas concentrations investigated in this chapter on the C-H-O Bachmann phase diagram.	135
Figure 5.3	Outline of Chapter 5.....	137
Figure 5.4	CVD diamond films with various morphologies deposited using the MCPR.	144
Figure 5.5	Morphology field map for total flow rate $f_t = 400$ sccm.	145
Figure 5.6	SEM pictures of the samples deposited at $f_t = 400$ sccm, $CH_4/H_2 = 0.60\%$, and (a) $T_s = 800^\circ C$, (b) $T_s = 850^\circ C$, (c) $T_s = 900^\circ C$, (d) $T_s = 950^\circ C$, and (e) $T_s = 1000^\circ C$	147
Figure 5.7	SEM pictures of the samples deposited at $f_t = 400$ sccm, $CH_4/H_2 = 1.50\%$, and (a) $T_s = 800^\circ C$, (b) $T_s = 850^\circ C$, (c) $T_s = 900^\circ C$, (d) $T_s = 950^\circ C$, and (e) $T_s = 1000^\circ C$	150
Figure 5.8	SEM pictures of the samples deposited at $f_t = 400$ sccm, $T_s = 850^\circ C$, and (a) $CH_4/H_2 = 0.6\%$, (b) $CH_4/H_2 = 1.0\%$, (c) $CH_4/H_2 = 1.50\%$, and (d) $CH_4/H_2 = 1.75\%$	153
Figure 5.9	Plot of grain size vs. T_s for $f_t = 400$ sccm and $CH_4/H_2 = 1.50\%$	155
Figure 5.10	Plot of grain size vs. CH_4/H_2 for $f_t = 400$ sccm and $T_s = 1000^\circ C$	156
Figure 5.11	Morphology field map for $f_t = 200$ sccm.....	160
Figure 5.12	SEM pictures of the samples deposited at $f_t = 200$ sccm, $CH_4/H_2 = 1.50\%$, and (a) $T_s = 700^\circ C$, (b) $T_s = 750^\circ C$, (c) $T_s = 800^\circ C$, (d) $T_s = 850^\circ C$, (e) $T_s = 900^\circ C$, and (f) $T_s = 1000^\circ C$	162
Figure 5.13	Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 200$ sccm and $CH_4/H_2 = 1.50\%$	165
Figure 5.14	SEM pictures of the samples deposited at $f_t = 200$ sccm, $T_s = 850^\circ C$, and (a) $CH_4/H_2 = 0.60\%$, (b) $CH_4/H_2 = 1.50\%$, (c) $CH_4/H_2 = 3.0\%$	166
Figure 5.15	SEM pictures of samples deposited at $f_t = 200$ sccm, $CH_4/H_2 = 2.0\%$, and (a) $T_s = 750^\circ C$ and (b) $T_s = 800^\circ C$	168
Figure 5.16	Plot of grain size vs. substrate temperature for $f_t = 200$ sccm with fixed at 1.50%	169

Figure 5.17

Figure 5.18

Figure 5.19

Figure 5.20

Figure 5.21

Figure 5.22

Figure 5.23

Figure 5.24

Figure 5.25

Figure 5.26

Figure 5.27

Figure 5.28

Figure 5.29

Figure 5.30

Figure 5.31

Figure 5.32

Figure 5.17	Morphology field map for $f_t = 100$ sccm.	171
Figure 5.18	SEM pictures of the samples deposited at $f_t = 100$ sccm, $CH_4/H_2 = 1.50\%$, and (a) $T_s = 700^\circ C$, and (b) $T_s = 1000^\circ C$	173
Figure 5.19	SEM picture a sample deposited at $f_t = 100$ sccm, $CH_4/H_2 = 0.60\%$ and $T_s = 850^\circ C$	174
Figure 5.20	Morphology field map for $f_t = 60$ sccm.	178
Figure 5.21	SEM pictures of the samples deposited at $f_t = 60$ sccm, $CH_4/H_2 = 1.50\%$, and (a) $T_s = 700^\circ C$, (b) $T_s = 750^\circ C$, (c) $T_s = 800^\circ C$, (d) $T_s = 850^\circ C$, (e) $T_s = 900^\circ C$, and (f) $T_s = 1000^\circ C$	180
Figure 5.22	Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 60$ sccm and $CH_4/H_2 = 1.50\%$	183
Figure 5.23	SEM pictures of the samples deposited at $f_t = 60$ sccm, $T_s = 850^\circ C$, and (a) $CH_4/H_2 = 0.50\%$, (b) $CH_4/H_2 = 1.0\%$, (c) $CH_4/H_2 = 1.50\%$, (d) $CH_4/H_2 = 2.0\%$, and (e) $CH_4/H_2 = 3.0\%$	184
Figure 5.24	SEM pictures of $\{111\}$ films with (a) smooth faces and (b) rough faces.	187
Figure 5.25	Grain size vs. T_s for $f_t = 60$ sccm and $CH_4/H_2 = 1.50\%$	188
Figure 5.26	Grain size vs. $CH_4/H_2\%$ for $f_t = 60$ sccm and $T_s = 850^\circ C$	189
Figure 5.27	Morphology field map for $f_t = 30$ sccm.	191
Figure 5.28	SEM pictures of sample deposited at $f_t = 30$ sccm, $CH_4/H_2 = 1.50\%$, and (a) $T_s = 700^\circ C$, (b) $T_s = 750^\circ C$, (c) $T_s = 850^\circ C$, and (d) $T_s = 900^\circ C$	192
Figure 5.29	SEM pictures of samples deposited at $f_t = 30$ sccm, $T_s = 850^\circ C$, and (a) $CH_4/H_2 = 0.60\%$, (b) $CH_4/H_2 = 1.50\%$, and (c) $CH_4/H_2 = 2.0\%$	194
Figure 5.30	Raman spectra for diamond films deposited at $CH_4/H_2 = 1.50\%$ and $f_t = 400$ sccm with $T_s =$ (a) $800^\circ C$, (b) $850^\circ C$, (c) $900^\circ C$, (d) $950^\circ C$, and (e) $1000^\circ C$	198
Figure 5.31	FWHM vs. T_s for $CH_4/H_2 = 1.5\%$ and $f_t = 400$ sccm.	201
Figure 5.32	Raman spectra for diamond films deposited at $CH_4/H_2 = 0.60\%$ and $f_t = 400$ sccm with $T_s =$ (a) $800^\circ C$, (b) $850^\circ C$, (c) $900^\circ C$, (d) $950^\circ C$, and (e) $1000^\circ C$	202

Figure 5.33 F

Figure 5.34 R
 $f_1 =$
(d)

Figure 5.35 F
and

Figure 5.36 R
and
(d)

Figure 5.37 FV
 $f_1 =$

Figure 5.38 R
 $f_1 =$
(d)

Figure 5.39 FW
and

Figure 5.40 A typ
 CH_2

Figure 5.41 Ram
 $f_1 =$
and

Figure 5.42 The
and C

Figure 5.43 Ram
scm
(e) 3.0

Figure 5.44 The p
scm a

Figure 5.45 A typ
 CH_2/H

Figure 5.46 Linear
scm to
 α val

Figure 5.33	FWHM vs. T_s for $CH_4/H_2=0.60\%$ and $f_t = 400$ sccm.	205
Figure 5.34	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 400$ sccm with $CH_4/H_2 =$ (a) 0.60%, (b) 1.0%, (c) 1.50%, (d) 1.75%, (e) 2.75%, and (f) 3.75%.....	206
Figure 5.35	FWHM vs. $CH_4/H_2\%$ for diamond films deposited at $f_t = 400$ sccm and $T_s = 850^\circ\text{C}$	209
Figure 5.36	Raman spectra for diamond films deposited at $CH_4/H_2 = 1.50\%$ and $f_t = 200$ sccm with $T_s =$ (a) 700°C , (b) 800°C , (c) 850°C , (d) 900°C , and (e) 1000°C	211
Figure 5.37	FWHM vs. substrate temperature for diamond films deposited at $f_t = 200$ sccm and $CH_4/H_2 = 1.50\%$	214
Figure 5.38	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 200$ sccm with $CH_4/H_2 =$ (a) 0.60%, (b) 1.50%, (c) 2.0%, (d) 3.0%.....	215
Figure 5.39	FWHM vs. $\%CH_4/H_2$ for diamond films deposited at $f_t = 200$ sccm and $T_s = 850^\circ\text{C}$	217
Figure 5.40	A typical Raman spectra of a sample deposited at $f_t = 100$ sccm, $CH_4/H_2 = 1.50\%$, and $T_s=850^\circ\text{C}$	218
Figure 5.41	Raman spectra for diamond films deposited at $CH_4/H_2=1.50\%$ and $f_t = 60$ sccm with $T_s =$ (a) 700°C , (b) 800°C , (c) 850°C , (d) 900°C , and (e) 1000°C	220
Figure 5.42	The plot of FWHM vs. T_s for diamond films deposited at $f_t = 60$ sccm and $CH_4/H_2 = 1.50\%$	223
Figure 5.43	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm with $CH_4/H_2 =$ (a) 0.50%, (b) 1.0%, (c) 1.50%, (d) 2.0%, (e) 3.0%, and (f) 4.0%.....	224
Figure 5.44	The plot of FWHM vs. CH_4/H_2 for diamond films deposited at $f_t = 60$ sccm and $T_s = 850^\circ\text{C}$	227
Figure 5.45	A typical Raman spectra of a sample deposited at $f_t = 30$ sccm, $CH_4/H_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$	228
Figure 5.46	Linear growth rate vs. substrate temperature and $CH_4/H_2\%$ for 400 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $CH_4/H_2\%$, $\mu\text{m/hr}$) coordinates	230

Figure 5.47 L
S
C

Figure 5.48 L
S
C

Figure 5.49 L
S
C

Figure 5.50 L
C
ir

Figure 5.51 σ_c
C

Figure 5.52 σ_c
C

Figure 5.53 σ_c
C

Figure 5.54 σ_c
C

Figure 5.55 σ_c
ar

Figure 5.56 SI
T

Figure 5.57 SI
T₁

Figure 5.58 SI
T₁

Figure 5.59 SI
T₁

Figure 5.60 SI
T₁

Figure 5.60 SE
T₁

Figure 5.47	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 200 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , CH_4/H_2 , $\mu\text{m/hr}$) coordinates.	232
Figure 5.48	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 100 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , CH_4/H_2 , $\mu\text{m/hr}$) coordinates.	233
Figure 5.49	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 60 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , CH_4/H_2 , $\mu\text{m/hr}$) coordinates.	235
Figure 5.50	Linear growth rate vs. (a) substrate temperature with $\text{CH}_4/\text{H}_2 = 1.50\%$ and (b) CH_4/H_2 with $T_s = 850^\circ\text{C}$. The α values are included in the plots. The total gas flow rate is fixed at 30 sccm.	236
Figure 5.51	%Carbon conversion efficiency vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for $f_t = 400$ sccm.	238
Figure 5.52	%Carbon conversion efficiency vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for $f_t = 200$ sccm.	240
Figure 5.53	%Carbon conversion efficiency vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for $f_t = 100$ sccm.	241
Figure 5.54	%Carbon conversion efficiency vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for $f_t = 60$ sccm.	244
Figure 5.55	% Carbon conversion efficiency vs. (a) substrate temperature, and (b) CH_4/H_2 for total gas flow rate fixed at 30 sccm.	245
Figure 5.56	SEM pictures of samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 8$ hours, (b) $t = 16$ hours, and (c) $t = 41$ hours.	250
Figure 5.57	SEM pictures of samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 16$ hours, and (b) $t = 24$ hours.	252
Figure 5.58	SEM pictures of samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 16$ hours, and (b) $t = 24$ hours.	253
Figure 5.59	SEM picture of SK132 sample deposited at: Step 1: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t_1 = 14.25$ hours. Step 2: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t_2 = 1.75$ hours.	254
Figure 5.60	SEM picture of SK133 sample deposited at: Step 1: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t_1 = 12$ hours. Step 2: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t_2 = 4.0$ hours.	255

Figure 5.61

Figure 5.62

Figure 5.63

Figure 5.64

Figure 5.65

Figure 5.66

Figure 5.67

Figure 5.68

Figure 5.69

Figure 5.70

Figure 5.71

Figure 5.72

Figure 5.73

Figure 5.74

Figure 5.61	Raman spectra of samples in set 1 (i.e., SK62, SK80, and SK70) deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 41$ hours.	257
Figure 5.62	Plot of FWHM vs. deposition time for samples in set 1 (i.e., SK62, SK80 and SK70); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$	259
Figure 5.63	Raman spectra of samples in set 2 (i.e., SK62, SK147, and SK153) deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 24$ hours.	260
Figure 5.64	Plot of FWHM vs. deposition time for samples in set 2 (i.e., SK62, SK147, and SK153); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$	262
Figure 5.65	Raman spectra of samples in set 3 (i.e., SK62, SK149, and SK150) deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 24$ hours.	263
Figure 5.66	Plot of FWHM vs. deposition time for samples in set 3 (i.e., SK62, SK149, and SK150); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$	265
Figure 5.67	Linear growth rate vs. deposition time for different sets of films deposited under $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$	267
Figure 5.68	Percent carbon conversion efficiency vs. deposition time for sample sets 1, 2, and 3 deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$	268
Figure 5.69	Morphology vs. flow rate for substrate temperature fixed at 850°C	271
Figure 5.70	SEM pictures of samples deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $f_t = 30$ sccm, (b) $f_t = 60$ sccm, (c) $f_t = 100$ sccm, (d) $f_t = 200$ sccm, (e) $f_t = 400$ sccm, and (f) $f_t = 600$ sccm.	272
Figure 5.71	Variation of the growth parameter with the total gas flow rate.	275
Figure 5.72	Structural quality vs. total gas flow rate with substrate temperature fixed at 850°C and $\text{CH}_4/\text{H}_2 = 1.50\%$	277
Figure 5.73	Plot of FWHM vs. total gas flow rate for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$	278
Figure 5.74	Linear growth rate vs. total gas flow rate for diamond films deposited at	

Figure 5.75

Figure 5.76

Figure 6.1

Figure 6.2

Figure 6.3

Figure 6.4

Figure 6.5

Figure 6.6

Figure 6.7

Figure 6.8

Figure 6.9

Figure 6.10

Figure 6.11

Figure 6.12

6
M
c
M
d
L
ch
M
SE
CH
(d)
SE
CH
(d)
Vari
samp
SEM

	$T_s = 850^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1.50\%$	279
Figure 5.75	%Carbon conversion efficiency vs. total gas flow rate for diamond films deposited at $T_s = 850^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1.50\%$	280
Figure 5.76	A 2-dimensional schematic demonstration of the Walff criterion [36]. The faster growing face (i.e., {100} in this example) is growing out of existence.	289
Figure 6.1	(a) The 5"quartz dome/3" substrate reactor configuration (Chapters 5). (b) The 4"quartz dome/2" substrate reactor configuration (Chapter 6).	301
Figure 6.2	Microwave cavity plasma reactor block diagram for the experiments described in this chapter. The dashed curve encircles the T_s , p , and P_t variables indicating that this triad of variables can be considered as a single variable for this investigation.	302
Figure 6.3	Operating road maps of the two reactor configurations under thermally floating arrangement.	304
Figure 6.4	Absorbed microwave power vs. substrate temperature for the two different reactor geometries.	305
Figure 6.5	Microwave volume power density vs. substrate temperature for two different reactor geometries.	306
Figure 6.6	Microwave area power density vs. substrate temperature for two different reactor geometries.	307
Figure 6.7	Locations of various methane gas concentrations investigated in this chapter on the C-H-O Bachmann phase diagram.	310
Figure 6.8	Morphology field map for total flow rate $f_t = 400$ sccm.	314
Figure 6.9	SEM pictures of the samples deposited at $f_t = 400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 950^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$	316
Figure 6.10	SEM pictures of the samples deposited at $f_t = 400$ sccm, $\text{CH}_4/\text{H}_2 = 0.60\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 950^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$	319
Figure 6.11	Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 400$ sccm and $\text{CH}_4/\text{H}_2 = 0.60\%$	322
Figure 6.12	SEM pictures of the samples deposited at $f_t = 400$ sccm, $T_s = 850^\circ\text{C}$,	

Figure 6.13

Figure 6.14

Figure 6.15

Figure 6.16

Figure 6.17

Figure 6.18

Figure 6.19

Figure 6.20

Figure 6.21

Figure 6.22

Figure 6.23

Figure 6.24

Figure 6.25

Figure 6.26

Figure 6.27

	and (a) $\text{CH}_4/\text{H}_2 = 0.60\%$, (b) $\text{CH}_4/\text{H}_2 = 1.0\%$, (c) $\text{CH}_4/\text{H}_2 = 1.50\%$, and (d) $\text{CH}_4/\text{H}_2 = 2.0\%$	323
Figure 6.13	Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 0.60\%$ and $f_t = 400$ sccm.	325
Figure 6.14	Morphology field map for total flow rate $f_t = 200$ sccm.	328
Figure 6.15	SEM pictures of the samples deposited at $f_t = 200$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 750^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 900^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$	330
Figure 6.16	SEM pictures of the samples deposited at $f_t = 200$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 1.0\%$, (b) $\text{CH}_4/\text{H}_2 = 1.50\%$, and T_s (c) $\text{CH}_4/\text{H}_2 = 2.0\%$	333
Figure 6.17	Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 200$ sccm.	335
Figure 6.18	Morphology field map for total flow rate $f_t = 60$ sccm.	338
Figure 6.19	SEM pictures of the samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 750^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 900^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$	340
Figure 6.20	Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 60$ sccm and $\text{CH}_4/\text{H}_2 = 1.0\%$	343
Figure 6.21	SEM pictures of the samples deposited at $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, and $\text{CH}_4/\text{H}_2 =$ (a) 0.50% , (b) 1.0% , (c) 1.50% , (d) 2.0% , and (e) 3.0%	344
Figure 6.22	SEM picture of a $\{100\}$ film with rough (jagged) edges.	347
Figure 6.23	SEM pictures of $\{111\}$ films with (a) rough faces and (b) smooth faces.	348
Figure 6.24	Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 60$ sccm.	349
Figure 6.25	Plot of average grain size vs. $\text{CH}_4/\text{H}_2\%$ for $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm.	350
Figure 6.26	Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 400$ sccm with $T_s =$ (a) 700°C , (b) 850°C , and (c) 1000°C	352
Figure 6.27	FWHM vs. substrate temperature for diamond films deposited at	

Figure 6.28

Figure 6.29

Figure 6.30

Figure 6.31

Figure 6.32

Figure 6.33

Figure 6.34

Figure 6.35

Figure 6.36

Figure 6.37

Figure 6.38

Figure 6.39

Figure 6.40

Figure 6.41

	$f_t = 400$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$	354
Figure 6.28	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 400$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 2.00%.	355
Figure 6.29	FWHM vs. $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $f_t = 400$ sccm and $T_s = 850^\circ\text{C}$	357
Figure 6.30	Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 200$ sccm with $T_s =$ (a) 750°C , (b) 850°C , and (c) 1000°C	359
Figure 6.31	FWHM vs. substrate temperature for diamond films deposited at $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$	361
Figure 6.32	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 200$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 3.00%.	362
Figure 6.33	FWHM vs. $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $f_t = 200$ sccm and $T_s = 850^\circ\text{C}$	364
Figure 6.34	Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 60$ with $T_s =$ (a) 750°C , (b) 850°C , and (c) 1000°C	366
Figure 6.35	Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 3.50%.	368
Figure 6.36	FWHM vs. $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $f_t = 60$ sccm and $T_s = 850^\circ\text{C}$	370
Figure 6.37	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 400 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates.	372
Figure 6.38	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 200 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates.	374
Figure 6.39	Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 60 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates.	375
Figure 6.40	Carbon conversion efficiency vs. substrate temperature and CH_4/H_2 for $f_t = 400$ sccm.	377
Figure 6.41	Carbon conversion efficiency vs. substrate temperature and CH_4/H_2 for $f_t = 200$ sccm.	378

Figure 6.42

Figure 6.43

Figure 6.44

Figure 6.45

Figure 6.46

Figure 6.47

Figure 6.48

Figure 6.49

Figure 6.50

Figure 6.51

Figure 6.52

Figure 6.53

Figure 6.54

Figure 6.42	Carbon conversion efficiency vs. substrate temperature and CH_4/H_2 for $f_t = 60$ sccm.	381
Figure 6.43	Morphology vs. total flow rate for substrate temperature fixed at 850°C	382
Figure 6.44	SEM pictures diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $f_t = 60$ sccm, (b) $f_t = 200$ sccm, and (c) $f_t = 400$ sccm.	383
Figure 6.45	Structural quality vs. total gas flow rate with substrate temperature fixed at 850°C and $\text{CH}_4/\text{H}_2 = 1.50\%$	385
Figure 6.46	Plot of FWHM vs. total gas flow rate for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$	386
Figure 6.47	Linear growth rate vs. total gas flow rate and $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $T_s = 850^\circ\text{C}$	387
Figure 6.48	%Carbon conversion efficiency vs. total gas flow rate and $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $T_s = 850^\circ\text{C}$	388
Figure 6.49	Morphology field maps for the 4" dome/2" substrate and the 5" dome/3" substrate reactor geometry configurations for $f_t = 400$ sccm.	391
Figure 6.50	Morphology field maps for the 4" dome/2" substrate and the 5" dome/3" substrate reactor geometry configurations for $f_t = 200$ sccm.	392
Figure 6.51	Morphology field maps for the 4" dome/2" substrate and the 5" dome/3" substrate reactor geometry configurations for $f_t = 60$ sccm.	393
Figure 6.52	Grain size vs. substrate temperature for the two reactor geometries for $\text{CH}_4/\text{H}_2 = 1.50\%$ and (a) $f_t = 60$ sccm, (b) $f_t = 200$ sccm, and (c) $f_t = 400$ sccm.	394
Figure 6.53	Variation of weight gain (mg./hr) with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	398
Figure 6.54	Variation of linear growth rate with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	399

Figure 6.5

Figure 6.56

Figure 7.1

Figure 7.2

Figure 7.3

Figure 7.4

Figure 7.5

Figure 7.6

Figure 7.7

Figure 7.8

Figure 7.9

Figure 7.10

Figure 7.11

a

L

C

T

P

SE

p =

(c)

SE

p =

Ran

and

FW

$H_2 =$

Ran

and (c)

Figure 6.55	Variation of percent carbon conversion efficiency with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	400
Figure 6.56	Variation of normalized percent carbon conversion efficiency (i.e., % carbon conversion efficiency/substrate area) with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	401
Figure 7.1	Microwave cavity plasma reactor block diagram utilized for CO-H ₂ diamond film deposition. The dashed curve encircles the T _s , p, and P _t variables indicating that this triad of variables can be considered as a single input variable for this investigation.	411
Figure 7.2	Effect of CO concentration on the substrate temperature for H ₂ = 400 sccm, and p = 50 torr.	412
Figure 7.3	SEM picture of the sample deposited at CO/H ₂ = 10%, H ₂ = 400 sccm, and p = 25 torr.	415
Figure 7.4	SEM picture of the sample deposited at CO/H ₂ = 10%, H ₂ = 100 sccm, and p = 35 torr.	416
Figure 7.5	Locations of various CO/H ₂ gas composition used in this chapter on the C-H-O Bachmann phase diagram.	417
Figure 7.6	The crystal habit common to majority of the crystals deposited under the parameter space investigated in this chapter.	419
Figure 7.7	SEM pictures of CO-H ₂ sample deposited at H ₂ = 400 sccm, p = 35 torr, and (a) CO/H ₂ = 10%, (b) CO/H ₂ = 20%, and (c) CO/H ₂ = 30%.	420
Figure 7.8	SEM picture of SK122_2 sample deposited at H ₂ = 400 sccm, p = 60 torr, and CO/H ₂ = 10%.	422
Figure 7.9	Raman spectra of diamond films deposited at H ₂ = 400, p = 35 torr, and CO/H ₂ = (a) 10%, (b) 20%, and (c) 30%.	424
Figure 7.10	FWHM vs. CO concentrations for CO-H ₂ diamond films deposited at H ₂ = 400 sccm and p = 35 torr.	426
Figure 7.11	Raman spectra of diamond films deposited at H ₂ = 400, CO/H ₂ = 20%, and (a) p = 35 torr, and (b) p = 45 torr.	427

Figure 6.55 V
g
st
st

Figure 6.56 V
(1)
g
st
st

Figure 7.1 M
d
a
c

Figure 7.2 E
s

Figure 7.3 S
a

Figure 7.4 S
a

Figure 7.5 L
C

Figure 7.6 T
F

Figure 7.7 S
I
(

Figure 7.8 S
I

Figure 7.9 I

Figure 7.10 I

Figure 7.11

Figure 6.55	Variation of percent carbon conversion efficiency with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	400
Figure 6.56	Variation of normalized percent carbon conversion efficiency (i.e., % carbon conversion efficiency/substrate area) with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.	401
Figure 7.1	Microwave cavity plasma reactor block diagram utilized for CO-H ₂ diamond film deposition. The dashed curve encircles the T _s , p, and P _t variables indicating that this triad of variables can be considered as a single input variable for this investigation.	411
Figure 7.2	Effect of CO concentration on the substrate temperature for H ₂ = 400 sccm, and p = 50 torr.	412
Figure 7.3	SEM picture of the sample deposited at CO/H ₂ = 10%, H ₂ = 400 sccm, and p = 25 torr.	415
Figure 7.4	SEM picture of the sample deposited at CO/H ₂ = 10%, H ₂ = 100 sccm, and p = 35 torr.	416
Figure 7.5	Locations of various CO/H ₂ gas composition used in this chapter on the C-H-O Bachmann phase diagram.	417
Figure 7.6	The crystal habit common to majority of the crystals deposited under the parameter space investigated in this chapter.	419
Figure 7.7	SEM pictures of CO-H ₂ sample deposited at H ₂ = 400 sccm, p = 35 torr, and (a) CO/H ₂ = 10%, (b) CO/H ₂ = 20%, and (c) CO/H ₂ = 30%.	420
Figure 7.8	SEM picture of SK122_2 sample deposited at H ₂ = 400 sccm, p = 60 torr, and CO/H ₂ = 10%.	422
Figure 7.9	Raman spectra of diamond films deposited at H ₂ = 400, p = 35 torr, and CO/H ₂ = (a) 10%, (b) 20%, and (c) 30%.	424
Figure 7.10	FWHM vs. CO concentrations for CO-H ₂ diamond films deposited at H ₂ = 400 sccm and p = 35 torr.	426
Figure 7.11	Raman spectra of diamond films deposited at H ₂ = 400, CO/H ₂ = 20%, and (a) p = 35 torr, and (b) p = 45 torr.	427

Figure 7.12

Figure 7.13

Figure 8.1

Figure 8.2

Figure 8.3

Figure 8.4

Figure 8.5

Figure 8.6

Figure 8.7

Figure 8.8

Figure 8.9

Figure 8.10

Figure 8.11

Figure 8.12

Figure 8.13

Figure 7.12	CO-H ₂ diamond film linear growth rate vs. CO/H ₂ and operating pressure. O represents the (p, CO/H ₂ %, um/hr) coordinates.	429
Figure 7.13	% Carbon conversion efficiency vs. pressure and CO/H ₂ %.....	430
Figure 8.1	Required patterns for CVD diamond films on tungsten disks.	439
Figure 8.2	Standard UV photolithographic method for patterning the diamond films on tungsten substrates using mask 1.....	443
Figure 8.3	Standard UV photolithographic method for patterning the diamond films on tungsten substrates using mask 2.....	444
Figure 8.4	Use of stainless steel shadow masks for selectively depositing diamond films on tungsten substrates.	445
Figure 8.5	Plasma Quest etch system [85].	446
Figure 8.6	Plasma etch procedure using shadow mask 1.....	447
Figure 8.7	Plasma etch procedure using shadow mask 2.	448
Figure 8.8	SEM picture of WSK1 sample deposited at $f_t = 400$ sccm, CH ₄ /H ₂ = 1.50%, p = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$) and $t_{\text{total}} = t_2 + t_5 = 24$ hours.....	453
Figure 8.9	Raman spectrum of a diamond film deposited on a tungsten substrate. Deposition condition: $f_t = 400$ sccm, CH ₄ /H ₂ = 1.50%, pressure = 36 Torr, and $t_{\text{total}} = 24$ hours.....	454
Figure 8.10	SEM pictures of SK179 and WSK1 samples deposited at $f_t = 400$ sccm, CH ₄ /H ₂ = 1.50%, and $T_s \sim 850^\circ\text{C}$ with $t_{\text{SK179}} = 8$ hours and $t_{\text{WSK1}} = 24$ hours.....	455
Figure 8.11	Raman spectra for diamond films deposited on (a) a silicon substrate, and (b) a tungsten substrate. Deposition condition: $f_t = 400$ sccm, CH ₄ /H ₂ = 1.50%, and $T_s \sim 850^\circ\text{C}$ with $t_{\text{SK179}} = 8$ hours and $t_{\text{WSK1}} = 24$ hours.....	456
Figure 8.12	(a) Plasma species in-flux on to the sample. (b) Thickness profile resulted when a shadow mask (i.e., shadow mask 1) is used for selective film growth.....	458
Figure 8.13	(a) and (b) Diamond film patterns formed via plasma etch.	459

1.1 Diamond

Diamond

thermal conduct

extreme hardne

such as very hig

GaAs [1]), hig

properties alio

semiconductors

some interestin

Natural d

researchers to

that diamond is

CHAPTER 1

Introduction

1.1 Diamond

Diamond possesses an unusual combination of extreme properties such as high thermal conductivity (approximately 5 times that of copper and 20 times that of silicon), extreme hardness, excellent infrared transparency, and excellent semiconductor properties such as very high breakdown electric field, high saturation velocity (i.e., 2.7 times that of GaAs [1]), high electron and hole mobility, and large band gap. These interesting properties allow diamond to have many potential applications in the fields of semiconductors, optics, opto-electronics, tool coating, etc. Table 1.1 includes a list of some interesting properties of diamond ([2], [3][4], [5], [6], [7], [8], [9], [10]).

Natural diamond is rare and expensive and its scarcity and high cost have motivated researchers to attempt to synthesize diamond ever since 1797 when Tennant discovered that diamond is a crystalline form of carbon.

Hardne

Mass d

Molar c

Specific

Therma

Bulk mo

Compre

Thermal

Refractiv

Dielectr

Electron

Hole mo

Breakdov

Electrica

Band gap

Lattice co

Transmitt

Electron

Table 1.1. Some properties of natural and (CVD) diamond

Property	Type IIa	CVD
Hardness, GPa	~90	80-90
Mass density, g/cm ³	3.515	2.8-3.5
Molar density, g atom/cm ³	0.293	0.23-0.29
Specific heat at 300 K, J/g	6.195	
Thermal conductivity at 298K, W/cm-K	20	10-20
Bulk modulus, N/m ²	4.4-5.9 x 10 ¹¹	~2.4
Compressibility, cm ² /kg	1.7 x 10 ⁻⁷	~5.7
Thermal expansion coefficient at 293 K, K ⁻¹	0.8 x 10 ⁻⁶	
Refractive index at 589.29 nm	2.41726	
Dielectric constant at 300 K	5.7±0.05	
Electron mobility (cm ³ V ⁻¹ s ⁻¹)	1800	
Hole mobility (cm ³ V ⁻¹ s ⁻¹)	1200	10-1000
Breakdown voltage (Vcm ⁻¹)	10 ⁷	
Electrical resistivity (Ω-cm)	>10 ¹²	
Band gap (eV)	5.5	~5.5
Lattice constant (Å)	3.57	3.57
Transmittancy in the UV range (nm) [8]	>225	>225
Electron saturation velocity (cm-sec ⁻¹) [9]	2x10 ⁷	

12 A brief history

A complete

requires knowledge

diamond, graphite

This section

structure.

Graphite

Graphite is the

structure. The

of 1.42 angstroms

angstroms [1].

the same as in

carbon crystal

The distance

(i.e., f.c.c.)

lattice as shown

carbon atom

respectively.

Chapter

particular are

Thermody

evident from the c

of color at different

1.2 A brief history of CVD diamond synthesis

A comprehensive understanding of the CVD diamond nucleation and growth process requires knowledge of atomic and crystal structure of various phases of carbon such as diamond, graphite, and amorphous carbon that might be produced by CVD processes. This section provides a brief description of various carbon phases and their associated structure.

Graphite, lonsdaleite, and diamond are different forms of crystalline carbon. Graphite is the most common form of carbon. Figure 1.1 shows the graphite lattice structure. The in-plane carbon atoms form sp^2 bonding with the nearest neighbor spacing of 1.42 angstrom. The repeating layers form pi bonds with the lattice constant of 6.707 angstroms [1]. In lonsdaleite structure the arrangement of carbon atoms in each plane is the same as in the cubic structure, but the planes are differently joined. This form of carbon crystal was first found in meteorites.

The diamond cubic lattice corresponds to two interpenetrating face cubic centered (i.e., f.c.c.) lattices. One lattice is displaced by $(1/4, 1/4, 1/4)$ with respect to the other lattice as shown in Figure 1.2. Each carbon atom is tetrahedrally (sp^3) bonded to four other carbon atoms. The lattice constant and bond length are 3.56 and 1.54 angstroms, respectively. A more in depth description of the diamond lattice structure is postponed until Chapter 3 where the cubic lattice structure in general and diamond structure in particular are studied.

Thermodynamically, diamond is stable relative to graphite only at high pressures, as evident from the carbon phase diagram shown in Figure 1.3 which shows various phases of carbon at different pressures and temperatures [3]. As shown in Figure 1.3 the graphite

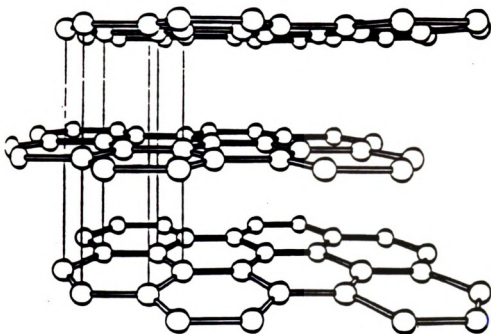


Figure 1.1. Graphite lattice structure.

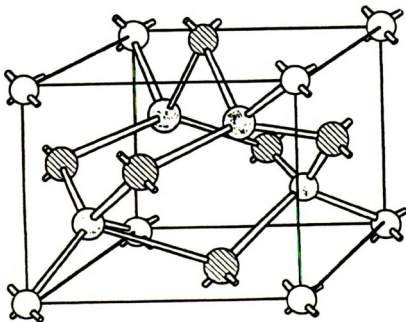


Figure 1.2. Diamond lattice structure.

10

1

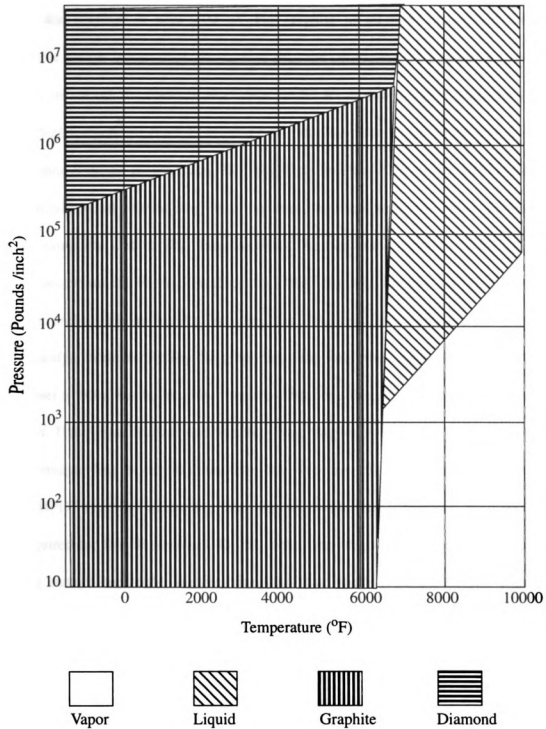
1

1

1

1

1 atm.



1 atm. = 14.7 Pound/inch² = 760 torr

Figure 1.3. Phase diagram of carbon [3].

phase is t

diamond

consider

by simpl

pressure

at Altem

using a

thermod

General

Pt. Fe-N

solvent-

much cl

Figure 1

ranges o

catalytic

those re

process

tempera

[16].

I

when in

that di

mixture

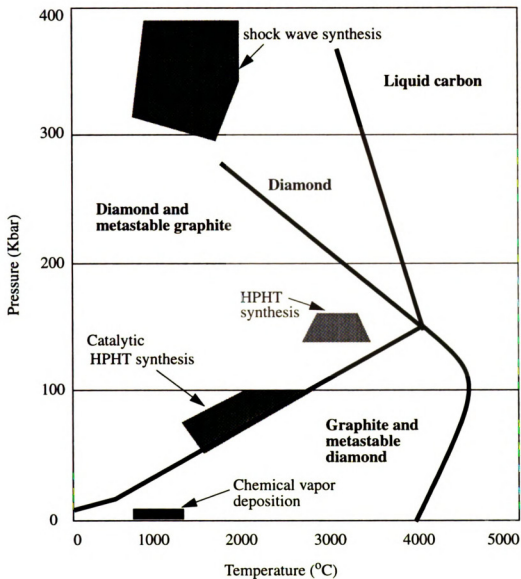
phase is thermodynamically stable at low pressures. The free energy difference between diamond and graphite is only 0.02 eV but graphite to diamond conversion faces a considerable kinetic barrier [10]. Because of this, the conversion of graphite to diamond by simply increasing the pressure was unsuccessful for over a hundred years until high pressure-high temperature (HPHT) synthesis methods were developed. In 1953 H. Liander at Alleman Svenska Elektriska A. B. (ASEA) in Sweden developed a HPHT process using a liquid metal solvent-catalyst at pressures and temperatures where diamond is thermodynamically stable [10]. Independently, Bundy and coworkers ([10], [11]) at General Electric succeeded in the synthesis of HPHT diamond in 1954. Fe, Ni, Cr, Co, Pd, Pt, Fe-Ni, and Co-Fe are among the transition metals that are used to react with the solvent-catalyst in order to make the graphite to diamond conversion occur at conditions much closer to the diamond-graphite transition line but at lower temperatures as shown in Figure 1.4. This Figure illustrates the carbon phase diagram with temperature and pressure ranges corresponding to various diamond synthesis processes. As illustrated in Figure 1.4 catalytic HPHT synthesis occurs at pressures much smaller and at temperatures lower than those required for HPHT synthesis. Direct conversion of graphite to diamond in HPHT processes though successful requires pressures that range from 50 to 100 kbar and temperatures that are in the range of 1300°C to 2300°C to overcome the kinetic barrier [10].

The breakthrough in the low pressure low temperature synthesis of diamond came when in 1949 W. G. Eversole of the Union Carbide Corporation in the U.S. discovered that diamond could be deposited on a substrate from a hydrocarbon gas or a CO/CO₂ mixture by chemical vapor deposition (CVD) where diamond is metastable with respect to

Pressure (Kbar)

1 bar ~

Figure 1.4. C.



1 bar ~ 1 atm. = 760 torr

Figure 1.4. Carbon phase diagram with temperature and pressure ranges corresponding to various diamond synthesis processes ([3], [10]).

graphite as

take place

is metastable

studies of

being unavailable

Physical Chemistry

and co-workers

synthesize

deposition

required for

graphite with

atm., respectively

rate of deposition

The

preferential

by Derjaguin

successful

deposition

been focused

processes

respect to

have been

for identification

graphite as illustrated in Figure 1.4. This Figure shows that CVD diamond synthesis can take place at very low pressures where thermodynamically graphite is stable and diamond is metastable. Eversole's effort started in 1949 and proceeded in parallel with the early studies of HPHT diamond synthesis. Working independently of one another and both being unaware of Eversole's work, B. V. Derjaguin and co-workers at the Institute of Physical Chemistry of the Academy of Science of the former U.S.S.R. and J. C. Angus and co-workers at Case Western Reserve University in the U.S. initiated efforts to synthesize low pressure diamond in 1968 [10]. They succeeded in low pressure co-deposition of diamond and graphite on diamond seed crystals. The deposition process required frequent interruptions of the deposition process in order to remove deposited graphite with hydrogen etching at temperatures and pressures greater than 1000°C and 50 atm., respectively or by oxidizing in air at atmospheric pressure [10]. The typical growth rate of diamond was less than 0.1 micron per hour.

The discovery and demonstration of the crucial role of atomic hydrogen in preferentially etching graphite and permitting high nucleation and growth rate of diamond by Derjaguin, Angus, and their co-workers led Derjaguin and his co-workers to the first successful low pressure deposition of diamond crystals on nondiamond substrates at a deposition rate $> 1\mu\text{m/hr}$ in the mid 1970's. Since mid 1980's, many research efforts have been focused on the low pressure synthesis of diamond using various CVD deposition processes. To date, low pressure diamond deposition (where diamond is metastable with respect to graphite) with linear growth rates in the order of hundreds of micron per hour have been achieved. Electron microscopy (for surface morphology), Raman spectroscopy (for identification of various phases of carbon), x-ray diffraction (for crystal structure),

and other

that these

The

polycrysta

incubation

surface, (i)

crystals, (i

growth of

Exp

shown th

Instead, t

diamond

The inter

metal can

activated

nucleatio

few min

depositio

Du

each oth

atoms fr

onto the

substrate

and other techniques have been utilized for characterization of these films and have shown **that** these films possess characteristics of the diamond structure.

The typical film growth process associated with the CVD assisted deposition of **polycrystalline** diamond films can be divided into several different steps [10]: (i) **incubation** period, (ii) three dimensional nucleation of individual crystallites on substrate **surface**, (iii) termination of surface nucleation and three dimensional growth of individual **crystals**, (iv) coalescence of individual crystals and formation of continuous film, and (v) **growth** of continuous film.

Experimental observations of diamond nucleation on non-diamond substrates have **shown** that diamond does not nucleate directly on a non-diamond substrate surface. **Instead**, the nucleation takes place on an intermediate layer which is formed between **diamond** and the non-diamond substrate during the period known as the incubation period. **The** intermediate layer formed during the incubation period is comprised of a-C, DLC, **metal** carbides, or graphite. This layer is formed as a result of the chemical interactions of **activated** gas species with the substrate surface. Such an intermediate layer provides **nucleation** sites for diamond crystallite growth. The incubation period may take from a **few** minutes up to hours, depending on surface pre-treatment, substrate materials, and **deposition** parameters [10].

During the nucleation step nuclei are formed and crystals grow independently of **each** other. The surface nucleation process may include the following events [10]: (1) **atoms** from the gas phase impinge upon the deposition substrate and become adsorbed **onto** the substrate surface. (2) The adsorbed atoms may desorb or may diffuse over the **substrate** surface and may bond to other surface atoms. (3) As time progresses, the surface

con-

dece-

con-

the-

con-

site

the

Th-

con-

CV

ce-

d-

re-

re-

re-

re-

re-

re-

re-

re-

re-

re-

concentrations of adsorbed atoms increases and clusters form. (4) These clusters grow or decay through statistical fluctuation in the adsorbed atom concentration. (5) There exists a critical cluster size above which it is more probable that a cluster will survive and grow than it will decay. The clusters whose size exceeds the critical size during the concentration fluctuation are called the stable clusters. The stable clusters provide suitable sites for growth either from the direct impingement of atoms from the gas phase or from the continued migration of the adsorbed atoms.

Nucleation will stop when crystals have nucleated on all available nucleation sites. Three dimensional growth of individual crystals continues until individual crystals coalesce and continuous film forms.

The detailed chemical mechanism of diamond CVD is not well understood. The CVD growth environment can be quite complex but it is well established that H_2 and carbon containing gases such as CH_4 , CH_3 , C_2H_2 , CO , CO_2 , etc. are required for CVD diamond deposition. Figure 1.5 illustrates the generalized schematic of the chemical processes in a CVD diamond reactor ([1], [3], [12]). As illustrated in Figure 1.5 the reactants (i.e., hydrogen and methane in this example) enter a region within which the molecular hydrogen gas is dissociated into atomic hydrogen (i.e., $H_2 \rightarrow 2H$). This can be accomplished by electron impact dissociation in a plasma or by thermal dissociation in a hot filament. The atomic hydrogen then reacts with carbon containing (i.e., hydrocarbon) gas and produces hydrocarbon radicals such as CH_3 (i.e., $CH_4 + H \rightarrow CH_3 + H_2$). The reactions between hydrocarbon radicals and atomic hydrogen and among hydrocarbon species continue and various species (i.e., CH_3 , CH_2 , C_2H_2 , CH , C_2H_6 , C_2H_4 , etc.) that are known to be the major elements of the gas phase reactions in CVD diamond are

created.

reactions

percent of

generally

reactions

slow bi-m

Figure 1.5. Gene

created. Figure 1.6 shows a schematic of the major elements of this complex set of reactions ([3], [12]). Typically, the hydrocarbon concentration constitutes only a few percent of the total gas concentration. Therefore, the hydrogen transfer reaction rates are generally much greater than the hydrocarbon reaction rates. The principal gas phase reactions involve the rapid hydrogen transfer reactions among the C_1 and C_2 species and slow bi-molecular hydrocarbon reactions forming C_x ($x \geq 2$) species [12].

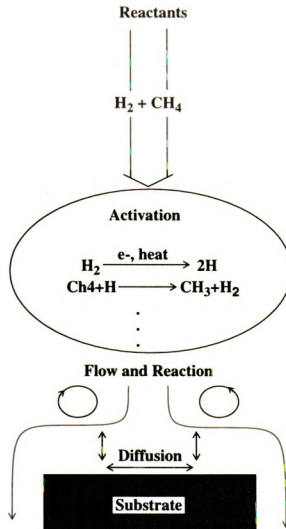


Figure 1.5. Generalized schematic of the chemical processes in a CVD diamond reactor ([1], [13]).

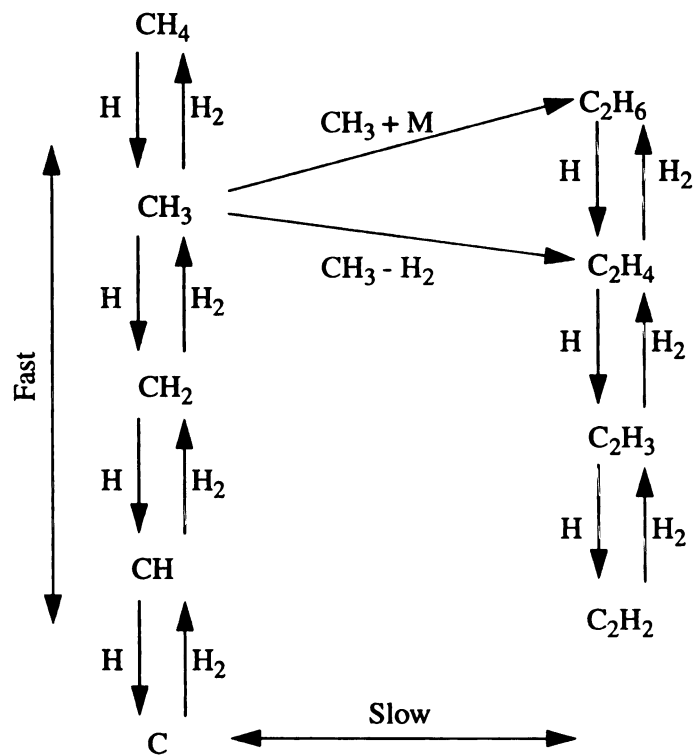


Figure 1.6. Schematic of the major elements of gas phase reactions in CVD diamond ([3], [12]).

large

react

vama

vama

vama

cons

geome

proced

upon in

of input

internal

I Indepe

1.3 A generic block diagram representation of diamond deposition reactors

A plasma assisted diamond CVD reactor is a very complex nonlinear system with a large number of variables. Figure 1.7 shows a generic block diagram of such a deposition reactor. As shown, the experimental variables can be divided into three groups of input variables (U), internal variables (X), and output variables (Y). The input variables are the variables which can be independently controlled by the reactor operator. These input variables are divided into three input sub-vectors (i.e., $U = [U_1, U_2, U_3]$) where U_1 consists of the macroscopic controllable input variables, U_2 consists of the reactor geometry variables, and U_3 consists of the variables that are associated with the deposition procedure and time. In general, as shown in Figure 1.7, output variables are dependent upon input and internal variables (i.e., $Y = g(U, X)$) while internal variables are functions of input variables (i.e., $X = f(U)$). For instance, for a microwave plasma reactor, the input, internal, and output variables include:

I. Independently controlled input variables, U :

(i) Macroscopic controllable input variables U_1 :

- (a) Input microwave power, P_t
- (b) Operating pressure, p
- (c) Total input gas flow rate, f_t
- (d) Gas composition, CH_4 / H_2 , CO_2 / H_2 , etc.

(ii) Reactor geometry variables, U_2 :

- (a) Cavity applicator construction, quartz tube size and shape, end feed gas vs. side feed gas, etc.
- (b) Substrate position and substrate holder design

Il Intern.

- (c) Electromagnetic excitation mode and cavity tuning
- (d) Reactor gas flow configuration
- (e) Vacuum system, pumping speed, volume, etc.
- (f) etc.

(iii) Deposition procedure and time variables, U_3 :

- (a) Substrate seeding procedure
- (b) Start-up and shut down procedure
- (c) Deposition time
- (d) Input power variation vs. time, etc.

II. Internal dependent variables, X :

- (i) Substrate temperature, T_s
- (ii) Gas residence time, t_r
- (iii) Discharge volume V_d , and deposition area, A_d
- (iv) Electric field strength and distribution within the reactor
- (v) Species flux onto the wafer
- (vi) Species flow patterns within the reactor
- (vii) Discharge energy distributions and temperatures
- (viii) Discharge absorbed power densities
- (ix) Mixture and densities of
 - (a) Charged species
 - (b) Excited species
 - (c) Atomic and molecular species
 - (d) Absolute densities and spatial variation of densities within the

III. Out

Associate

The second

The
understand
the influen
input and
performanc
understand

reactor

III. Output variables, Y can be divided into two sets Y_1 and Y_2 . The first set Y_1 is associated with the film properties:

- (i) Surface morphology
- (ii) Grain size
- (iii) Film structural quality (sp^3 phase vs. sp^2 phase)
- (iv) Film uniformity
- (v) Film texture
- (vi) Film electrical resistivity
- (vii) Etc.

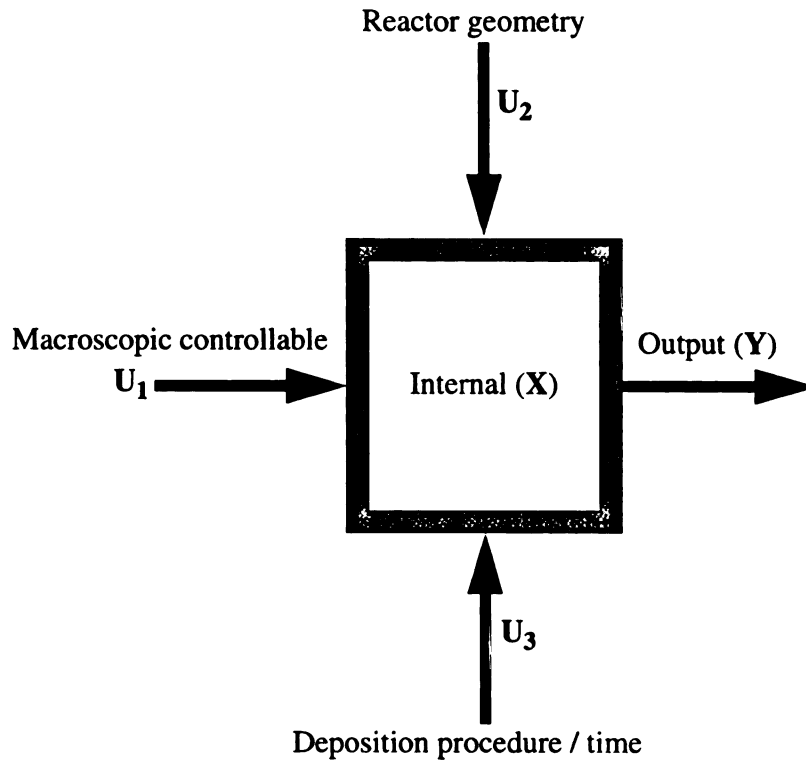
The second set Y_2 is associated with the reactor performance variables such as:

- (i) Film growth rate
- (ii) Carbon conversion efficiency
- (iii) Specific energy or energy efficiency

The large number of experimental input and internal variables indicate that understanding a reactor's behavior is a very complex problem. One needs to understand the influence of each variable on the output performance and the relationships between input and internal variables in order to have a precise knowledge of the reactor performance. Only through a careful experimental parametric study of a reactor can one understand the reactor's deposition behavior.

Mac

In ge



$\mathbf{U}$ = Input variables
 $\mathbf{X}$ = Internal variables
 $\mathbf{Y}$ = Output variables

In general:

$\mathbf{X} = \mathbf{f}(\mathbf{U})$, where: $\mathbf{U} = [\mathbf{U}_1, \mathbf{U}_2, \mathbf{U}_3]$ and
 $\mathbf{U}_1 = (u_1, u_2, u_3, \dots, u_k)$
 $\mathbf{U}_2 = (u_{k+1}, u_{k+2}, \dots, u_q)$
 $\mathbf{U}_3 = (u_{q+1}, u_{q+2}, \dots, u_r)$

$\mathbf{Y} = \mathbf{g}(\mathbf{U}, \mathbf{X})$, where:
 $\mathbf{Y} = (y_1, y_2, y_3, \dots, y_p)$
 $\mathbf{X} = (x_1, x_2, x_3, \dots, x_n)$

Figure 1.7. A generic block diagram for deposition reactors.

consisting

carbon and

by the con

may requi

application

It has bee

diamond c

conditions

another di

step in gro

the films.

quality (sp

diamond f

deposition

output film

understand

used to de

between a

variables he

ze associa

Microwave

1.4 Motivation

CVD diamond films all exhibit a generally similar, polycrystalline morphology consisting of randomly oriented crystals and containing a varying amount of non-diamond carbon and defects. Thus the films have a wide range of properties which are determined by the conditions under which the films are deposited. Each application of CVD diamond may require diamond films with specific properties. For instance, electronic and thermal applications of diamond film require that the defects associated with the films be minimal. It has been established (see Chapter 3) that planar and line defects are abundant in diamond crystals with {111} facet structure which grow under certain set of deposition conditions while these defects are not present in {100} structure which grow under another different set of deposition conditions. Thus the morphology control is a crucial step in growing diamond films that are to be used in electrical and thermal applications of the films. A different application may require diamond films with a certain structural quality (sp^3 vs. sp^2 phase), electrical resistivity, crystal size and/or film thickness. A diamond film with these desired characteristics may be synthesized if the correct deposition conditions are known. Therefore, it is imperative to understand how a reactor's output film properties (Y) are mapped into its input (U) and internal (X) variables (i.e., understand the $Y = g(U, X)$ and $X = f(U)$ relationships) if that reactor is to be repeatedly used to deposit diamond films with specific properties. Understanding the relationship between a reactor's output film characteristics (Y) and its input (U) and internal (X) variables helps understand and control the diamond synthesis and the growth process that are associated with that reactor. Establishing such an experimental understanding of the Microwave Cavity Plasma Reactor has been a major motivation behind the research

presented

15 Object

The

CVD dia

operating

conducted

internal v

In p

experimen

variables

Y_1

Y_2

and the m

and the geo

presented in this research.

1.5 Objectives of the research

The main objective of this investigation was to better understand how to control the CVD diamond growth synthesis of the Microwave Cavity Plasma Reactor (MCPR) [14] operating in the moderate pressure (20-80 torr) regime. A detailed parametric study was conducted in order to understand the relationship between output variables and input/internal variables of the MCPR reactor.

In particular, the objective of the research was, through a series of many separate experiments, to develop an understanding of the relationships between the reactor output variables $Y = [Y_1, Y_2]$

Y_1 :

- (1) Film morphology
- (2) Grain size
- (3) Structural quality (sp^3 phase vs. sp^2 phase)

Y_2 :

- (1) Linear growth rate
- (2) Carbon conversion efficiency
- (3) Specific energy

and the macroscopic controllable input variables (U_1):

- (1) Operating pressure, p
- (2) CH_4/H_2 and CO/H_2 concentrations
- (3) Total gas flow rate, f_t

and the geometry (U_2) and deposition procedure and time variables (U_3) of the microwave

cavity P

The

For inst

structure

1.6 Diss

A re

microwa

presente

propertie

literature

with the

procedu

In Chap

output v

5th quart

only can

(U₁) in

output fi

achieved

utilized

CH₂ is

input var

cavity plasma reactor.

The relationships between $Y_1 \leftrightarrow Y_2$ and $Y_{1i} \leftrightarrow Y_{1j}$ were also to be established.

For instance, the relationship between a certain film morphology (i.e., {100}) and structural quality and/or carbon conversion efficiency was to be established.

1.6 Dissertation outline

A review of some plasma assisted deposition reactors (i.e., microwave plasma tubular, microwave bell-jar, microwave jet, microwave cavity plasma reactors, and hot filament,) is presented in Chapter 2. Chapter 3 presents a literature review on the diamond film properties and reactor performance vs. deposition conditions. It also gives an in-depth literature review of various structural defects (line defect, planar defect, etc.) associated with the diamond structure. Chapter 4 describes the experimental system, experimental procedures and parameter space, and measurement methodologies utilized in this thesis. In Chapter 5 the experimental results that relate the microwave cavity plasma reactor's output variables ($Y = [Y_1, Y_2]$) to several input and internal variables are presented for a 5" quartz dome/3" substrate reactor geometry (U_2). The methane gas (i.e., CH_4) is the only carbon containing gas that is utilized as a macroscopically controllable input variable (U_1) in the experiments presented in Chapter 5. The effect of deposition time, t on the output film properties is also presented in Chapter 5. In Chapter 6 the experimental results achieved when a different reactor geometry (i.e., 4" quartz dome/2" substrate) (U_2) was utilized for diamond deposition is presented. As with Chapter 5, the methane gas (i.e., CH_4) is the only carbon containing gas that is utilized as a macroscopically controllable input variable (U_1) in the experiments presented in Chapter 6. Chapter 7 presents the

experimental.

no CH_4 gas.

It should be

CO gas to ex

only a prelim

§ presents the

diamond film

developed to

presents a su

and detailed

asked to read

experimental results of the preliminary exploration of the CO-H₂ diamond deposition (i.e., no CH₄ gas). The 5" quartz dome/3" substrate reactor geometry was utilized in this work. It should be emphasized that only a limited number of experiments were conducted with CO gas to explore CO-H₂ diamond deposition and the data presented in Chapter 7 reflect only a preliminary exploration of the diamond deposition with CO and H₂ gases. Chapter 8 presents the deposition process methodology and the experimental results for depositing diamond films on tungsten substrates. This chapter also discusses the technique that was developed to improve the adhesion of diamond film on tungsten substrates. Chapter 9 presents a summary of the experimental results of this thesis research. This thesis is long and detailed and readers who would like to read the results without reading the details are asked to read this summary chapter.

CHAPTER 2

A Review of Deposition Reactors

2.1 Introduction

This chapter presents a review of some deposition reactors and compares the reactors' performances.

Presently there are several deposition reactors which are utilized for diamond deposition. Some of these are Microwave Plasma Tubular, DC Plasma, DC Jet, Flame, Hot Filament, Microwave Cavity Plasma Reactor (MCPR), RF Thermal, Bell-Jar microwave, and Microwave Jet reactors. A microwave reactor (i.e., MCPR) is experimentally examined in this research to determine its output film properties (Y_1) and deposition performance (Y_2). Therefore, in this chapter the emphasis is placed on microwave reactors. For the sake of brevity only the Microwave Plasma Tubular, Bell-Jar Microwave, Microwave Jet, and Microwave Cavity Plasma reactors among the microwave reactors and Hot Filament among other types of reactors are described in this chapter. For comparison purpose, this chapter however provides a summary of the performance of many other reactors. The criteria for comparison will be linear growth rate ($\mu\text{ m/hr}$), weight gain (mg./hr), deposition area (cm^2), carbon conversion efficiency, and energy efficiency (mg./KW-hr). The definitions and methods of calculation of these output variables (Y) are given in detail in Chapter 4.

Th
through
this mac

22 Micr

Fig
configur
the com
substrat
plasma a
arrangen
silica tub
and can
it is etch
dioxide
disadvan
because
wave gu

Typ
are as fo
1-400) to
flow rate
wafer, an

The Michigan State University microwave plasma deposition machine is utilized throughout this research for its output film properties and deposition performance. Thus this machine is described in a greater detail.

2.2 Microwave plasma tubular reactor

Figure 2.1 shows the schematic drawing of a microwave plasma tubular reactor. This configuration was popular at the early stages of microwave reactor development and still is the commonly used microwave reactor in research. The substrate is placed on a plate (substrate holder) which is inserted from the bottom of a silica tube. The substrate and plasma are contained within the tube. The plate may be equipped with cooling or heating arrangements so that an independent substrate temperature control may be achieved. A silica tube is used because it is vacuum compatible, does not absorb microwave radiation, and can operate at temperatures up to 1200 °C. A disadvantage of using silica tube is that it is etched by hydrogen plasma when the tube walls are touched by the discharge. Silicon dioxide is then incorporated in the film. This configuration suffers from another disadvantage of being limited to a small substrate size (diameter ≤ 3 cm) [1]. This is because the diameter of the silica tube is limited by the maximum size of the rectangular wave guide.

Typical diamond film deposition conditions for a microwave plasma tubular reactor are as follows ([1], [14]): excitation frequency (U_1) = 2.45 GHz, operating pressure (U_1) = 1–400 torr, methane concentration (U_1) = 0.1 - 5.0% (i.e., $CH_4/H_2 = 0.1 - 5.0\%$), total gas flow rate (U_1) = 50 - 500 sccm, tube diameter (U_2) = 4.0 cm, substrate (U_2) = silicon wafer, and substrate temperature (X) = 400 - 1000°C. Linear growth rate (Y_2) of $\sim 3 \mu m/$

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

hr with deposition area of $\sim 3 - 6 \text{ cm}^2$ and weight gain (Y_2) of $\sim 3 - 6 \text{ mg./hr}$ are reported in the literature.

2.3 Bell-jar microwave reactor

The schematic drawing of a Bell-Jar microwave reactor is shown in Figure 2.2. The reactor consists ([1], [14]) of a cylindrical wave guide, a quartz bell jar, an adjustable substrate holder, a rectangular wave guide, and an antenna. Input gas is fed into the bell jar through an input gas tunnel and the microwave energy is introduced into the cylindrical wave guide through a rectangular wave guide and an antenna. The microwave energy dissociates the input gas which is mainly comprised of hydrogen, hydrocarbon (i.e., methane), and possibly oxygen gases and forms a ball-like discharge (i.e., plasma) above the substrate. The tuning of the cavity is changed by vertical position of the substrate holder arrangement and influences the intensity and position of the plasma ball [1]. Substrate heating is primarily done by species recombination on the substrate but an external substrate heating or cooling arrangement may also be utilized to independently heat or cool the substrate.

Typical diamond film deposition conditions for a bell-jar microwave reactor are as follows ([1], [14]): operating pressure (U_1) = 40 - 70 torr, methane concentration (U_1) = 0.50 - 5.0% (i.e., $\text{CH}_4/\text{H}_2 = 0.50 - 5.0\%$), and total gas flow rate (U_1) = 200 - 600 sccm, substrate (U_2) = Si, substrate temperature (X) = 850 °C - 1030 °C. Linear growth rate (Y_2) of $\sim 3.5 \mu \text{ m/hr}$ with deposition area of $\sim 12.5 \text{ cm}^2$ and weight gain (Y_2) of 15.4 mg./hr are reported.

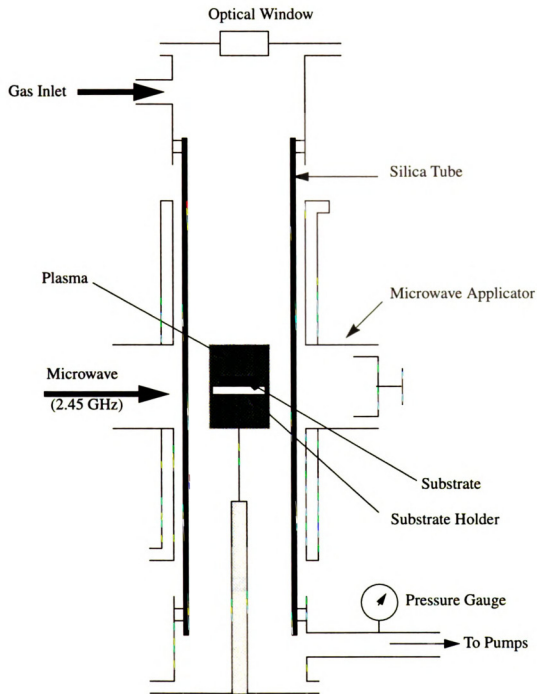


Figure 2.1. Schematic drawing of a tube-style microwave plasma CVD reactor [1].

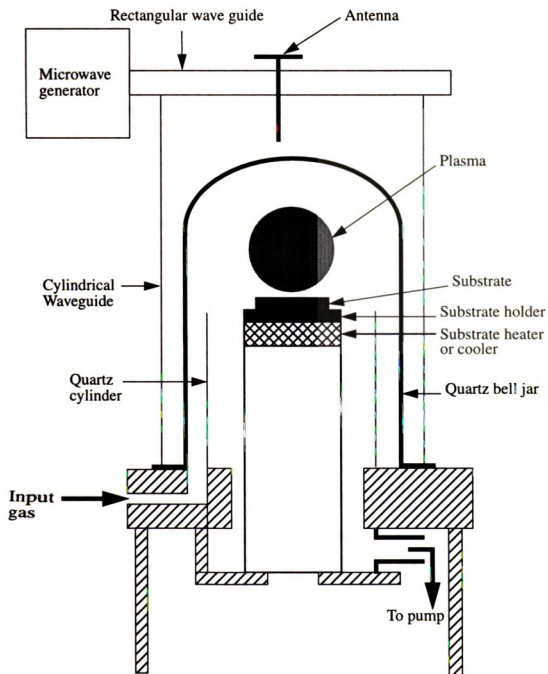


Figure 2.2. Schematic drawing of microwave Bell-Jar reactor ([1], [14]).

1

2

3

4

5

6

7

8

9

10

11

12

13

2.4 Microwave jet reactor

Figure 2.3 illustrates a schematic drawing of a microwave jet reactor ([14], [15]). Microwave energy, which creates a plasma which in turn dissociates the input gas, is supplied by a 2.45 GHz, 5 KW microwave generator. A microwave discharge is created at high pressure (greater than 0.50 atmosphere) and is located at the end of the center conductor. The input gas which is normally a mixture of hydrogen, hydrocarbon, and possibly oxygen gases is dissociated near the jet nozzle where a microwave high pressure arc discharge is created and the dissociated gas flows into the deposition chamber where the substrate is located. The substrate is placed on a water cooled substrate holder. Diamond film is deposited when plasma species react on the substrate surface. The diameter of the inner and outer conductors in the coaxial wave guides are 20 and 57.2 mm, respectively and they are water cooled to prevent thermal evaporation.

Typical diamond growth conditions are [15]: microwave power (U_1) = 3.8 - 4.2 KW, excitation frequency (U_1) = 2.45 GHz, H_2 flow rate (U_1) = 2×10^4 sccm, Ar/H_2 (U_1) = 50%, CH_4/H_2 (U_1) = 2.0%, O_2/H_2 (U_1) = 2.0%, operating pressure (U_1) = 1 atm. (760 torr), substrate (U_2) = Si, and substrate temperature (X) = 890 - 930 °C. High linear growth rate (Y_2) of $\sim 12 \mu m/hr$ with small deposition area of $\sim 2.5 cm^2$ and weight gain (Y_2) of $\sim 10.5 mg/hr$ are reported in the literature.

2.5 Hot filament reactor (HFCVD)

Figure 2.4 depicts a hot filament CVD configuration ([1], [14]). The reactor consists of an SiO_2 chamber, a substrate holder, filament(s), substrate heater, and if desired, a

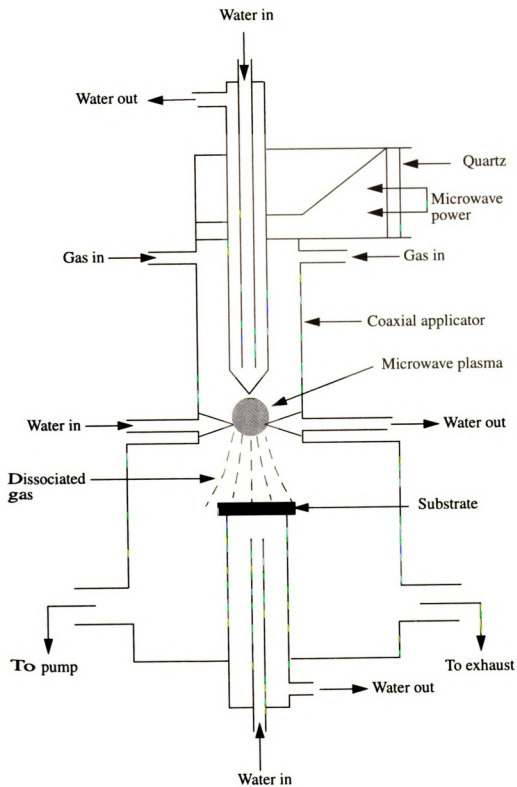


Figure 2.3. Schematic drawing of microwave jet reactor ([14], [15]).

st

n

el

N

f

de

Al

me

is

ad

HF

Fl

to

of

car

dis

det

betw

199

sons

subst

excl

substrate bias arrangement. Atomic hydrogen is produced by passing H_2 over a hot filament with temperature between $1800\text{ }^{\circ}\text{C}$ and $2400\text{ }^{\circ}\text{C}$. The filament is heated by an electric current. The feed gas which is normally a mixture of hydrogen, hydrocarbon and possibly other gases is dissociated when it is heated by the hot filament. The substrate is placed near the hot filament ($0.5\text{ -}2\text{ cm}$ from the filament [10]) and diamond film is deposited on the substrate where the dissociated gas species react on its surface. Various kinds of refractory metals such as tungsten, tantalum, and rhenium are used as filament material. Multiple filaments may be utilized to increase the deposition area. The substrate is usually independently heated to a temperature between $500\text{ }^{\circ}\text{C}$ and $1000\text{ }^{\circ}\text{C}$. Among advantages of this reactor configuration are its simplicity and relative ease of scaling. The HFCVD is an appropriate choice if deposition of very pure film is not mandatory. Filament erosion and breakage during the deposition process and film contamination due to filament erosion are among the disadvantages of this reactor type. Long-term stability of the filament is marred primarily by the corrosion of the filament and the formation of carbides on the filament during the deposition period which causes the filament to sag or distort [10]. This leads to non-uniform temperature distribution over the substrate which is detrimental to film uniformity.

A bias voltage ($>120\text{ V}$) may be employed in the HFCVD method. It is applied between substrate and filament with substrate being positive with respect to the filament [10]. Electrons emitted from the filament accelerate toward the substrate while heavier ions are repelled by the positively charged substrate. The impact of electrons with substrate enhances the reactivity of graphite (if formed) with atomic hydrogen through excitation of π electrons and fragmentation of hydrocarbon species at or near the substrate

2-1

2-1

2-1

(1)

2-1

U₁

U₁

Y₂

2-1

2-1

26.1

26.1

2-1

2-1

2-1

2-1

2-1

2-1

2-1

surface [10]. The biasing mechanism enhances nucleation density, improves the growth rate, and permits deposition of diamond at lower substrate temperatures [10]. It however, may be detrimental to the film quality [10].

Typical diamond film deposition conditions for a hot filament reactor are as follows ([10], [14]): operating pressure (U_1) = 10 - 100 torr, CH_4/H_2 (U_1) = 0.1 - 2%, total gas flow rate (U_1) = 100 sccm, filament temperature (U_1) = 2000°C - 2400°C, filament voltage (U_1) = 30 V, filament current (U_1) = 28 A, heater voltage (U_1) = 70 V, and heater current (U_1) = 6.5 A, substrate (U_2) = Si, substrate temperature (X) = 700-1000°C, deposition rate (Y_2) = 0.3 -20 μ m/hr, typical deposition rate (Y_2) = 1 μ m/hr for high quality films, deposition area of ~ 6.5 cm² (up scalable), and weight gain (Y_2) of 1.35 mg./hr are reported.

2.6 Microwave cavity plasma reactor (MCPR)

2.6.1 Basic description of the reactor

In order to make it possible to deposit diamond films on large surface areas, three generations of 7 inch Microwave Cavity Plasma Reactors (MCPR7) have been designed at Michigan State University. Jie Zhang [14] provides a detailed description of the three generations of MCPR reactor design and their performance. Due to a number of problems associated with the first and second generation of the MCPR7s (i.e., near field effect problem caused by using side feed assembly and O-ring over heating problem, respectively) [14], the most advanced generation (i.e., third generation) of the MCPR7s was used for diamond deposition in this research. In what follows a basic description of

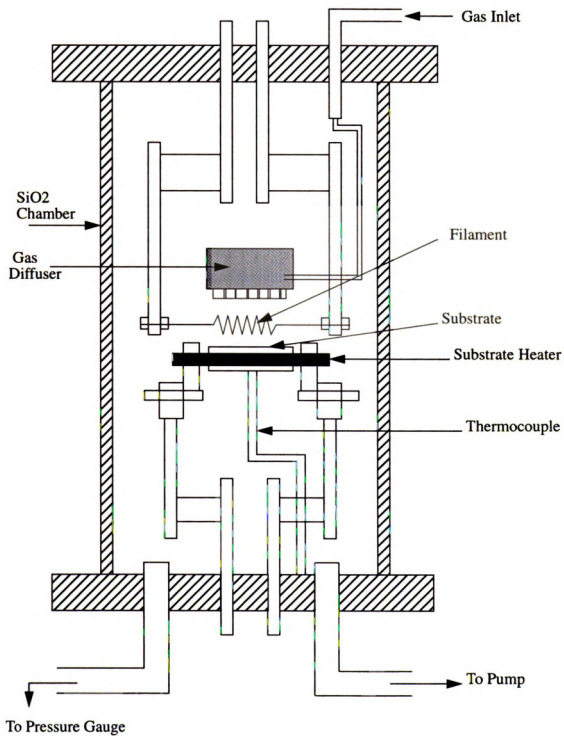
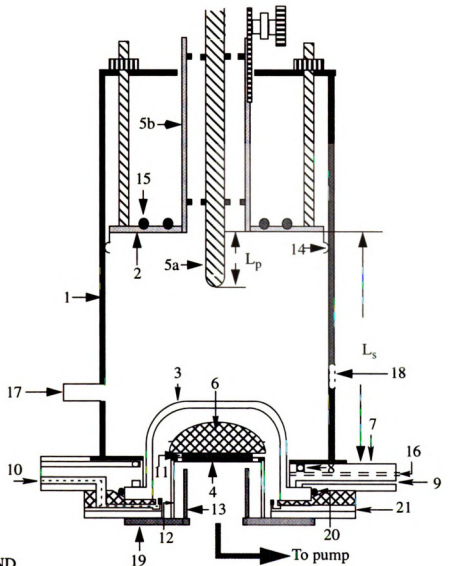


Figure 2.4. Schematic drawing of a Hot filament CVD reactor ([1], [14]).

th
S
d
A
co
m
st
w
s
co
at
ple
the
pl
me
me
M
co
sb
sy
in o
of th
19

this reactor is provided. Figure 2.5 shows a schematic drawing of the most advanced generation (i.e., third generation) of MCPR7 configuration. In what follows a basic description of this reactor is provided. Figure 2.5 shows a schematic drawing of the most advanced generation (i.e., third generation) of MCPR7 configuration. The reactor mainly consists of the following components: a cylindrical cavity (1) with an inner diameter of 7 inches which forms the outer conducting shell of the cavity applicator, a water cooled sliding short (2) which forms the top end of the cavity and is electrically shorted to cavity walls via a finger stock (14), a quartz dome (3) with a sealing O-ring (20) around it, a substrate holder assembly (4), an adjustable coaxial power input port (5), and a water cooled base plate (7). Water cooling of the sliding short and the base plate is done via annular water cooling channels (8, 15). There is also an air cooling channel (9) on the base plate and a cooling air inlet (17) on the cavity wall. Atmospheric air is then forced through the air inlet (17) to cool the quartz dome. Several ports (16) are incorporated in the base plate for laser diagnosis of microwave discharge (i.e., hydrogen translational temperature measurement). A screen window (18) is cut into the cavity wall for substrate temperature measurement and for viewing the plasma. It also serves as the cooling air outlet. Microwave power is coupled into the cavity applicator through a 1 5/8 inch adjustable coaxial wave guide (5) which consists of a coupling probe (5a) and its outer conductor (5b). The sliding short (2) can be moved back and forth along the longitudinal axis of the cylindrical cavity walls changing the electrical and physical height of the cavity applicator in order to excite the desired electromagnetic mode and also to achieve optimal matching of the incident microwave power (i.e., to minimize reflected power). An input gas tunnel (10) leads the reactive gases through the gas distribution plate (21) into the quartz dome



LEGEND

- | | |
|--------------------------|-----------------------------|
| (1) Cavity | (12) Quartz tube |
| (2) Sliding short | (13) Metal tube |
| (3) Quartz dome | (14) Finger stock |
| (4) Substrate holder | (15) Cooling water |
| (5) Coaxial cable | (16) Laser port |
| (6) Plasma discharge | (17) Cooling air inlet |
| (7) Base plate | (18) Viewing window |
| (8) Water cooling tunnel | (19) Metal plate |
| (9) Air cooling tunnel | (20) Sealing O-ring |
| (10) Gas input tunnel | (21) Gas distribution plate |
| (11) Substrate | |

Figure 2.5. MCPR-3 reactor under forced flow configuration.

where the microwave fields produce a microwave discharge (i.e., microwave plasma) (6) in the proximity of the substrate. The microwave plasma consists of a mixture of dissociated charged species, electrons, and neutral gases. The substrate (11) is placed on top of a substrate holder (4) which is supported by a quartz tube (12). Quartz tubes of different heights may be used to change the position of the substrate with respect to the plasma. A metal tube (13) which serves as a resonance breaker is placed inside the quartz tube. The metal tube prevents the plasma discharge from forming underneath the substrate by reducing the electric field underneath the substrate. The metal tube (13) and quartz tube (12) are placed on a metal plate (19) which has ~ 1" in diameter hole in its center to pass the hot gases from within the quartz dome (3) to the pump. L_s and L_p denote the cavity length and the probe length, respectively. The MCPR7 design creates a hemisphere shaped discharge over the substrate. The reactor is mounted on a vacuum chamber with chamber outlet leading to vacuum pump [14].

The MCPR7 reactor utilizes a flow pattern regulator for the substrate holder (4) as shown in Figure 2.6. The flow pattern regulator is a plate with a series of holes which directs the gas flow as it flows through the plasma and the substrate. This configuration increases the uniformity of the deposition by influencing the shape of the plasma discharge by changing the flow pattern into the plasma discharge [14].

2.6.2 Approximate determination of the empty cavity electromagnetic modes

The MCPR creates a microwave discharge when it is excited in a single cavity electromagnetic mode. Figure 2.7 shows an empty circular cavity of length L_s (in z direction) and radius a . For such a cavity the choice of the excitation mode depends on the

200

200

200

excitation frequency f_0 and the cavity radius a and length L_s . The relationship between the cavity radius and length and the excitation frequency f_0 are obtained from the hertz potential functions as follows [16].

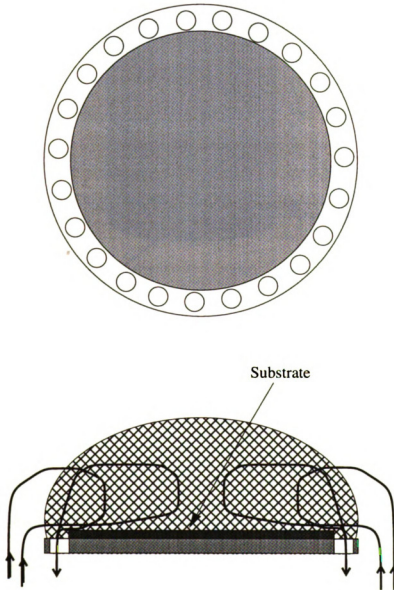


Figure 2.6. Flow pattern regulator (4) with substrate (11) [14].

TE

E

This po

π

∇

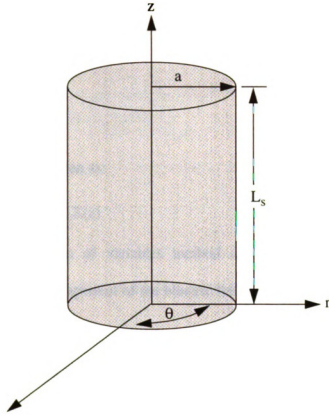


Figure 2.7. An empty circular cavity of length L_s and radius a .

(i) TE_{nml} modes:

$\mathbf{E}$ and $\mathbf{H}$ fields of TE_{nml} modes are obtained from a magnetic Hertz potential π_h .

This potential is related to the Hertz potential by the following equations.

$\pi_h = z \pi_h$ where

$\nabla^2 \pi_h + k^2 \pi_h = 0$ or in the cylindrical coordinate system

the ec

1

1

where

2

2

condit

this ec

2

where

(ie. k

7

radius

(

where

n

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \pi_h}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \pi_h}{\partial \theta^2} + \frac{\partial^2 \pi_h}{\partial z^2} + k^2 \pi_h = 0$$

where $k = \omega \sqrt{\mu \epsilon}$, ω is the operating frequency, μ is the permeability and ϵ is the dielectric permittivity inside the cavity.

$$\mathbf{E} = -j\omega\mu \nabla \times \pi_h$$

$$\mathbf{H} = k^2 \pi_h + \nabla (\nabla \cdot \pi_h)$$

where $\pi_h(r, \theta, z)$ can be written as:

$$\pi_h(r, \theta, z) = R(r) \cdot \Theta(\theta) \cdot Z(z)$$

Applying the separation of variables method and using appropriate boundary conditions (i.e., tangential component of the electric field is zero on a perfect conductor) this equation simplifies to:

$$\pi_h(r, \theta, z) = A J_n \left(\frac{\rho'_{nm}}{a} r \right) \begin{pmatrix} \cos n\theta \\ \sin n\theta \end{pmatrix} \sin \frac{l\pi}{L_s} z$$

where J_n is the Bessel function of the first kind of order n , $\rho'_{nm} = m^{\text{th}}$ root of $J'_n(x) = 0$

(i.e., $k_r = \frac{\rho'_{nm}}{a}$), and $k_z = \frac{l\pi}{L_s}$.

The relationship between resonant frequency f_0 and the cavity length, L_s and cavity radius, a is determined from the following equation:

$$(f_0)_{nml} = \frac{v_c}{2\pi} \left\langle \left(\frac{\rho'_{nm}}{a} \right)^2 + \left(\frac{l\pi}{L_s} \right)^2 \right\rangle^{\frac{1}{2}} \quad \text{For TE}_{nml} \text{ modes} \quad (\text{eqn. 2.1})$$

where

$$n = 0, 1, 2, 3, \dots$$

$$m = 1, 2, 3, \dots$$

$$l = 1, 2, 3, \dots$$

and $v_c = \frac{1}{\sqrt{\mu\epsilon}}$ is the speed of light.

(ii) TM_{nml} modes:

$$\pi_e(r, \theta, z) = BJ_n(k_r r) \begin{pmatrix} \cos n\theta \\ \sin n\theta \end{pmatrix} \begin{pmatrix} \cos k_z z \\ \sin k_z z \end{pmatrix}$$

and

$$\mathbf{E} = k^2 \pi_e + \nabla (\nabla \cdot \pi_e)$$

$$\mathbf{H} = j\omega\epsilon \nabla \times \pi_e$$

Using appropriate boundary conditions, the electric Hertz potential equation simplifies to:

$$\pi_e(r, \theta, z) = BJ_n\left(\frac{\rho_{nm}}{a}r\right) \begin{pmatrix} \cos n\theta \\ \sin n\theta \end{pmatrix} \cos \frac{l\pi}{L_s} z$$

and the relationship between resonant frequency f_o and the cavity length, L_s and cavity radius, a is determined from the following equation:

$$(f_o)_{nml} = \frac{v_c}{2\pi} \left\langle \left(\frac{\rho_{nm}}{a} \right)^2 + \left(\frac{l\pi}{L_s} \right)^2 \right\rangle^{\frac{1}{2}} \quad \text{For } TM_{nml} \text{ modes} \quad (\text{eqn. 2.2})$$

where

$$n = 0, 1, 2, 3, \dots$$

$$m = 1, 2, 3, \dots$$

$$l = 0, 1, 2, 3, \dots$$

and $\rho_{nm} = m^{\text{th}}$ root of $J_n(x)=0$, and $v_c = \frac{1}{\sqrt{\mu\epsilon}}$ is the speed of light.

Figure 2.8 shows the excitation frequency vs. cavity length mode diagram of an ideal 7 inch diameter empty cavity [14]. Each curve is determined from (eqn. 2.1) or (eqn. 2.2) by plotting f_0 vs. L_s for various TE_{nml} and TM_{nml} modes. Each mode was experimentally evaluated for its potential to deposit CVD diamond films at discharge pressures of 30-80 torr [14]. The mode diagram of Figure 2.8 shows what mode(s) are excited at a given excitation frequency and cavity length, L_s for cavity diameter fixed at 7". For instance, it illustrates that for the frequency fixed at 2.45 GHz, TE_{111} , TM_{011} , $TE_{211}, \dots$, TE_{113} modes are excited as the cavity length is changed from $L_s \sim 7$ cm to $L_s \sim 20$ cm. Therefore, through a careful adjustment of the cavity length and radius it is possible to achieve the desired excitation mode. The current MCPR reactor is utilizing end feed probe coupling. In end feed probe coupling TM (i.e., TM_{011} , TM_{012} , and TM_{013} , etc.) modes are easily excited. In the case of the TM_{011} mode of excitation the coupling probe is located close to the top surface of the quartz dome. This is evident from the mode diagram of Figure 2.8 which shows that the cavity length must be fixed at ~ 7 cm (i.e., $L_s = 7$ cm) if TM_{011} mode is to be excited. From the schematic drawing of the reactor shown in Figure 2.5 it can be seen that this will put the microwave coupling probe very close to the top of the quartz dome. This allows the near field of the coupling probe to influence the shape of the discharge under high power conditions. The microwave coupling probe's strong near field attracts the plasma to the top of the quartz dome and causes the dome to over heat and melt. Therefore, to eliminate this near field effect, cavity length is adjusted so that only TM_{013} mode is excited (i.e., microwave coupling probe is further away from

the quartz dome top). It was determined by Jie Zhang [17] that the TM_{013} mode was a suitable electromagnetic mode for exciting an almost hemispheric discharge that is formed in contact with the substrate, away from the dome walls. Figure 2.9 shows the field patterns of TM_{011} and TM_{013} modes. For a cavity under discharge loaded conditions excited in the TM_{013} mode the cavity length, L_s is adjusted to approximately 21.6 cm and the probe length L_p is adjusted to about 3.2 cm [14].

2.7 Examples of various reactors' film characteristics

Table 2.1 includes a summary of a selected set of film characteristics of various reactors [14]. Figure 2.10 illustrates the linear growth rate ($\mu\text{m/hr}$) for different diamond CVD methods vs. gas temperature in their activation zones [25]. It shows that a linear growth rate between $\sim 0.05 \mu\text{m/hr}$ and $\sim 1000 \mu\text{m/hr}$ is achievable depending on the deposition method used.

2.8 A common feature among various diamond CVD reactors

Despite a considerable variations in terms of film properties (i.e., growth rate, uniformity, etc.) that exist among various CVD deposition reactors, Bachmann [25] shows that all CVD diamond deposition reactors have one thing in common; regardless of the CVD diamond deposition method, low pressure diamond synthesis is only feasible within a well-defined area of the so called C-H-O phase diagram. Bachmann has introduced a C-H-O diagram that provides a common feature for all major CVD diamond deposition methods. Figure 2.11 shows the Bachmann C-H-O phase diagram. The phase diagram shows that low pressure diamond synthesis is only feasible within a well-defined area of

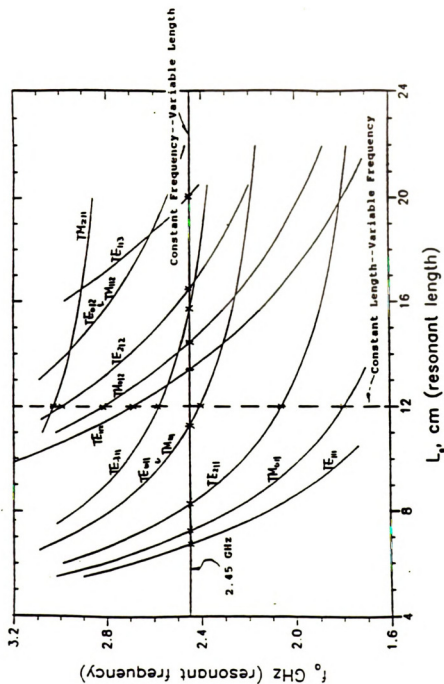


Figure 2.8. Mode diagram of an ideal 7 inch cavity [14].

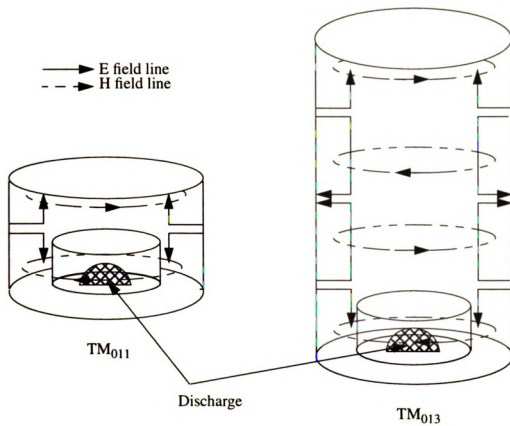


Figure 2.9. Field patterns of discharge loaded TM_{011} and TM_{013} modes [14].

Table 2.1. A summary of film characteristics of various reactors.

Reactor	Linear growth rate ($\mu\text{ m/hr}$)	Deposition area (cm^2)	Weight gain (mg./hr)	Energy efficiency (mg./KW-hr)	% Carbon conversion efficiency
Hot Filament [18]	0.6	6.4	1.35	1.04	0.32
DC Plasma ([19], [20])	20	0.25	1.76	0.56	13.7
DC Jet [21]	900	2	632	57	1.97
Flame [22]	60	0.28	5.9	n/a	0.009
RF Thermal [23]	60	3	63	1.05	0.2
Tubular MW [24]	3.0	3-6	3-5	4.3-8.6	n/a
Bell-Jar MW [25]	3.5	12.5	15.4	10.3	4.2
MW Jet ([15], [26])	12	2.5	10.53	2.6	0.055
Microwave Plasma Cavity [14]	0.55	81	14.8	6.73	5.5
Microwave Plasma Cavity High pressure [27]	6.27	20.3	44.7	14.5	7.7
Microwave Plasma Cavity Intermediate pressure	0.663	45.6	10.40	4.14	5.42

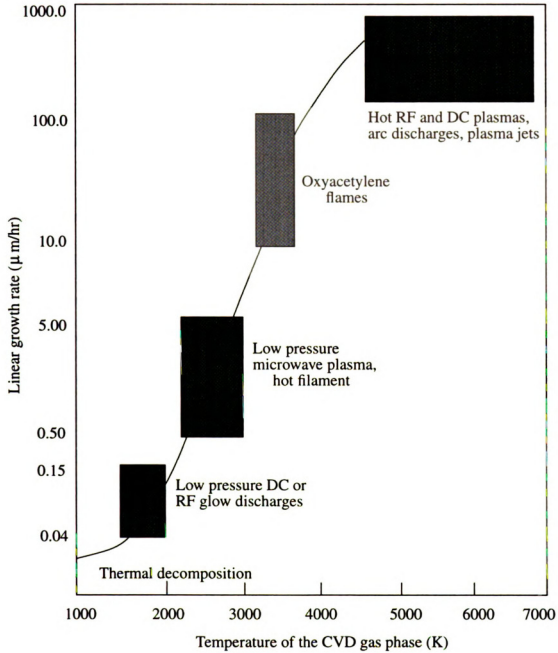


Figure 2.10. Linear growth rate (m/hr) for different diamond CVD methods vs. gas temperature in their activation zones [25].

the diagram. The rule for C-H-O phase diagram construction is to calculate the carbon: hydrogen: oxygen ratios of the corresponding gas phases which allow the calculation of the coordinates of data points in the atomic C-H-O phase diagram. For instance, pure carbon monoxide is comprised of 50% C and 50% O. Hence it is located on the C-O side of the triangle at 0.50. A gas mixture comprised of 400 sccm H_2 (i.e., 800 sccm H) and 40 sccm CO is found at

$$X_{C-O} = C/(C+O) = 40/(40+40) = 0.50$$

$$X_{H-C} = H/(H+C) = 800/(800+40) = 0.952$$

$$X_{O-H} = O/(O+H) = 40/(40+800) = 0.048$$

which is located on the CO line at the lower left corner of the Bachmann phase diagram.

Finally a gas mixture of 200 sccm H_2 and $CH_4/H_2=2.0\%$ has:

$H=400$ sccm from hydrogen flow

$CH_4/H_2 = 2.0\%$ or $CH_4 = 8$ sccm or $C = 8/5 = 1.6$ sccm and $H = 4 \times 1.6 = 6.4$ sccm,

Therefore, $H/(H+C) = (400+6.4)/((400+6.4)+1.6) = 0.9961$

This point is found on the lower end of the $H/(H+C)$ side of the Bachmann triangle.

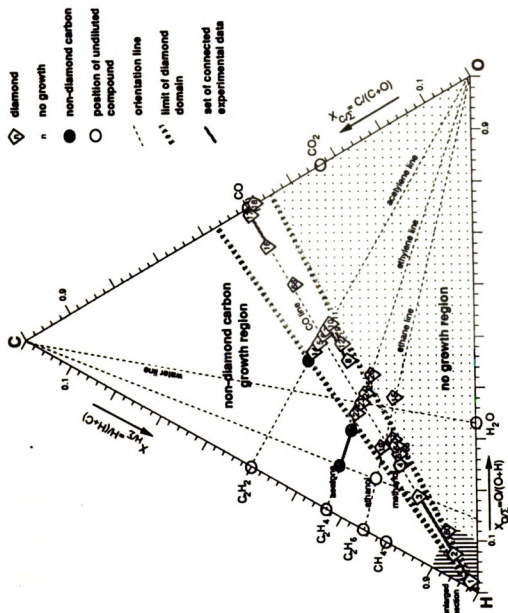


Figure 2.11. Atomic C-H-O diamond deposition phase diagram developed by Bachmann [25].

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

CHAPTER 3

Literature Review on Film Properties vs. Deposition Conditions

3.1 Introduction

In order to understand why certain morphology, structural quality, texture, and other characteristics of a film occur under certain conditions, it is necessary to understand the crystal lattice from its structural point of view. For example, to understand why {111} facets are rough and have high growth rates while {100} facets are smooth and have low growth rates or why a certain film texture develops, it is necessary to understand why and how defects get incorporated into the lattice and how they affect certain crystal characteristics. Establishing a link between the internal characteristics of the diamond crystal and its various properties is the purpose of this chapter.

3.2 Textures and morphologies of CVD diamond films

Texture direction is by definition the direction of fastest growth. Texture development can be explained by the van der Drift competitive growth model [28]. According to this model, in the case of CVD layers it appears to be necessary to consider as a property the vertical (perpendicular to substrate) growth rate of the individual crystals, the rate at which the highest point of the crystal rises. The larger the vertical growth rate, the greater the probability of survival. Randomly oriented nuclei grow competitively on

the substrate. With increasing film thickness, more and more grains are overgrown and buried by adjacent grains. Only those crystals with maximum vertical growth rate will survive and determine the final texture-morphology/morphologies of the film. The result is a pronounced fiber texture where the fiber axis equals the direction of fastest growth and the degree of texturing increases with increasing film thickness as shown in Figure 3.1.

Morphology, structural quality, and other properties of CVD diamond films depend strongly on the deposition conditions. Through a careful adjustment of these conditions it is possible to optimize the properties of diamond films for specific applications. According to Clausing ([29], [30]) (HFCVD method), Wild ([31], [32]) (MWPCVD method), and Spitsyn [8] (CTR method), crystal shapes can be used to determine growth rates in various crystallographic directions. For isolated untwinned crystals, they describe

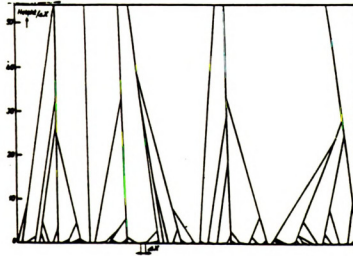


Figure 3.1. The van der Drift competitive growth model [28].

how the relative growth velocities in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions determine crystal shape. They define a growth parameter $\alpha = \sqrt{3} V_{100} / V_{111}$ with V_{100} and V_{111} as the growth rates in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively. The α values range between 1 for a cube and 3 for an octahedron. Figure 3.2 shows crystal shapes for different α values ([10], [31], [32]). The longest direction in a cube is the $\langle 111 \rangle$ diagonal ($\alpha=1$), the longest direction in the cubo octahedron is the $\langle 110 \rangle$ direction ($\alpha = 1.5$), and the longest direction in the octahedron is the $\langle 100 \rangle$ diagonal ($\alpha = 3$). Therefore, according to the van der Drift theory, for films grown with $\alpha = 1$ a $\langle 111 \rangle$ texture, for films with $\alpha = 1.5$ a $\langle 110 \rangle$ texture, and for films with $\alpha = 3$ a $\langle 100 \rangle$ texture will develop.

The structural quality of diamond films is shown to be dependent on the details of growth on $\{111\}$ and $\{100\}$ facets. Films with $\{111\}$ facet show rough surfaces and contain extensive twinning and stacking fault features while the crystals in the $\{100\}$ faceted films are smooth and free of planar defects but contain point defects in grain boundaries ([33], [34], [35]).

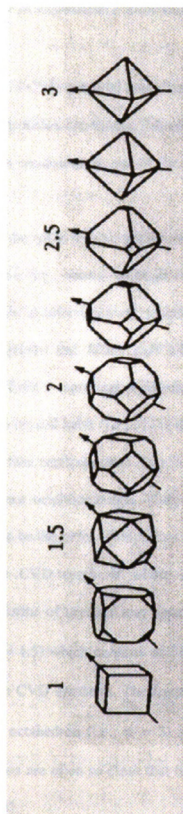


Figure 3.2. Various crystal habits and their corresponding $\alpha = \sqrt{3} V_{100} / V_{111}$ values ($\{10\}$, $\{31\}$, $\{32\}$).

3.3 Reacto

3.3.1 Film

3.3.1.1 Mo

Surfa

links crys

morpholog

requiremen

Diam

under equi

diamonds)

followed b

crystallizat

also shows

the cube (f

energy res

{111}, {10

Under

equilibrium

cubo octah

formed unc

(i.e., $\alpha =$

$\langle 111 \rangle$ and

form in a sin

3.3 Reactor output variables $Y = [Y_1, Y_2]$ vs. deposition conditions

3.3.1 Film properties (Y_1) vs. deposition conditions

3.3.1.1 Morphology

Surface morphology of CVD diamond is proven to be an indication of its quality. It links crystal structure to deposition conditions. Therefore, a detailed understanding of film morphology vs. deposition conditions is crucial for developing films that meet specific requirements.

Diamond belongs to the cubic crystal system and based on the Wulff criterion [36], under equilibrium condition (i.e., natural or High Pressure High Temperature (HPHT) diamonds), the most stable diamond growth planes are the octahedral $\{111\}$ planes followed by cube $\{100\}$ planes and finally roof like $\{110\}$ planes. Provided that the crystallization takes place from a vapor and equilibrium conditions persist, Hartman [37] also shows that octahedron crystal habit (i.e., $\{111\}$ faces) is energetically favorable over the cube ($\{100\}$ faces) for face cubic centered (f.c.c.) structures assuming that most of the energy resides in the nearest neighbor bonds. With this assumption, Hartman finds the $\{111\}$, $\{100\}$, and $\{110\}$ to be the order of important (energetically favorable) facets.

Under low pressure CVD synthesis where diamond is metastable (i.e., non-equilibrium state), other forms of crystals may form and even dominate. In particular, cubo octahedron (i.e., $\alpha = 1.5$) which consists of $\{111\}$ and $\{100\}$ facets is frequently formed under low pressure CVD synthesis. The frequent appearance of cubo octahedron (i.e., $\alpha = 1.5$) instead of octahedron (i.e., $\alpha = 3$) indicates that the growth rate along $\langle 111 \rangle$ and $\langle 100 \rangle$ directions are often so close that both $\{111\}$ and $\{100\}$ crystal planes form in a single crystal [34].

1

!

2

6

1

2

三

泡

2

5.

5.

515

3.3.1.2 Film morphology vs. deposition condition

In what follows, the experiments performed by several researchers to relate diamond film surface morphology to deposition conditions are presented. Methane concentration in hydrogen and substrate temperature are known to be fundamental in shaping the crystal habit. Most literature concentrates primarily on the influence of these two factors on the film morphology.

Zhu and Stoner [34] in their systematic study of the morphology of tubular MPCVD (see Figure 2.1 for the reactor schematic drawing) diamond synthesis on Si substrates, developed the field map of Figure 3.3. As shown, the {111} facets were found most often in the films deposited at high substrate temperatures and low methane concentrations. The medium substrate temperatures and medium methane concentrations favored {100} morphology. The hills and valley structure corresponds to defects facilitated growth related to the secondary nucleation [34]. Low T_s produced amorphous carbon phase while graphite phase was produced at high T_s . Graphite was shown to nucleate at grain boundaries. Both planar defects (twins and stacking faults) and graphite were shown to form preferentially on {111} planes of diamond.

Wild, Koidl, and their colleagues [31] investigated morphology of diamond films prepared by a tubular MPCVD system (Figure 2.1). They grew diamond films with various morphologies and textures. They developed Figure 3.4 (a) and (b) which related the growth parameter $\alpha = \sqrt{3} \cdot \frac{V_{100}}{V_{111}}$ to the CH_4/H_2 and the substrate temperature, respectively. $\alpha = 3$ resulted in the octahedral crystal habit which shows {111} morphology and <100> texture. By lowering α to a value slightly less than 3, they showed

that the tips of the octahedra were truncated by $\{100\}$ facets (i.e., $\{100\}$ - $\langle 100 \rangle$ film). The α reduction was accomplished by lowering the CH_4 / H_2 or by increasing the substrate temperature. This means that the $\{111\}$ morphology was associated with higher methane concentrations and lower substrate temperatures while the $\{100\}$ morphology was favored at lower methane concentrations and higher substrate temperatures.

Kobashi and his colleagues [38] indicated that in their tubular microwave plasma CVD diamond synthesis (see Figure 2.1 for reactor schematic drawing), the film morphology changed from primarily $\{111\}$ faces to primarily $\{100\}$ faces as methane concentration was increased from $\text{CH}_4 / \text{H}_2 < 0.40\%$ to $0.40 \leq \frac{\text{CH}_4}{\text{H}_2} \leq 1.20\%$ and further increase in the methane concentration in hydrogen led to an entirely structureless film

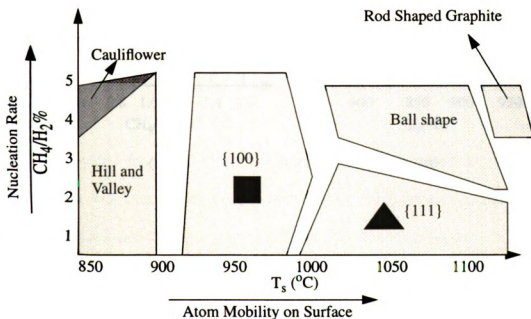


Figure 3.3. The field map of morphology vs. methane concentration and substrate temperature by Zhu and Stoner [34].

$\alpha = \sqrt{3} V_{100} / V_{111}$ Growth parameter

$\alpha = 1$, Cube

$\alpha = 1.5$, Cubo octahedron

$\alpha = 3$, Octahedron

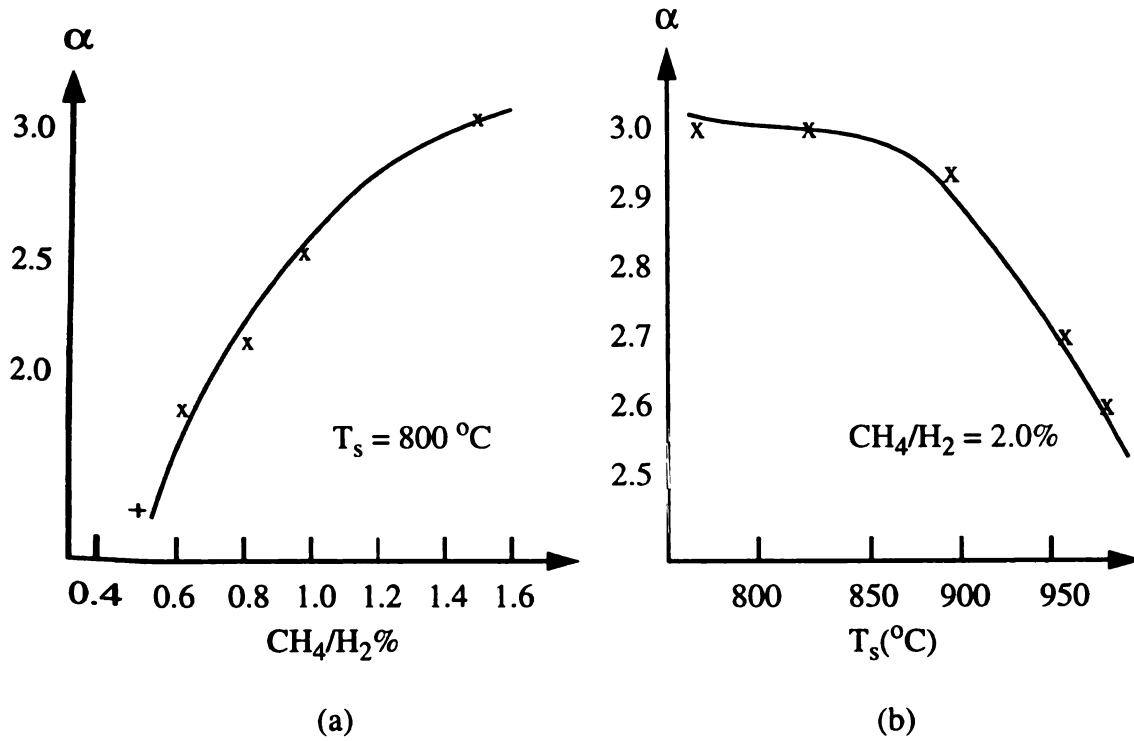


Figure 3.4. Growth parameter as a function of: (a) $\text{CH}_4/\text{H}_2\%$ with $T_s = 800^\circ\text{C}$, and (b) substrate temperature, T_s with $\text{CH}_4/\text{H}_2\% = 2.0\%$ [31].



surface consisting of merely microcrystallites. In their studies, the Si substrate was placed in a quartz tube which penetrated perpendicularly to a rectangular wave guide. They fixed substrate temperature at 800°C, H₂ flow rate at 100 sccm, microwave power at 350 Watts, pressure at 30 torr, microwave frequency at 2.45 GHz, and deposition time at 7 hours and obtained the field map of Figure 3.5 which related the morphology to CH₄ / H₂%. They also indicated that at the high methane concentrations where {100} facets appeared, the growth rate of {111} faces was so high that they were no longer stable. Further, they demonstrated that the diamond films grew cyclically through the microcrystallites formation followed by the formation of well defined faces. For methane to hydrogen concentration of 1.20% they observed that after 3 hours of growth, the substrate was fully covered with small {100} facet grains with some small crystals in the background. After 8.3 hours, the {100} facets had become larger in size and were covered with small crystals, an indication that a secondary growth had taken place. After 11.3 hours, the small crystals had disappeared almost completely and the surface was covered by crystallites with {100} facet of different sizes. After 17.3 hours, a third stage of growth in the form of small crystallites had occurred. The small crystallite growth was observed to begin in between the {100} facets and cover the entire surface. These small crystallites had vanished after 44.8 hours of growth and well defined {100} features had covered the surface. This cycle was shown to repeat over the 59.8 hours of experiments.

Hiromu Shiomi and his coworkers[39] used tubular MPCVD diamond synthesis method (see Figure 2.1 for reactor schematic drawing) with Si (100) substrate placed on a quartz holder in the middle of the quartz tube reactor. The 2.45 GHz microwave used was guided through a three-stub tuner to the quartz tube. The experimental conditions were as

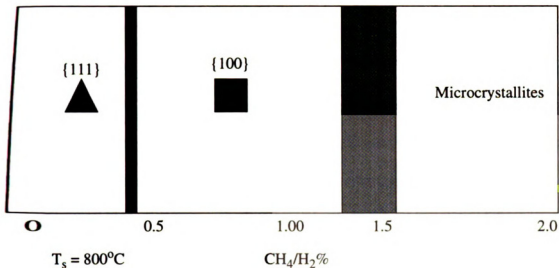


Figure 3.5. Morphology vs. CH_4 / H_2 field map developed by Kobashi [38].

follows: H_2 flow rate = 100 sccm, microwave power = 300 Watts, pressure = 40 torr, substrate temperature = 830°C , and deposition time = 2 hours. They varied the methane concentration in hydrogen from 1.0% to 8.0%. At $\text{CH}_4/\text{H}_2 = 1.0\%$, crystals with cubo octahedral shapes with primarily {111} surface morphology were obtained. At $\text{CH}_4/\text{H}_2 = 2.0\%$, the film surface were covered almost equally by both {100} and {111} facets. For $\text{CH}_4/\text{H}_2 > 3.0\%$, the surface was covered primarily by {100} facets. At $\text{CH}_4/\text{H}_2 = 6.0\%$, the {100} facets became small and were surrounded with rough facets with no well-defined crystallographic planes. Finally at $\text{CH}_4/\text{H}_2 = 8.0\%$, the entire surface lacked well-defined crystallographic planes. Since the crystal planes are bounded by the slow growing planes, the data indicated that $V_{100} > V_{111}$ for $\text{CH}_4/\text{H}_2 = 1.0\%$, $V_{100} \sim V_{111}$ for $\text{CH}_4/\text{H}_2 = 2.0\%$, and $V_{100} < V_{111}$ for $\text{CH}_4/\text{H}_2 > 3.0\%$. Furthermore, for $\text{CH}_4/\text{H}_2 = 6.0\%$, macro-Raman showed

graphitic components while micro-Raman showed no graphitic components. This indicated that graphitic components existed along the boundaries of the grains.

Using a tubular MWCVD technique, Williams and Glass [40] showed that {111} faceted diamond crystals were predominant at $\text{CH}_4/\text{H}_2 = 0.30\%$ while for $\text{CH}_4/\text{H}_2 = 1.0\%$ and 2.0% , the {100} morphology was favored. In their experiments, the microwave from a 2.45 GHz power supply were guided by a rectangular wave guide through an isolator and a three-stub tuner to a quartz tube reaction chamber having an inner diameter of 40 mm. The n-type Si (111) substrate was placed in the quartz tube in the path of the rectangular wave guide and the following experimental conditions were used: Substrate temperature = 800°C , microwave power = 300 - 350 Watts, and pressure = 30 torr. No data on the H_2 flow rate was provided. They further observed growth steps on both the {111} and {100} facets. Secondary nucleation was observed on the {111} facets while for the {100} faceted films, secondary nucleation was observed mainly between the grains (i.e., rough {111} and smooth {100} facets).

Lee Chow and his colleagues [41] showed that for $\text{CH}_4/\text{H}_2 < 0.40\%$ {111} and for $0.40\% < \text{CH}_4/\text{H}_2 < 1.20\%$ {100} morphology dominated. A 2.45 GHz tubular MWCVD system with microwave power <100 Watts, pressure = 30 - 80 torr, and substrate temperature = 680°C - 750°C was utilized. The substrates were n-type Si (100) and the substrate holder was made of high purity graphite. Moreover, they showed that under intensified ion bombardment which was accomplished by raising the sample in the chamber or by increasing the power, {100} diamond films could be grown on top of microcrystallites ball-like particles under the suitable conditions (i.e., $\text{CH}_4/\text{H}_2 = 1.50\%$,

substrate temperature = 680°C - 750°C and pressure = 30 - 80 torr).

To examine the surface morphology of a CVD diamond layer grown on another CVD diamond layer in a tubular MWCVD system, Kobashi and his coworkers [42] deposited a second layer of diamond on top of the first layer. The first layer was deposited on Si substrate and consisted of diamond film with {111} faces for $\text{CH}_4 / \text{H}_2 < 0.40\%$ and {100} faces for $0.40 \leq \frac{\text{CH}_4}{\text{H}_2} \leq 1.20\%$ and no well-defined facets were obtained beyond $\text{CH}_4 / \text{H}_2 = 1.20\%$. For the second layer, the first layer was grown with $\text{CH}_4 / \text{H}_2 = 2.50\%$ (i.e., structureless microcrystallites) for 3 hours. The second layer was deposited for 14 hours. The concentration of methane in hydrogen was varied between 0.20% to 2.0%. The morphological features of the second layer was quite different from those of the first layer in that no {111} facets were observed on the second layer and the {100} morphology appeared for $1.0 \leq \frac{\text{CH}_4}{\text{H}_2} \leq 1.20\%$.

In an AStex Inc. microwave reactor (see Figure 2.2 for schematic drawing) with frequency = 2.45 GHz, forward power = 700 Watts, reflected power < 5 Watts, pressure = 30 torr, and $\text{CH}_4 / \text{H}_2 = 0.40\%$, Haq [43] deposited diamond on Si (100) substrates. For deposition performed at 816°C substrate temperature, a poor micro-structure was obtained. At 716°C, the {111} facets were predominant while at 516°C, {100} and {110} facets were favored.

Utilizing their microwave plasma CVD system (Figure 3.6), Yoon-Kee and colleagues [44] observed that with increasing substrate temperature, diamond film surface morphology changed from {100} to {111}. With increasing methane concentration, film

m

M

22

S

E

10

a

10

1

10

00

00

cr

sy

ac

te

h

in

d

{

morphology changed from {100} facets to cauliflower.

The films grown in a Hot Filament CVD (see Figure 2.4 for schematic drawing) by Matsumoto and his colleagues [45] showed predominantly {100} planes at high substrate temperatures while lower temperatures favored {111} morphology.

In growing diamond with Chemical Transport Reaction (CTR) mechanism (schematic drawing of the CTR system was not provided), Spitsyn [8] related the crystal habit of the diamond crystals growing on substrates not forming carbides (i.e., Cu, Au,...) to hydrocarbon supersaturation on the surface by relating the crystal habit to the ratio $\alpha / (\sqrt{3}) = V_{100} / V_{111}$ of growth rates in <100> and <111> directions and showing that lowering the supersaturation changed the habit from octahedron ($\alpha \geq 3$) to cube ($\alpha = 1$). He further showed that supersaturation decreased as crystallization temperature increased which means that the increase in temperature changed the crystal shape from octahedron (only {111} faces) to cube (only {100} faces) via intermediate cubo octahedron (both {111} and {100} faces) forms ($\alpha = 1.5$). Figure 3.7 represents the crystal habit versus crystallization temperature as was proposed by Spitsyn. In his CTR system, octahedra grew at ~800 °C and cubo octahedra at ~1000°C. Cubic habit, according to the figure, required a still higher temperature. If achieving such high temperatures was not feasible, the growth of such crystals could be accomplished at lower hydrocarbon supersaturation (i.e., reduced CH₄). Twinning probability was shown to increase with supersaturation in the CTR synthesis. In summary, in the CTR synthesis of diamond carried out by Spitsyn, low substrate temperatures and high CH₄/H₂% resulted in {111} morphology while high substrate temperatures and low CH₄/H₂% favored {100}

morphology.

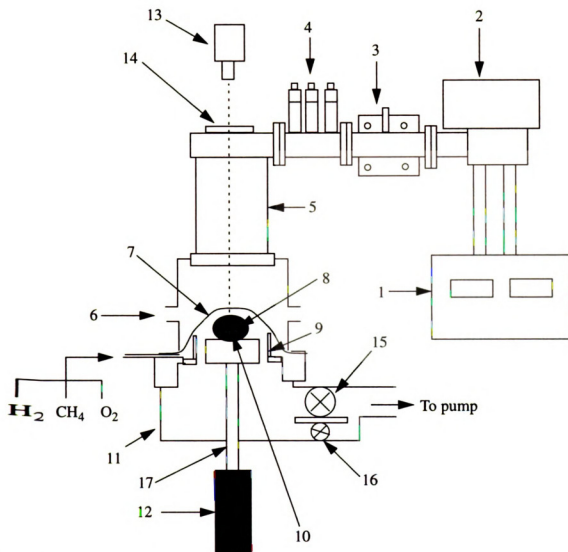
In summary, Zhu (MPCVD), Kobashi (MPCVD) Hiromu Shiomi (MPCVD), William-Glass (MPCVD), and Lee Chow (MPCVD) showed that low CH_4/H_2 concentrations resulted in {111} morphology and high CH_4/H_2 favored {100} morphology while Spitsyn (CTR) and Wild-Koidl (MPCVD) showed the opposite result; low CH_4/H_2 favored {100} morphology, high CH_4/H_2 favored {111} morphology. With regard to the substrate temperature, Zhu, Yoon, and Haq (AStex MPCVD) showed that {100} and {111} morphologies were associated with low and high temperatures, respectively, while Spitsyn, Wild-koidl, and Matsumoto (HFCVD) showed the opposite results.

Finally, it is reported that [34] impurities can greatly affect the growth morphology due to their contribution to the surface free energy. Surface free energy is not only a function of the atomic structure of the surface but also a function of all the interactions between the gas phase environment and the surface.

H.

LE
1. N
2. N
3. C
4. 3
5. S
6. A
7. C
8. F
9. C

Fig
Yo



LEGEND

- | | |
|-----------------------------------|------------------------------------|
| 1. Microwave power controller | 10. Substrate |
| 2. Microwave source | 11. Stainless steel vacuum chamber |
| 3. Circulator/Directional coupler | 12. Linear positioner |
| 4. 3-stub tuner | 13. Optical pyrometer |
| 5. Symmetric plasma coupler | 14. Plasma view port |
| 6. Air cooling ports | 15. Main valve |
| 7. Quartz dome (6" diameter) | 16. Pressure control |
| 8. Plasma | 17. Substrate holder/heater |
| 9. Gas diffuser ring | |

Figure 3.6. Schematic drawing of the microwave plasma CVD system utilized by Yoon-Kee and colleagues [44].

331.

meas

shift

natura

qualit

the Ra

Z

compo

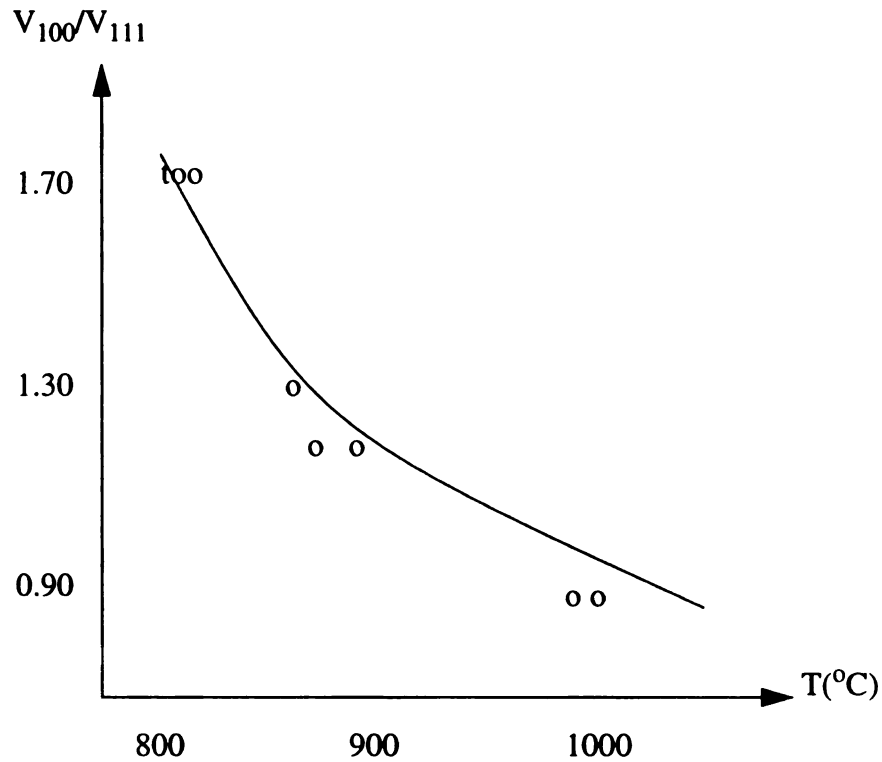


Figure 3.7. Crystal habit vs. crystallization temperature [8].

3.3.1.3 Structural quality vs. deposition condition

Full Width at Half Maximum (FWHM) of Raman spectra is widely used as a **measure** of the structural quality of diamond films. Natural diamond shows a sharp Raman **shift** at 1332 cm^{-1} with FWHM in the range of 2 cm^{-1} . Smaller (i.e., closer to that of the **natural** diamond) values of measured FWHM of a diamond film mean that they have better **quality** than diamond films with larger values of FWHM. A more in-depth description of **the Raman** effect and causes of the FWHM widening is given in Chapter 4.

Zhu and Stoner (tubular MPCVD) [34] observed a decrease in sp^2 bonding **component** (shown by Raman analysis) as CH_4/H_2 decreased indicating that the defect

concentration and CH_4/H_2 concentration were directly proportional to one another. The defect sizes were shown to decrease as CH_4/H_2 increased. Williams and Glass [40] observed that the defect density increased with the methane concentration. The low defect density at low methane concentrations was attributed to the lower growth rate at the low methane concentrations which allow a less defective/strained film to grow. The observation was also related to the decreased sp^2 bonding component (indicated by Raman) at low methane concentrations.

Kobashi [38] also observed that the diamond peak about 1332 cm^{-1} (indicated by Raman spectra) decreased and the concentration of non-diamond components (i.e., graphite) increased as methane concentration increased in its respective range of 0.30% - 2.0%. The increase of the graphitic peak ($\sim 1550\text{ cm}^{-1}$) and the decrease and/or widening of the diamond peak ($\sim 1332\text{ cm}^{-1}$) as methane concentration was increased is reported by other researchers ([1], [40], [46]), as well.

Yoon-Kee and colleagues [44] observed that FWHM obtained from Raman spectra of diamond films increased with substrate temperature (in the range of 700°C - 900°C) and with CH_4/H_2 . This is shown in Figure 3.8. They also demonstrated that the FWHM of the diamond films increased with pressure ($p = 15 - 64\text{ torr}$).

R. G. Buckley and colleagues (HFCVD) [47] demonstrated that with other deposition conditions fixed, the Raman line about 1332 cm^{-1} was broadened as the pressure ($p = 5 - 100\text{ torr}$) was decreased. The line broadening was attributed to the density of lattice defects, i.e., lattice defects increased as pressure was decreased.

Figur
Yoon

33.21

33.21

C

conce

conditi

section

Z

[14] sh

diamon

hydroge

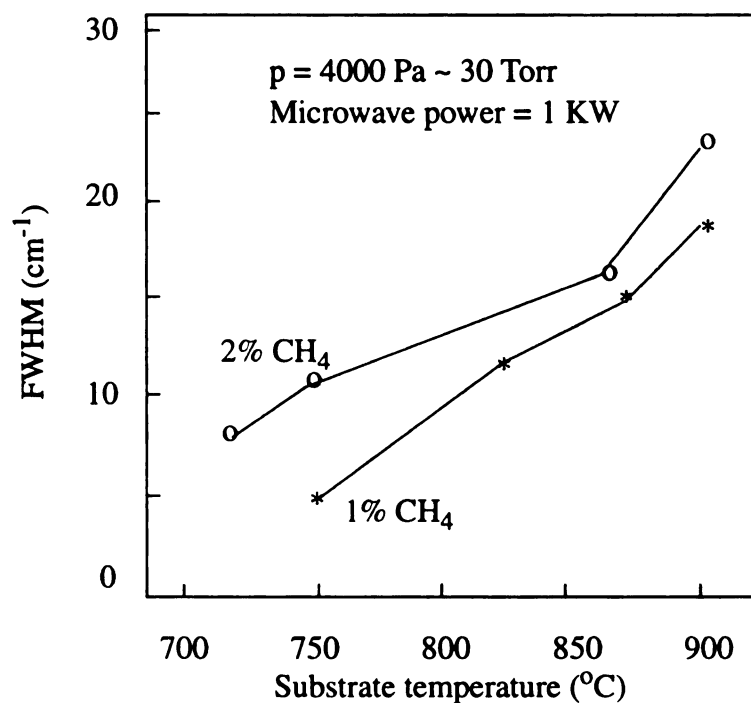


Figure 3.8. FWHM vs. substrate temperature and methane concentration obtained by Yoon-Kee [70].

3.3.2 Reactor performance (Y_2) vs. deposition conditions

3.3.2.1 Growth rate vs. deposition condition

CVD diamond film growth rate has been shown to change with methane concentration in hydrogen. A detailed investigation of growth rate vs. deposition conditions has been carried out by K. P. Kuo [27] and is only briefly studied in this section.

Zhu [34] achieved a lower growth rate at lower methane concentration. Jie Zhang [14] showed that at $H_2 = 400$ sccm and T_s (i.e., substrate temperature) = 900 °C, CVD diamond film linear growth rate and weight gain increased with methane concentration in hydrogen up to $CH_4/H_2=1.50\%$ and decrease beyond this point. For $H_2 = 400$ sccm, $T_s =$

950

at CH

for F

were

after

Liou

up to

obser

Figur

incre

and p

syste

3.07

powe

subst

was a

powe

tempe

tempe

950 °C, and $\text{CH}_4/\text{H}_2 \in [0.75, 1.75]\%$, he showed that linear growth rate was maximum at $\text{CH}_4/\text{H}_2 = 1.25\%$. He observed a similar behavior with respect to substrate temperature; for $\text{H}_2 = 200$ sccm, $\text{CH}_4/\text{H}_2 = 2.0\%$, and $T_s \in [750, 950]^\circ\text{C}$, the linear growth rate and weight gain increased with substrate temperature up to $T_s = 850^\circ\text{C}$ and decreased afterward.

In diamond deposition by bell jar MPCVD system, manufactured by AStex Inc., Liou and colleagues [46] observed that growth rate increased with methane concentration up to $\text{CH}_4/\text{H}_2 = 3.0\%$ and decreased beyond this point as shown in Figure 3.9 (a). They observed a monotonic increase in growth rate with substrate temperature as shown in Figure 3.9 (b). They also determined that graphitic component in the film increased with increasing methane concentration. In their study, total gas flow rate, microwave power, and pressure were found to have no significant effect on the growth rate.

Yoon-Kee and colleagues [44] observed that in their microwave plasma CVD system, diamond film growth rate vs. methane concentration was maximized at $\text{CH}_4/\text{H}_2 = 3.0\%$ to result in $0.70 \mu\text{m/hr}$ growth rate. Substrate temperature, pressure, and microwave power were fixed at 800°C , 30 torr, and 1.0 KW, respectively. The growth rate vs. substrate temperature showed a similar trend, it was maximized around 850°C where it was approximately $0.70 \mu\text{m/hr}$ when $\text{CH}_4/\text{H}_2 = 2.0\%$, pressure = 30 torr, and microwave power = 1.0 KW were used. They attributed the decrease in growth rate vs. substrate temperature to the enhanced etching of diamond and non-diamond components at high temperatures.

Walter and Russell [48] showed that on copper substrates, for $T_s = [700, 1100]^\circ\text{C}$,

diamond film thickness experienced an increases with T_s up to $T_s \sim 950^\circ\text{C}$ and decreased beyond this substrate temperature.

In epitaxial growth of diamond film on cubic boron nitride (cBN) surface by DC glow discharge CVD experiments conducted by Guangtian Zou and his colleagues [49], an increase in growth rate from $0.50\ \mu\text{m/hr}$ to $1.0\ \mu\text{m/hr}$ was observed as methane concentration in hydrogen was increased from 0.30% to 0.60%.

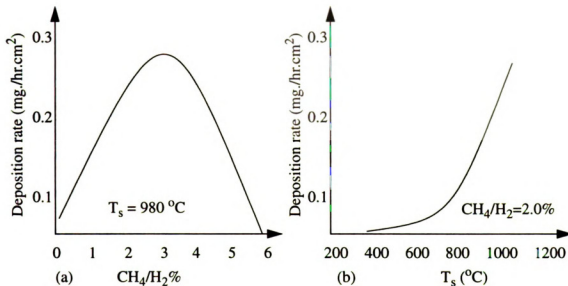


Figure 3.9. The deposition rate vs. (a) $\text{CH}_4/\text{H}_2\%$ and (b) substrate temperature for AStex bell jar MPCVD reactor examined by Liou [46].

3.3.3 Concluding remarks

A deposition reactor is a complex system of many experimental variables and exact relationships between deposition reactors' output, internal, and input variables have not been well-defined. At present time there are no simple or complex theories or models to describe the complex relationships between reactors' many experimental variables.

Diff

var

con

me

ac

m

m

li

hi

ac

sp

in

in

in

v

u

e

-

o

Different reactors display different relationships between output (Y) and input (U) variables. Even when performance of similar reactors, i.e., tubular microwave CVD, are compared important differences in output film properties and performance such as film morphology vs. the input variables are observed. For instance, in open literature, CH_4/H_2 and substrate temperature, T_s have been identified as the primary factors that influence the morphology of diamond films. However, from Figure 3.10 which summarizes the film morphology vs. CH_4/H_2 and T_s (i.e., called morphology field map) of the preceeding literature review of film morphology vs. deposition conditions, it is seen that a specific film morphology (i.e., {100}) belongs to different areas in this morphology field map (i.e., areas over which a specific film morphology is formed do not coincide) even when one specific reactor (i.e., tubular microwave CVD) is considered. This suggests that all the important experimental variables have not been identified and controlled in these investigations and that in addition to CH_4/H_2 and T_s , there are other variables that influence the diamond film morphology. In the preceeding discussion, film morphology was taken as an example of the output film properties and it is shown in this dissertation that other film properties and reactor performance variables (i.e., structural quality, growth rate, etc.) also depend on many other variables including reactor geometry (U_2) variables. Thus, finding the experimental relationships between output variables ($Y = [Y_1, Y_2]$) and input ($U = [U_1, U_2, U_3]$) and internal (X) variables of a deposition reactor requires a more thorough investigation. Chapters 4 through 7 present such a thorough investigation of the microwave cavity plasma reactor (MCPR) whose schematic diagram is shown in Figure 2.5.

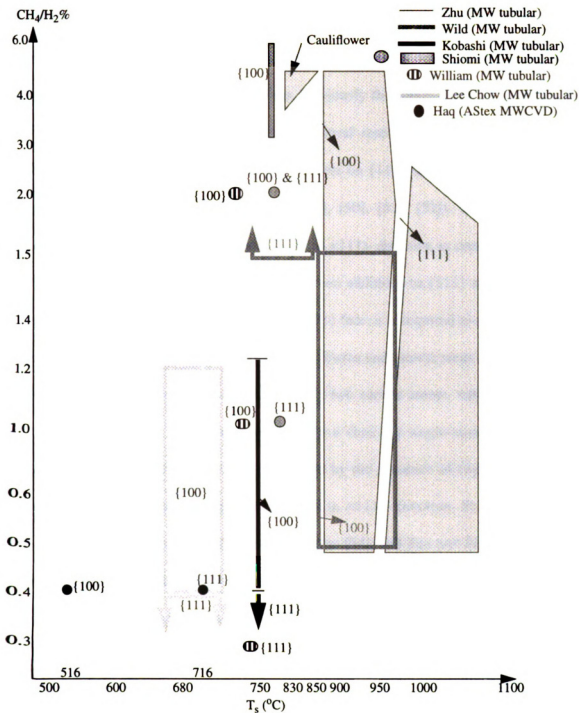


Figure 3.10. Summary of morphology vs. deposition conditions for various reactors/experiments.

3.4 Structural defects

The relationships between the external surface morphology and internal structure perfection is of great importance in designing experimental conditions to develop relatively perfect structures of diamond films. Obviously the $\{100\}$ faces are the desirable faces for smooth and defect free structures. Several researchers have investigated the causes of existence of defects and surface roughness on $\{111\}$ facets and the smoothness and defect free structure on $\{100\}$ facets ([29], [50], [51], [52]). Clausing [29] has developed models to show why growth is faster in $\langle 111 \rangle$ direction as compared to $\langle 100 \rangle$ direction. The models are based on the ways carbon additions to $\{111\}$ and $\{100\}$ facets take place. According to the models, for a flat $\{111\}$ face, it is required to add three carbon atoms in order to form a complete structural ring. Twins and growth steps make it possible to grow on $\{111\}$ faces with the addition of only two carbon atoms. After the two atom addition has been made, growth may continue in a chain by single-atom addition. This means that growth on $\{111\}$ faces are facilitated by the presence of twins and stacking faults which in turn means that growth is faster in $\langle 111 \rangle$ direction. Similar arguments have been made by Everson and Tamor [53], Angus [54], and Zhu and Stoner [34] which show that growth is facilitated by defects. On the other hand, for a new $\{100\}$ layer to form, a carbon atom can only be added in one way and that no twins or stacking faults can arise. It can only go to the correct lattice position. Point defects may be incorporated in to these growing facets, but planar defects can not. This could account for relatively slower growth rate in $\langle 100 \rangle$ direction [29].

To further understand the reason for incorporation of twins and stacking faults in the diamond structure, let's consider an f.c.c. (face centered cubic) lattice. The diamond cubic

lattice corresponds to two interpenetrating f.c.c. lattices, one of which is displaced by $(1/4, 1/4, 1/4)$ with respect to the other as shown in Figure 1.2. The primitive unit cell vectors are the same as the ones associated with a single f.c.c. lattice. Therefore, to a large extent it suffices to understand the dislocations, twinning and faults in a single f.c.c. structure. The result can safely be extended to the diamond structure. Dislocations, twinning and stacking faults in f.c.c. structures are briefly described in the following sub-sections.

3.4.1 Dislocations ([55], [56], [57], [58], [59])

Dislocations, or line imperfections, in crystal solids are defects that cause lattice distortion centered around a line. The two main types of dislocations are the edge and screw types. In a crystal, an edge dislocation is created by the insertion of an extra half plane of atoms into the lattice or by removing a half plane of atoms (Figure 3.11). The screw dislocation can be formed in a perfect crystal by applying upward and downward shear stresses to regions of a perfect crystal which have been separated by a cutting plane (Figure 3.12 (a) and (b)).

Dislocations are non-equilibrium defects and store energy in the distorted region of the crystal lattice around the dislocation. The displacement distance of the atoms around the dislocation is called the slip or Burgers vector $\mathbf{b}$. Figure 3.13 (a) and (b) illustrate the definition of the Burger vector $\mathbf{b}$. We draw in the defective crystal a clockwise Burger circuit S-1-2-3-F, which encloses the dislocation (Figure 3.13 (a)). Then we draw the same circuit in the perfect reference lattice, as shown in Figure 3.13 (b). The vector required to close the lattice circuit (vector $\mathbf{FS}$) is defined as the Burger vector (i.e., $\mathbf{b} = \mathbf{FS}$). Alternatively, we can draw in the defective crystal a clockwise circuit which would be

ch

vec

tra

con

The

par

per

dis

vec

Bu

also

seq

mo

dire

on

ame

ass

vec

closed in the perfect reference crystal (i.e., $\mathbf{b} = \mathbf{SF}$) as shown in Figure 3.14 (a) and (b).

In the simple cubic crystals, the Burger vectors are the shortest lattice translation vectors which join two points in the lattice. A dislocation whose Burger vector is a lattice translation vector is called a perfect or unit dislocation.

In a simple f.c.c. structure (Figure 3.15 (a) and (b)), the atoms are situated at the corners of the unit cell and at the centers of all cube faces in sites of the type $1/2, 1/2, 0$. The atoms are closest to one another along the various $\langle 110 \rangle$ directions. The lattice parameter is $a = 2r\sqrt{2}$ where r is the atomic radius. If dislocations are to be restricted to be perfect dislocations (due to misfit energy, with the exception of some special cases, all dislocations in crystals are expected to be perfect dislocations [57]) the smallest Burgers vectors possible in f.c.c. crystals point along various $\langle 110 \rangle$ directions. The length of these Burgers vectors is the distance from the center of one atom to the center of the next atom along any of $\langle 110 \rangle$ directions. This means that $\mathbf{b} = \frac{a}{2} \langle 110 \rangle$ and $b = \frac{a}{\sqrt{2}}$ [55].

The stacking sequence of $\{100\}$ and $\{110\}$ planes is ABABAB... and the stacking sequence of $\{111\}$ planes is ABCABCABC.... The atoms in the $\{111\}$ planes are in the *most* close-packed arrangement possible for spheres and contain three close-packed directions 60° apart [56].

For f.c.c. structure it has been observed experimentally that slip takes place primarily on $\{111\}$ planes along $\langle 110 \rangle$ directions ([55], [56], [57]). This can be attributed to the amount of stored energy associated with dislocations. The amount of stored energy associated with a dislocation is proportional to the square of the magnitude of its Burger vectors $\mathbf{b}$ (i.e., $E \propto b^2$). Lets consider stored energies along different directions.

Along the $\langle 110 \rangle$ directions:

$$\mathbf{b} = \frac{a}{2} \langle 110 \rangle$$

$$b = \frac{a}{2} (1^2 + 1^2 + 0^2)^{1/2} = \frac{a}{\sqrt{2}}$$

$$E \propto b^2 = \frac{a^2}{2}$$

Along the $\langle 100 \rangle$ directions:

$$\mathbf{b} = a \langle 100 \rangle$$

$$b = a(1^2 + 0^2 + 0^2)^{1/2} = a$$

$$E \propto b^2 = a^2$$

Along the $\langle 111 \rangle$ directions:

$$\mathbf{b} = a \langle \sqrt{3} \ \sqrt{3} \ \sqrt{3} \rangle = \sqrt{3} a \langle 111 \rangle$$

$$b = a(3 + 3 + 3)^{1/2} = 3a$$

$$E \propto b^2 = 9a^2$$

As the calculations show, the amount of stored energy associated with a dislocation of $\langle 100 \rangle$ Burgers vector is twice as great as the $\langle 110 \rangle$ Burgers vector and the amount of stored energy associated with $\langle 111 \rangle$ Burgers vector is nine times greater than that of $\langle 110 \rangle$ Burgers vector. Therefore, dislocations along $\langle 110 \rangle$ directions are energetically favorable and can be introduced into the crystal with greater ease.

It has been observed ([55], [56], [57], [58]) that with rare exceptions, slip occurs only on the $\{111\}$ planes. It can be shown that there is a lower energy associated with the dislocations of the type $\frac{a}{2} \langle 110 \rangle$ that lie on $\{111\}$ planes. Figure 3.16 shows appearance

of several crystal planes. Since slip involves the sliding of close-packed planes of atoms over each other, a simple experiment [56] can be made to see how this can occur. Figure 3.17 shows the close-packed form of one layer, A, of $\{111\}$. A second layer (layer B) can rest in the sites marked B. Consider the movement of the layers when they are sheared over each other to produce a displacement in the slip direction. Due to the stacking arrangement, it is energetically more favorable for B atoms instead of moving from one B site to the next B site *over* the top of the A atoms, to move first to the nearby C site along the “valley” between the two A atoms and then to the new B site via a second valley. This can be shown by the following energy calculations [56]:

As shown in Figure 3.17:

$$\mathbf{b}_1 = \mathbf{b}_2 + \mathbf{b}_3$$

or
$$\frac{1}{2}\langle 110 \rangle = \frac{1}{6}\langle 211 \rangle + \frac{1}{6}\langle 12\bar{1} \rangle$$

Considering stored energies:

$$E(\mathbf{b}_1) = \frac{a^2}{2}$$

$$E(\mathbf{b}_2) = \frac{a^2}{36}(2^2 + 1^2 + 1^2) = \frac{a^2}{6}$$

$$E(\mathbf{b}_3) = \frac{a^2}{36}(1^2 + 2^2 + (-1)^2) = \frac{a^2}{6}$$

From the above calculations:

$$E(\mathbf{b}_2) + E(\mathbf{b}_3) < E(\mathbf{b}_1)$$

which means that the type $\frac{a}{2}\langle 110 \rangle$ dislocations that lie on $\{111\}$ planes may *lower* their

energy by splitting into new dislocations called partial (or Shockley) dislocations (i.e., splitting reaction is energetically favorable). It is due to the special stacking arrangements of $\{111\}$ planes that the splitting and hence energy lowering occurs. The stacking arrangements of $\{100\}$ and $\{110\}$ planes (Figure 3.16) do *not* allow such reactions. Therefore, the $\{111\}$ planes may be considered as the *only* slip planes for dislocations. A more complete discussion on dislocations and their interactions in the f.c.c. lattice is given in [60].

To sum up, from the preceding discussions it can be concluded that generally the $\{111\}$ planes are prone to occurrence of line and plane defects.

3.4.2 Stacking faults in an f.c.c. lattice

A stacking fault is a planar defect in a region in a crystal where a regular sequence has been interrupted. The stacking sequence of $\{100\}$ and $\{110\}$ planes is *ABABAB...* and that of $\{111\}$ planes is *ABCABCABC...*. These are evident from Figure 3.16 which illustrates the appearance of a single layer of several crystal planes. As shown in the Figure, for $\{100\}$ and $\{110\}$ planes, a second layer of atoms could find only one site to rest if the close-packed arrangement is required. This means that stacking faults are not expected in planes with *ABABAB...* sequence. However, for $\{111\}$ planes, occurrence of stacking faults is probable. Consider an atomic plane of atoms of $\{111\}$ planes (plane A) illustrated as hard spheres in Figure 3.18 [55]. As shown, the second plane of atoms could be placed on top of the plane A in two different ways so that the maximum packing density of the spheres is achieved. The two possible arrangements for the second layer are labeled *B* and *C*. It is possible to add a third layer of atoms again in two different ways consistent

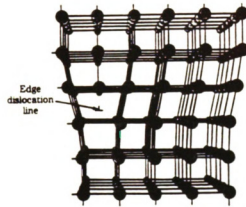


Figure 3.11. Edge dislocation in a crystallite lattice [58].

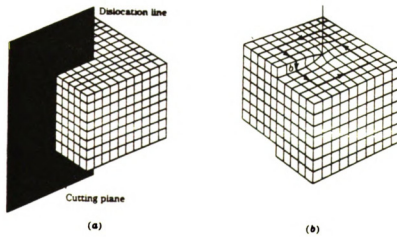


Figure 3.12. (a) and (b). Screw dislocation in a crystallite lattice [58].

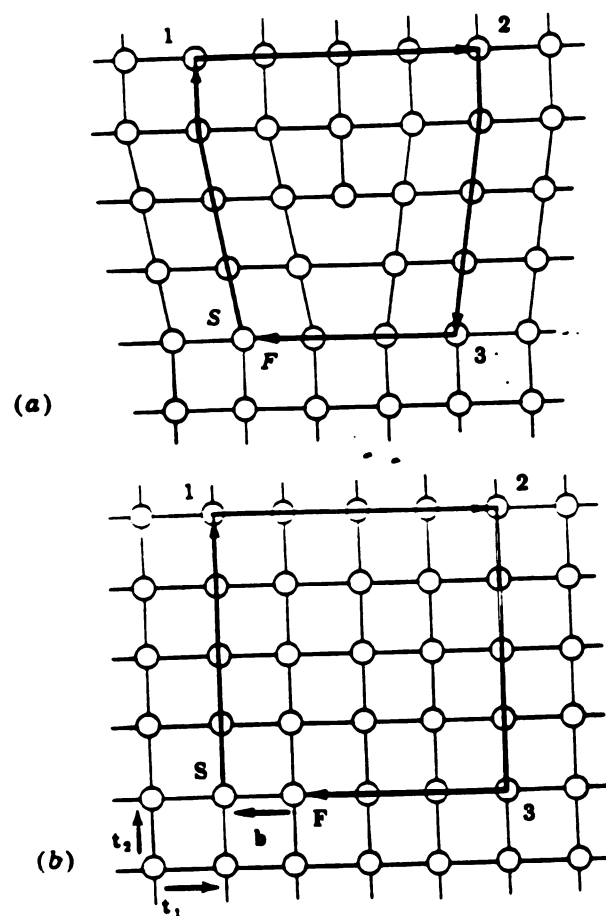


Figure 3.13. (a) A real crystal and (b) a perfect reference crystal [57].

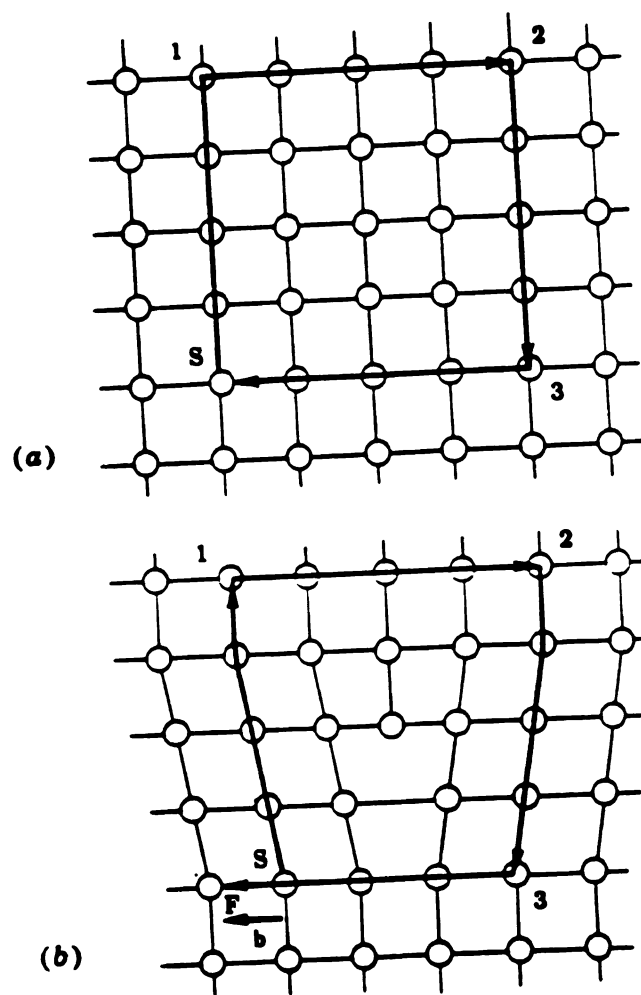


Figure 3.14. (a) A perfect reference crystal and (b) a real crystal [57].

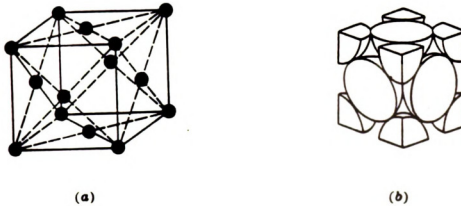


Figure 3.15. F.c.c. unit cell (a) atomic site model, and (b) hard-sphere model [58].

with the requirement of maximum packing. The atoms of the third layer may be directly over those of the first layer. In this case when the sequence of the third layer is repeated, we have either *ABABABA* or *ACACACA*. Either construction produces the hexagonal close-packed structure shown in Figure 3.19 (a). Alternatively atoms of the third layer may be placed so that they are not directly over atoms in either of the two preceding layers. This arrangement results in *ABCABCABC* or *ACBACBACB* structure as shown in Figure 3.19 (b). A stacking fault results if in some region(s) of $\{111\}$ planes the stacking sequence of *ABCABCABC...* form is interrupted. Dislocations in $\{111\}$ planes could induce such faults. As discussed in the preceding section, a perfect dislocation splits into two partial dislocations. This is further evident from Figure 3.20 [59]. The decrease in the total energy after splitting reaction indicates that there is an interaction between the two partial dislocations and that the two partial dislocations repel each other and tend to move

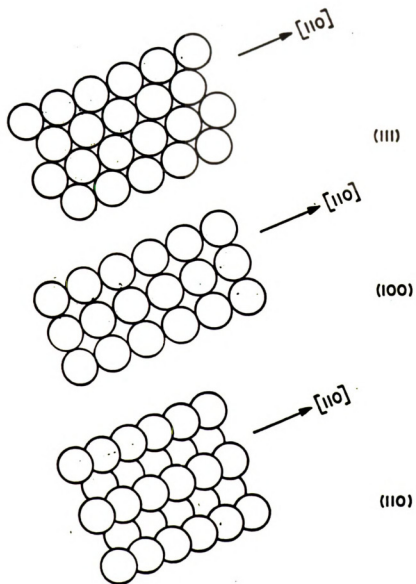


Figure 3.16. Appearance of (111) , (100) , and (110) crystal plane [55].

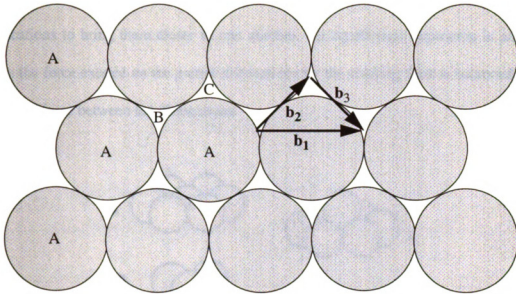


Figure 3.17. Layer displacement in $\{111\}$ planes [56].

as far apart as possible. Such a repulsive force causes the atoms of the part of the plane bounded between the partials to shift to a different site (i.e., site C). As a result, the stacking sequence of $\{111\}$ planes outside the dislocation will be $ABCACABC...$ and between the partial dislocations $ABCACABC...$ which is an indicative of a stacking fault in that region. Figure 3.21 [59] shows the separation of the two partial dislocations and the appearance of a stacking fault in the region between the two partial dislocations. Since atoms of the faulted region are not at the same locations they would normally occupy in a perfect lattice, there is a surface energy associated with a stacking fault. This energy determines how far apart the two partial dislocations could be. The repulsive force between the partial dislocations decreases with increase in the distance between them. On

the contrary, the stacking fault energy increases with the separation distance between the partial dislocations. To lower the energy, the stacking fault exerts energy on the partial dislocations to bring them closer to one another. An equilibrium separation is achieved when the force exerted on the partial dislocations by the stacking fault is balanced by the repelling force between the dislocations.

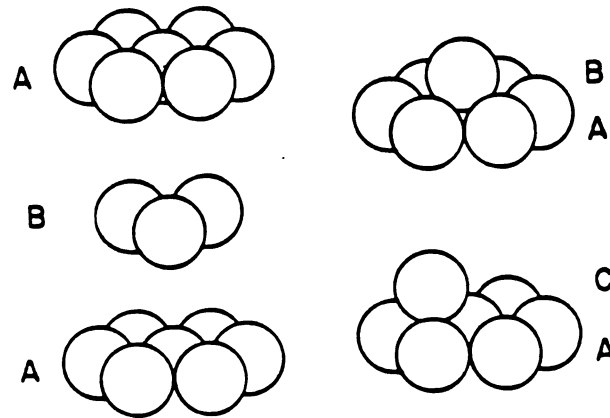


Figure 3.18. Stacking of close-packed atomic layers [55].

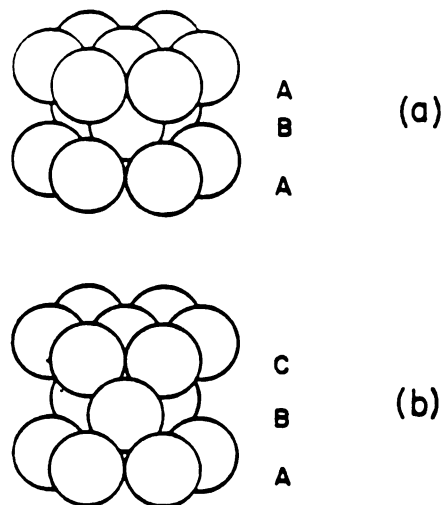


Figure 3.19. (a) Hexagonal close-packed and (b) face centered cubic [55].

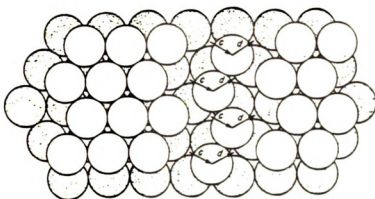


Figure 3.20. Partial dislocation in an f.c.c. lattice [59].

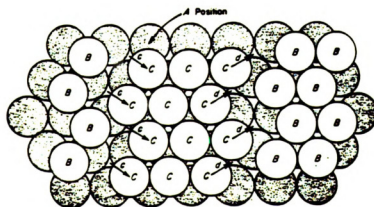


Figure 3.21. Separation of two partial dislocations [59].

3.4.3 Intrinsic and extrinsic stacking faults in an f.c.c. lattice ([55], [56], [57], [58], [59])

Figure 3.22 illustrates an intrinsic and an extrinsic stacking fault. If there is only *one* break in the stacking sequence, the resulting fault is called an intrinsic stacking fault. This is equivalent to removing a plane from the stacking sequence. For example, in an f.c.c. lattice with the sequence $ABCABCABCABC\dots$ if the plane B and all the planes *above* B undergo a displacement by the vector $1/6 [\bar{2}11]$, the plane B will move into a C position (i.e., $B \rightarrow C$) and the planes above B undergo similar displacement (i.e., $C \rightarrow A$, $A \rightarrow B$, $B \rightarrow C$ and so on). The resultant sequence is of the form $ABCA|CABCABC\dots$ (the symbol $|$ shows where the break occurs). An extrinsic stacking fault refers to the occurrence of *two* breaks in the stacking sequence. An extrinsic fault results from insertion of an extra plane into the sequence. As an example, having an intrinsic fault, if the plane C and all the planes *below* C are displaced by the vector $1/6 [2\bar{1}\bar{1}]$ (i.e., $C \rightarrow B$, $B \rightarrow A$, $A \rightarrow C$, and so on) the $ABCA|CABCABC\dots$ sequence changes to $CABA|CABBC$ and the stacking fault is extrinsic.

3.4.4 Twinning in an f.c.c. lattice ([55], [56], [57], [58], [59], [61])

In a crystal, deformation twinning is a process in which a portion of the crystal, as a result of the motion of partial dislocations, suffers a change in its original orientation and becomes a mirror image of the rest of the crystal (called parent). Figure 3.23 shows the formation of a twin from an un-distorted single crystal [57].

A coherent twin can be created if a partial dislocation of Burger vectors moves across each $\{111\}$ plane contained in a portion of an f.c.c. lattice. For example [57] if a

partial dislocation of Burger vectors $1/6 [\bar{2}11]$ displaces the B plane and all planes above it (as discussed in the intrinsic stacking faults) and the displacement continues plane by plane above A , a coherent twin forms. This process is shown below:

Original perfect crystal: $ABCABCA^{\wedge}BCABC\dots$ (^ indicates where plane displacement begins)

Plane B moves to C $ABCABCA^{\wedge}CABCA$

The process continues $ABCABCAC^{\wedge}BCAB$

$ABCABCACB^{\wedge}ABC$

$ABCABCACBA^{\wedge}CA$

$ABCABCACBAC^{\wedge}B$

The final stacking sequence is $ABCABClACBACB$ which is that of a coherent twin. Figure 3.24 portrays the twinned region. Reference [61] provides a thorough discussion on the subject of twinning mechanism.

A growing twin produces a tilt when it reaches a flat surface [56]. It should be noted that intrinsic and extrinsic stacking faults and twinning preserve the close-packed requirement, so that the nearest bonds are not disturbed. According to the interatomic-force laws [57], most of the atomic binding energy resides in the nearest neighbor bonds. Therefore, all the above faults have small surface energies compared to surfaces containing deformed or dangling bonds (such as grain boundaries and free surfaces).

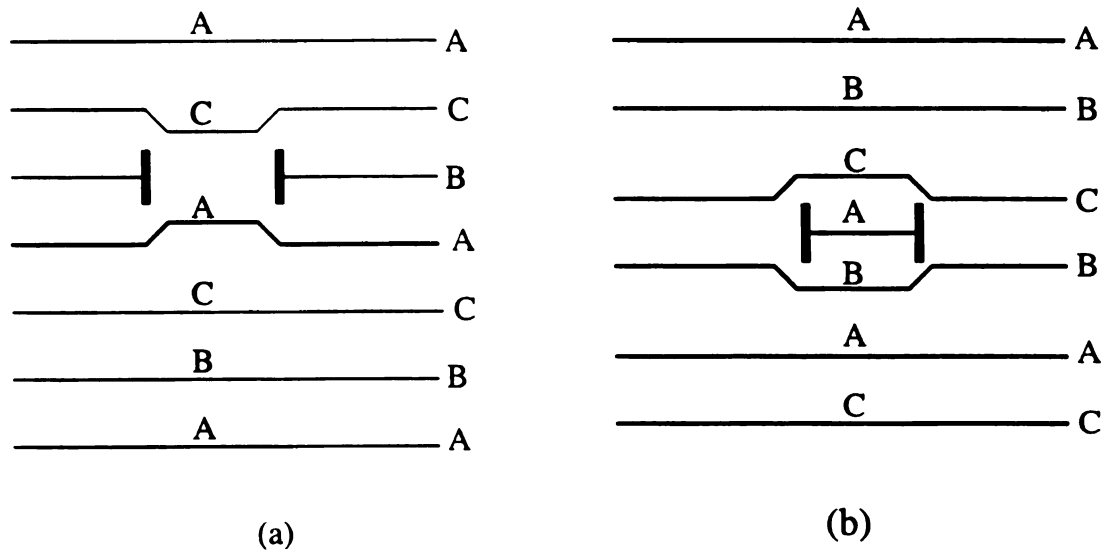


Figure 3.22. (a) an intrinsic and (b) an extrinsic stacking fault [57].

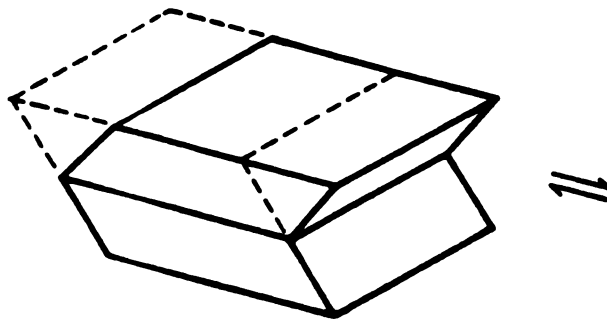


Figure 3.23. Twin formation (solid lines) from an un-distorted single crystal (dashed lines) [57].

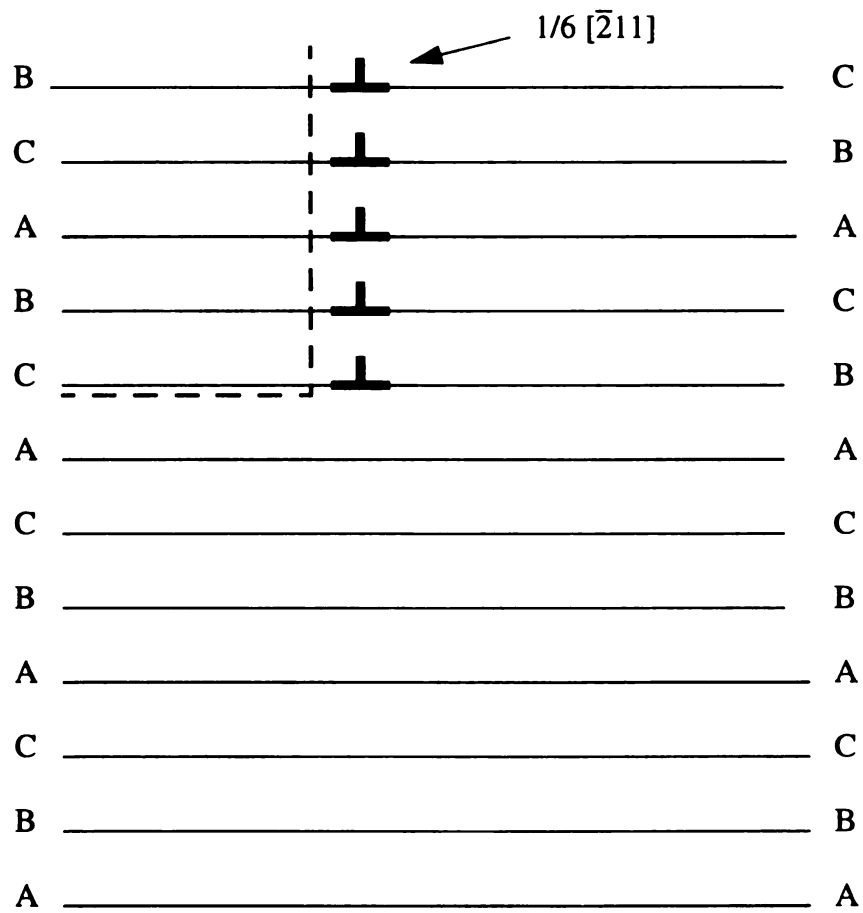


Figure 3.24. Stacking sequence of twin [61].

3.4.5 Dislocations, stacking faults, and twinning in diamond structure

The covalent bond formed by two atoms sharing electrons is strongly localized and directional. Of many covalent crystals, the cubic structure of diamond, silicon and germanium is one of the simplest and most widely studied. Dislocations in these semiconductors affect both electrical and mechanical properties. For diamond the primitive-unit cell vectors are the same as the ones associated with a single f.c.c. lattice. Thus the *perfect* dislocation Burgers vectors for the diamond cubic lattice are the *same* as those in the f.c.c. lattice. The diamond cubic structure can be conveniently described by a stacking sequence of $\{111\}$ planes in the form of $AaBbCcAaBbCc...$ ([56], [57], [62]) as shown in Figure 3.25. Atoms of adjacent layers of the same letter such as Aa lie directly over each other. Planar defects involve the insertion or removal of *pairs* of layers of the same index (i.e., Bb) which means that such faults do *not* change the tetrahedral bonding. All other faults (i.e., faults formed between adjacent layers of the same letter) disturb the nearest neighbor covalent bondings (i.e., do not restore tetrahedral bonding) and are expected to have high energy. Because the layers must be added or removed in pairs, we can drop the double-index notation and describe the packing by the sequence $ABCABCABC.....$ where each letter refers to a pair of layers of the same index. This sequence is the same as the sequence associated with a simple f.c.c. structure, hence the stacking faults in the diamond lattice are the *same* as in the f.c.c. lattice. Occurrence of defects (stacking faults, twinnings, and dislocations) primarily on $\{111\}$ planes of natural and CVD diamond (homoepitaxial as well as polycrystalline) have been reported by many researchers ([29], [30], [31], [34], [35], [53],[54] and ([62] - [70])).

From the fact that dislocations can occur only between the pair of the same index

(i.e., Bb), it is expected to observe lower stacking fault energy (relative to surface and grain boundary energies) in diamond structure than in a simple f.c.c. This is because in the covalent diamond structure, most of the binding energy resides in the *nearest* neighbor bonds and as seen in the Figure 3.25 only one bond is disturbed when a dislocation takes place [57].

This concludes the discussion on the structural defects in f.c.c. crystals. Next section provides a brief insight into some important surface reactions (i.e., surface reconstruction) which affect the morphological formation of CVD films.

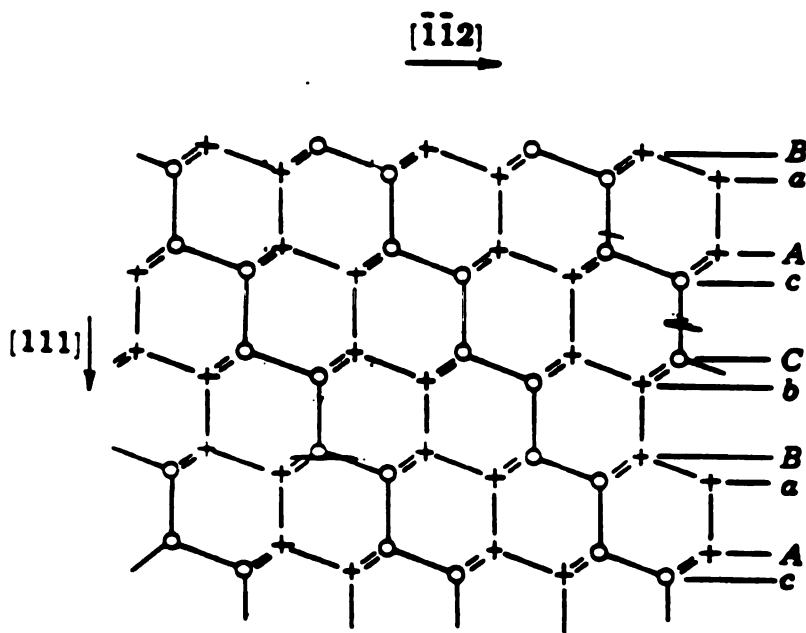


Figure 3.25. Diamond cubic lattice structure normal to $(1\bar{1}0)$. O represents atoms in the plane of the paper and + represents atoms in the plane below [57].

3.5 Surface reconstruction in CVD crystals

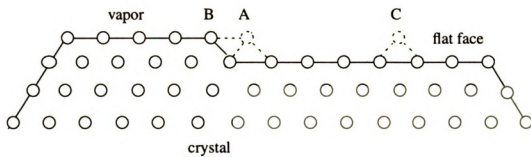
3.5.1 Periodic bond chain theory and surface reconstruction in crystals

In the field of crystal growth, the crystal surface is generally merely considered as a truncated bulk crystal. This assumption forms the basis of the Periodic Bond Chain (PBC) theory formulated by Hartman ([37], [70], [71]) which is often used to relate surface morphologies to crystallographic structures. Using PBC theory, Hartman classified crystal morphologies to crystallographic structures. Using PBC theory, Hartman classified crystal faces into three categories: (i) F-faces (flat), where each growth layer of minimal thickness (called slice) is made up of two or more interconnected PBC's. These flat faces are the most slowly growing ones and growth proceeds via a step mechanism. Figure 3.26 (a) illustrates the formation of a flat face. The PBC at the step A has a greater probability of being deposited than PBC's at C, when the PBC's parallel to the considered face are bonded by strong bonds A-B. This means that there must be at least one more PBC parallel to the face. Hence, layer growth is possible when the layer contains two or more PBC's. (ii) S-faces (stepped), the growth layer is made up of a parallel array of only one type PBC. In this case the PBC's are not connected by strong bonds which implies that S faces are purely made up of steps. Figure 3.26 (b) shows the formation of an S face. The PBC's are not bonded and the layer growth does not occur because the probability of deposition of another PBC is the same everywhere. The growth rate is faster than that of an F face because deposition of new PBC's occur simultaneously. (iii) K-faces (kinked), if in the growth layer no PBC's occur. These faces are atomically rough and no nucleation barrier exists for growth. This means that they have the highest possible growth rate and do not show steps.

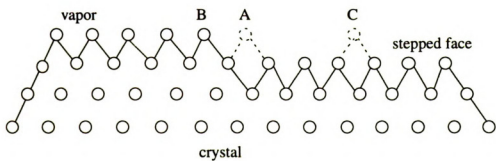
Figure 3.27 shows the projection of diamond's f.c.c. structure along $[\bar{1}10]$ direction

[71]. There is one type of strong covalent bond between carbon atoms at $[0, 0, 0]$ and at $[1/4, 1/4, 1/4]$. This bond, together with the covalent bond between atoms at $[1/4, 1/4, 1/4]$ and $[1/2, 1/2, 0]$, forms the period of PBC $[1/2 \ 1/2 \ 0]$. Thus there are zigzag PBC's in $\langle 110 \rangle$ directions (the same holds for Si, Ge, and GaAs [50]). In Figure 3.27, each circle represents a carbon atom. Adjacent PBC's are bonded in slice d_{111} , not in d_{220} . Layer d_{004} is too thin to contain a PBC. This is because the thickness of a slice is determined by the crystallographic extinction conditions [71] according to which the minimum thickness of $\{001\}$ growth layer equals $1/4$ unit lattice length for the diamond structure and $1/2$ a unit lattice length for the zinc blende structure (Figure 3.28) [71]. Because of the very thin $\{001\}$ slice thickness in the diamond structure (also true for Si and Ge) no PBC fits into it which means that the $\{001\}$ faces of diamond Si, and Ge are K-type ([50], [71]). Therefore, (111) is a F face, (110) is a S face, and (001) is a K face. This in turn means that according to the PBC theory, $\{111\}$ faces must be smooth and have the slowest growth rate, $\{110\}$ faces must have the intermediate growth rate, and $\{100\}$ faces must be rough, have the fastest growth rate, and no growth steps should occur on them.

The observed behavior of the $\{001\}$ faces of Si, C, Ge, and GaAs grown under various conditions is in conflict with quite a lot of experimental evidence and show a clear contradiction to PBC predictions. Experimental results show that $\{001\}$ faces grow relatively slow [29], they do show growth steps [50], and they are smooth.



(a)



(b)

Figure 3.26. (a) Formation mechanism of a flat face. Each circle represents a PBC seen end on. (b) Formation mechanism of an S face. No bond exists between adjacent PBC's (between A and B) [71].

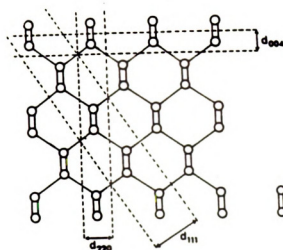


Figure 3.27. Projection of diamond structure along $[\bar{1}10]$. Each circle represents a carbon atom. Adjacent PBC's are bonded in slice d_{111} , not in d_{220} . In the layer d_{004} no PBC occurs [71].

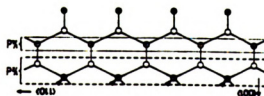


Figure 3.28. Projection of $\{001\}$ face along $\langle 110 \rangle$ showing the unit slices for the diamond ($0.25d$) and the zinc blende structure ($0.5d$) [50].

Th

explain

where t

with re

crystal

situation

dangli

config

recons

Ge. G

crystal

unreco

with t

Count

introd

bonds

expans

proves

I

neighb

1) rec

stabiliz

3.5.2 F-like behavior due to surface reconstruction

The contradiction between the PBC theory and experimental observations could be explained by accepting that the $\{001\}$ surfaces reconstruct into the (2×1) reconstruction where the surface atoms lower their energy by dimerization and occupy different positions with respect to the bulk phase. On the surface of growing crystals, the truncation of bulk crystals leaves a surface with dangling bonds which lead to an energetically unfavorable situation. Surface reconstruction is carried out in a way by which the surface can eliminate dangling bonds and the surface atoms rearrange themselves into a new periodic configuration so as to reduce its surface energy ([50], [51]). Somorjai [72] shows that reconstruction takes place in the covalently bonded surfaces of semiconductors (i.e., Si, Ge, GaAs, InSb, etc.). Giling and Van Enckevort [50] show that surface recombinations on crystal growth processes account for smoothness of $\{100\}$ facets. Figure 3.29 (a) shows an unreconstructed $\{001\}$ surface. Figure 3.29 (b) shows the same unreconstructed surface with the addition of a growth island having a thickness of half a lattice parameter. Counting the dangling bonds reveals that the surface energy is not altered by the introduction of the island (no island: 120 dangling bonds, with island: 120 dangling bonds). This means that the edge free energy is equal to zero, the growth island does not expand over the surface and hence the surface is rough and does not show steps. This proves that the unreconstructed $\{001\}$ face is a K-face (in agreement with PBC model).

In the (2×1) reconstructed model an extra bond is formed at the surface between neighboring atoms as shown in Figure 3.20 (a). This means that on the $\{001\}$ face the (2×1) reconstruction creates an extra PBC and therefore contributes to a crystallographic stabilization of this surface. This pairing model reduces the number of dangling bonds by

50%

bone

slow

(dim)

1) re

grow

than

islan

intro

islan

surfa

dime

of th

Amo

not s

faces

is un

the s

nonre

termi

50% (unreconstructed surface: 120 dangling bonds, reconstructed surface: 60 dangling bonds) which in turn results in a considerable reduction of the surface free energy. The slow growth of $\{001\}$ faces can now be understood, for addition of new atoms extra bonds (dimer bonds) must be broken. The formation of an extra bond is a unique property of (2 x 1) reconstructed $\{001\}$ surface [50].

Figure 3.30 shows the same reconstructed $\{001\}$ surface with the addition of a growth island. With the growth island included, the number of dangling bonds is larger than for the reconstructed face without the island (with island: 68 dangling bonds, without island: 60 dangling bonds). This shows that a non-zero edge free energy is created with the introduction of a growth island. As a result of the non-zero edge free energy, the growth island expands along the surface (i.e., a growth step) and gives rise to a smooth (F - type) surface. The observed F-like behavior of $\{001\}$ faces can be understood in terms of the dimer model.

Giling and van Enckevort [50] argue that stabilization and thus the F - like character of the $\{001\}$ faces can not be due to some specific adsorptions instead of reconstruction. Among their reasons one may include: (i) the calculations and experiments performed did not show the coverage of crystal faces by impurities and (ii) The F-like behavior of $\{001\}$ faces is very similar under a wide range of different experimental environments, so that it is unlikely that every time the same impurity is present.

In support of the surface reconstruction on $\{100\}$ surfaces, Kobashi [38] illustrates the schematic structures of a nonreconstructed $\{111\}$ surface terminated by hydrogen, a nonreconstructed $\{111\}$ surface terminated by CH_3 , and a nonreconstructed $\{100\}$ surface terminated by hydrogen (Figure 3.31 (a) - (c)) and proceeds with the following arguments:

for $\{111\}$ surface terminated by hydrogen, there is no interference between hydrogen atoms. In a CH_3 terminated $\{111\}$ surface, the possible interference between the adjacent CH_3 groups can be eliminated by the rotation of CH_3 groups about the C-C bonds. For a $\{100\}$ surface, however, the hydrogen to hydrogen distance between the adjacent CH_2 groups is 1.7 angstrom which is smaller than the 2 angstrom interatomic H-H atoms of H_2 . Therefore, in reality it seems very unlikely to have a nonreconstructed $\{100\}$ hydrogen terminated surface. The preceding discussion suggests that the F-like character of diamond like structures is an intrinsic property of their faces induced by reconstruction.

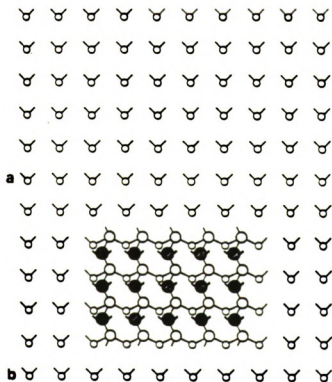


Figure 3.29. An unreconstructed $\{001\}$ surface with (a) no growth island: 120 dangling bonds and (b) with growth island: 120 dangling bonds. Thickness of island=0.5d [50].

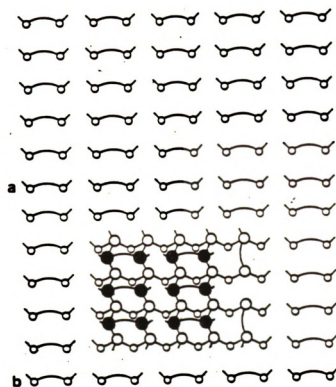


Figure 3.30. A (2 x 1) reconstructed {001} surface with (a) no growth island: 60 dangling bonds and (b) with growth island: 68 dangling bonds. Thickness of island=0.5d [50].

3.5.3 The orientation of growth steps on reconstructed {001} faces

The step direction on reconstructed {001} directions can be determined by the total free energy on these faces. Figure 3.32 (a) and (b) show growth steps parallel to $\langle 110 \rangle$ and $\langle 100 \rangle$ directions, respectively. Counting the number of dangling bonds in both Figures shows that their number and thus the total edge free energy is higher for island (b) than for (a). In addition, the total number of atoms included in (b) is about 50% of the number in (a). Therefore, configuration (a) has a lower total free energy and thus is more

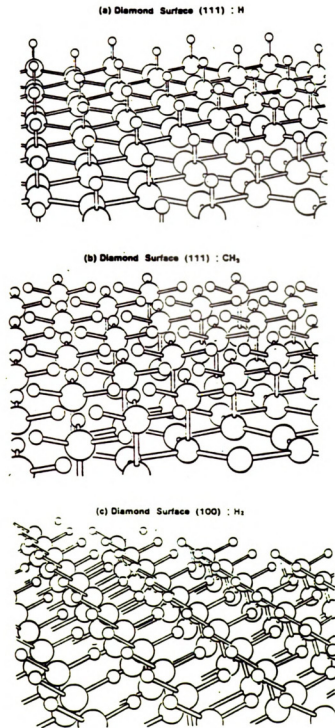


Figure 3.31. Schematic structure of hydrogen-chemisorbed diamond surfaces: (a) (111): H, (b) (111): CH₃, and (c) (100): H₂ [38].

stable. Figure 3.33 (a) and (b) illustrate how a $\langle 110 \rangle$ step is formed [51]. Surface atoms rearrange themselves into (2×1) dimer rows normal to $\langle 110 \rangle$ (Figure 3.33 (a)). Then the alternate dimer rows are reconstructed perpendicular to the old ones, which bring about a $\langle 110 \rangle$ step indicated by a dashed line (Figure 3.33 (b)). The occurrence of step growth mechanism on $\{001\}$ surfaces are also shown by Badzian [67] which shows that the step type growth is along $\langle 110 \rangle$ directions, by Everson and Tamor [53], by Zhu and Stoner [34], by Kobashi [38] and by Lee Chow [41]. Spitsyn [8] and Williams [40] indicate that step growth mechanism takes place on both $\{100\}$ and $\{111\}$ surfaces.

Okada [51] points out from the results of some calculations that CH_2 radical might migrate along the $\langle 110 \rangle$ direction on the (2×1) reconstructed $\{100\}$ planes under CVD diamond growth conditions because of the low migration barrier. Although the precursor cannot be restricted to CH_2 , it suggests that the growth along $\langle 110 \rangle$ on the reconstructed $\{100\}$ planes is kinetically favorable.

3.5.4 Growth steps and reconstruction on $\{111\}$ planes

Formation of growth steps on $\{111\}$ planes of diamond have been reported by some researchers ([32], [40], [50], [51], [52]). The step directions normal to step edges on $\{111\}$ were shown to be $[\bar{1}\bar{1}2]$ oriented. The $\langle 112 \rangle$ step on the (111) surface is crystallographically identical with the (100) plane $[3/11]$ which means that each atom at the $\langle 112 \rangle$ steps on an unreconstructed (111) plane has two dangling bonds and the $(111)\langle 112 \rangle$ steps have the slowest lateral growth rate. Figure 3.34 (a) shows a top view of unreconstructed $\{111\}$ planes. On these unreconstructed $\{111\}$ planes where PBC theory applies at the crystal surface, an atom on a $[11\bar{2}]$ step site of the crystal surface has three

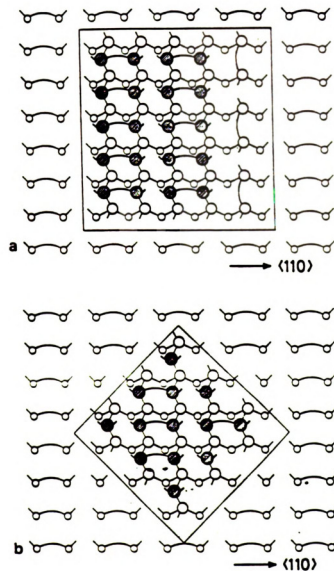
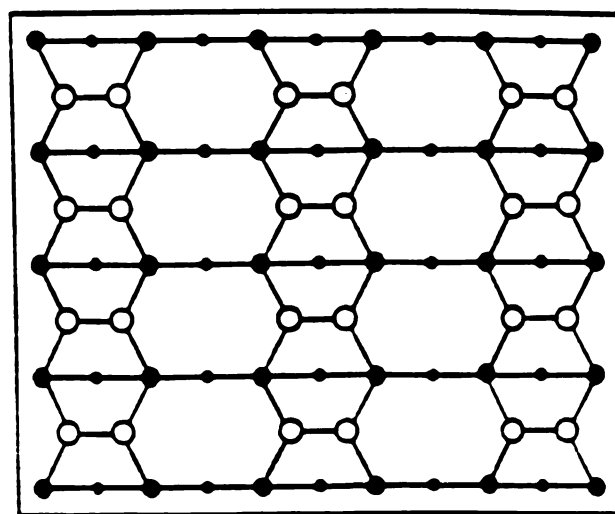
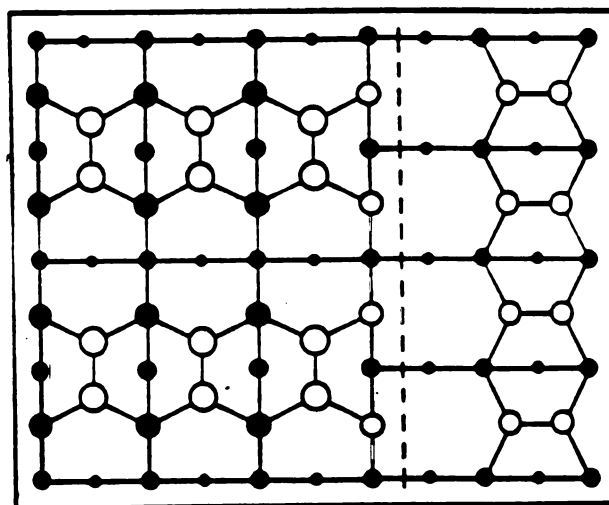


Figure 3.32. Difference in energy (i.e., number of dangling bonds and number of atoms included in nucleus) of unit thickness ($0.5d$) growth islands of different orientations, (a) Edges parallel to $\langle 110 \rangle$: 50 atoms in nucleus, 90 dangling bonds over the whole surface area, (b) Edges parallel to $\langle 100 \rangle$: 30 atoms in nucleus, 100 dangling bonds [50].



→ $\langle 110 \rangle$
(a)



→ $\langle 110 \rangle$
(b)

Figure 3.33. Top view of (a) the (2 x 1) reconstructed {100} planes; (2 x 1) dimer rows normal to $\langle 110 \rangle$ are rearranged, (b) the alternate (2 x 1) dimer rows perpendicular to the previous ones. A $\langle 110 \rangle$ step indicated by the dashed lines is formed. Open circles represent atoms with dangling bonds. Large filled circles represent upper terrace atoms [51].

bonds with neighbor atoms and has one dangling bond, whereas an atom on a $[\bar{1}\bar{1}2]$ step site is connected with two bonds and has two dangling bonds. Accordingly, the velocity of the step movement to $[\bar{1}\bar{1}2]$ must be higher than that to $[11\bar{2}]$ (i.e., the lateral growth rate must be the slowest in the $[11\bar{2}]$ direction). This was shown to be in conflict with the resultant growth steps on $\{111\}$ which showed the opposite behavior (i.e., the lateral growth rate was the slowest in the $[\bar{1}\bar{1}2]$ direction). In addition, the PBC theory applied to an unreconstructed surface predicts that the growth steps on $\{111\}$ planes should be a regular triangle whose sides have the same directions of the outline of the $\{111\}$ planes as shown in Figure 3.35 [73], whereas, the step directions observed [51] were opposite to those predicted from the PBC theory. These conflicts may be explained by accepting that the (100), (2 x 1) reconstruction occurs on $\{111\}$ surfaces as well as on $\{100\}$ surfaces ([50], [51], [52]). Giling and van Enckevort [50] and Okada [51] have discussed $\langle 112 \rangle$ step reconstruction mechanism on (111) due to the (100), (2 x 1) reconstruction. Figure 3.34 (b) shows a top view of reconstructed $\{111\}$ planes where a (100), (2 x 1) type reconstruction has taken place at the $[\bar{1}\bar{1}2]$ step. As shown, an atom on the reconstructed $[\bar{1}\bar{1}2]$ step site has one additional bond and $[\bar{1}\bar{1}2]$ steps become more stable because the number of the dangling bonds decreases from two to one. The reconstruction at the $[11\bar{2}]$ step is geometrically less favorable than at the $[\bar{1}\bar{1}2]$ step. As a result, the lateral growth rate is the slowest in the $[\bar{1}\bar{1}2]$ directions; hence the $\{111\}$ faces are likely to be roughened. The observed growth steps [51] were shown to be consistent with this model.

Eiichi Kondoh [52] points out that the dimer structure on the (100), (2 x 1) surface is closely related to hydrogen atoms in the growing environment. Accordingly, (100), (2 x 1) structure can be expected to be broken by hydrogen irradiation when the gas-phase H

concentration is high. The {100}-preferred morphology of microwave plasma CVD diamond films at higher methane concentration (see the section on morphology vs. deposition conditions) is believed to be due to a smaller concentration of atomic hydrogen in methane rich environment in which the (100), (2 x 1) structure is preserved [52]. At high atomic hydrogen concentration, almost all the surface bonds may be saturated with hydrogen atoms which then prevent surface reconstruction, so that both {100} and {111} faces would have the primitive (1 x 1) structure and the competition between the growth rates of {100} and {111} faces results in a {111}-dominant structure [52] since {111} faces have faster growth rate due to the formation of twins as explained in [29].

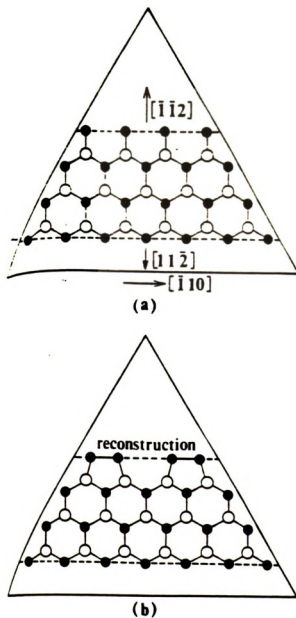


Figure 3.34. Top view of (a) the unreconstructed $\{111\}$ planes. Each $[\bar{1}\bar{1}2]$ step atom has two dangling bonds, whereas $[11\bar{2}]$ step atom has one dangling bond, (b) the $[\bar{1}\bar{1}2]$ step reconstructed $\{111\}$ planes. $[\bar{1}\bar{1}2]$ step atoms have one additional bond. Closed circles and open circles represent atoms with one bond directed downwards and atoms with one bond directed upwards, respectively [51].



Figure 3.35. Morphology of diamond as expected from the PBC theory [73].

CHAPTER 4

Experimental System, Experimental Procedures, Experimental Parameter Space and Measurement Methodologies

4.1 Introduction

This chapter describes the experimental system, experimental procedures and parameter space, and measurement methodologies utilized in this thesis.

4.2 Experimental system: Michigan State University microwave plasma deposition machine

Figure 4.1 shows various components of the Michigan State University Microwave Plasma Deposition machine. These components include (i) microwave cavity plasma reactor (MCPR) and process chamber, (ii) vacuum pump and the gas flow control system, (iii) microwave power supply and microwave waveguide/transmission system, and (iv) computer controller. The microwave cavity plasma reactor was described in Section 2.6. Other components of the microwave deposition machine are described in the following subsections.

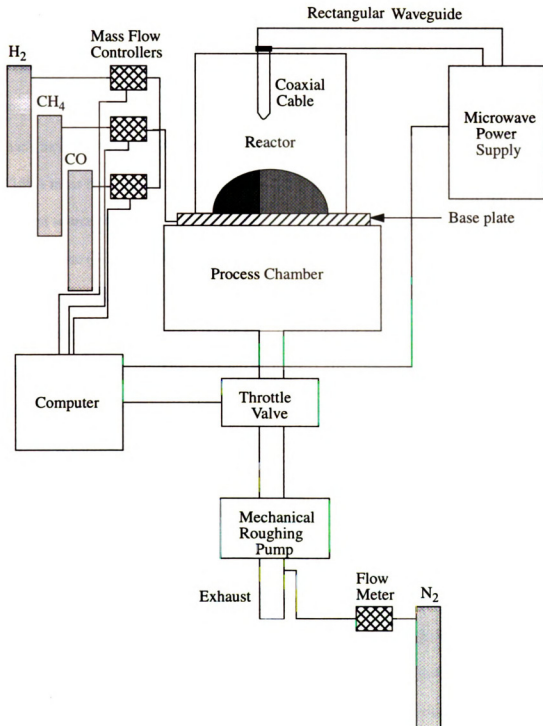


Figure 4.1. Various components of the M.S.U microwave plasma deposition machine.

4.2.1 Vacuum pump and the gas flow control system

Figure 4.2 displays a simplified schematic drawing of the vacuum pump and the gas flow systems of the M.S.U microwave plasma deposition machine. A detailed description of the vacuum pump and the gas flow control systems of the deposition machine is provided in reference [14]. The source gases consist of H_2 (1), CH_4 (2), and CO (3) gases which have a purity of 99.999%, 99.99%, and 99.9%, respectively. Three MKS type 11159A mass flow controllers along with a MKS type 247C power supply/digital readout/set point source (4) are utilized for gas flow control. The gases are mixed before they enter the base plate (5). Chamber (6) pressure is controlled by a MKS 6 inch throttle valve (7). A varian manual throttle valve (8) is installed and used to manually control the pressure of the chamber (6) if the automatic throttle valve becomes dysfunctional. The manual throttle valve is normally open and the chamber (6) pressure is controlled by the automatic throttle valve. The pressure in the process chamber (6) is measured by an MKS Baratron type 122A 1000 Torr full scale high pressure gauge (9). This pressure gauge is connected to the chamber (6) through an isolation valve (10) so that the gauge can be isolated from the chamber whenever not in use. An ALCATEL 2033 type mechanical roughing pump (11) is used to pump down the chamber pressure to ~ 0.01 Torr. The pump pressure is measured by an MKS type 286 thermal conductivity vacuum gauge TC_1 (12). Nitrogen (13) is used for system vent to bring the chamber (6) pressure into the atmospheric pressure. It is also used for exhaust (14) purge because H_2 (1) and CH_4 (2) gases used in experiments are flammable and nitrogen gas (12) with flow rate of twenty (or more) times of total flow rate is needed to dilute the exhaust gas mixture in the exhaust pipe so that the resultant gas mixture is no longer flammable.

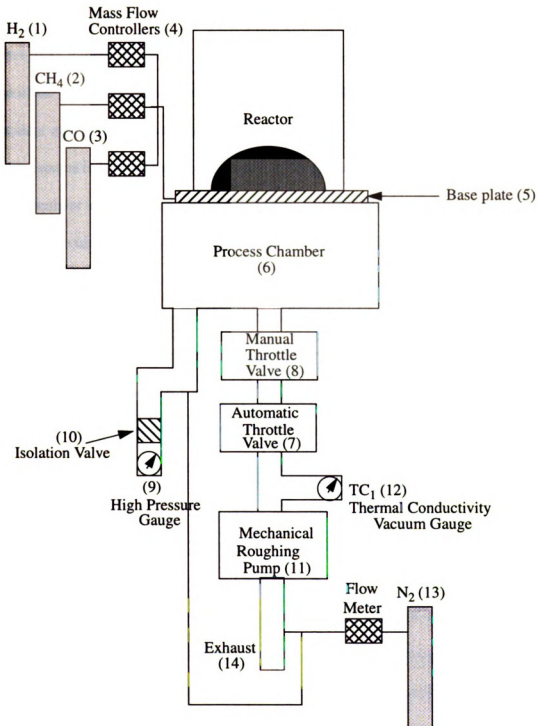


Figure 4.2. Vacuum pump and the gas flow system of the M.S.U microwave plasma deposition machine.

4.2.2 Microwave power supply and microwave waveguide/transmission system

Figure 4.3 shows a schematic drawing of the microwave power supply and waveguide circuit. It consists of a 2.45 GHz variable microwave power source (1), a circulator (2) a matched dummy load (3), a dual-directional power coupler (4), and incident and reflected power meters (5) and (6). The microwave power supplied by the power source is incident on the microwave cavity applicator (7) after it propagates through the circulator and the dual-directional power coupler. Should there exist a mismatch between the impedances of the cavity applicator and the wave guide, some of the incident power is reflected back from the cavity applicator and propagates in the opposite direction of the incident power. It travels through the dual-directional coupler and is directed by the circulator into the matched dummy load where it is absorbed and dissipated as thermal energy. The circulator and the matched dummy load prevent the propagation of the reflected power back into the power supply where it may damage the source.

The microwave power source used was a Cober (model no. S6F/4503) 2.45 GHz, 6 kW power source.

4.2.3 Computer controller

A computer is used to monitor the operating conditions of the reactor. It controls experiment time and shut down sequence of the experiments. It also monitors the safety of the system. The system operating pressure along with reflected and input power readings are used as input signals to the computer. The flow chart of the computer monitoring program is shown in Figure 4.4 [14]. As shown, the experimental run time, reflected power upper limit, and the operating pressure are set first. The experimental system is then

enabled to allow the microwave power to turn on and the feed gases to flow. It also allows the automatic throttle valve to operate in an automatic mode in order to control the pressure of the system. During the experiment, a checking loop compares the pressure, reflected microwave power, and timer with the pre-set values to determine the state of the experiment. An emergency shut down of the microwave power and feed gas is performed if at any time during the experiment, the operating pressure and/or reflected microwave power exceed the pre-set values. It also performs shut down if the power supply and/or the base plate cooling water is shut down. The automatic throttle valve is then closed in order to isolate the vacuum pump from the process chamber.

4.2.4 Microwave cavity plasma reactor (MCPR) general operational performance

The reactor is said to be under thermally floating configuration if no external substrate cooler or heater is utilized. This method of reactor operation is utilized throughout this thesis. Under the thermally floating configuration the operating pressure p , substrate temperature T_s , and microwave power P_t are interrelated. These three variables are interdependent and thus they can be considered as essentially one variable. Figure 4.5 displays the very repeatable experimental non-linear relationships between these three variables for the 5" quartz dome/3" substrate reactor geometry configuration. As shown, the substrate temperature T_s is very sensitive to variations in pressure p and only varies slowly with variations in the absorbed microwave power P_t . The discharge volume V_d is sensitive to both the variations in absorbed microwave power P_t and pressure p . For a fixed pressure p , the discharge volume increases with the absorbed microwave power. For a fixed absorbed microwave power P_t , the discharge volume decreases with pressure p . The

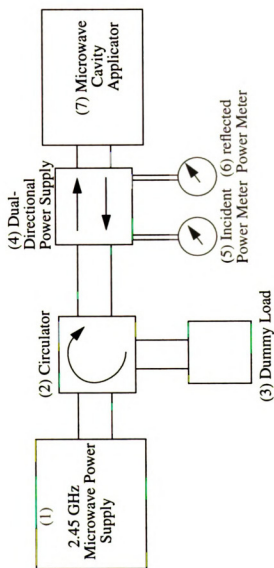


Figure 4.3. Microwave power supply and waveguide circuit [14].

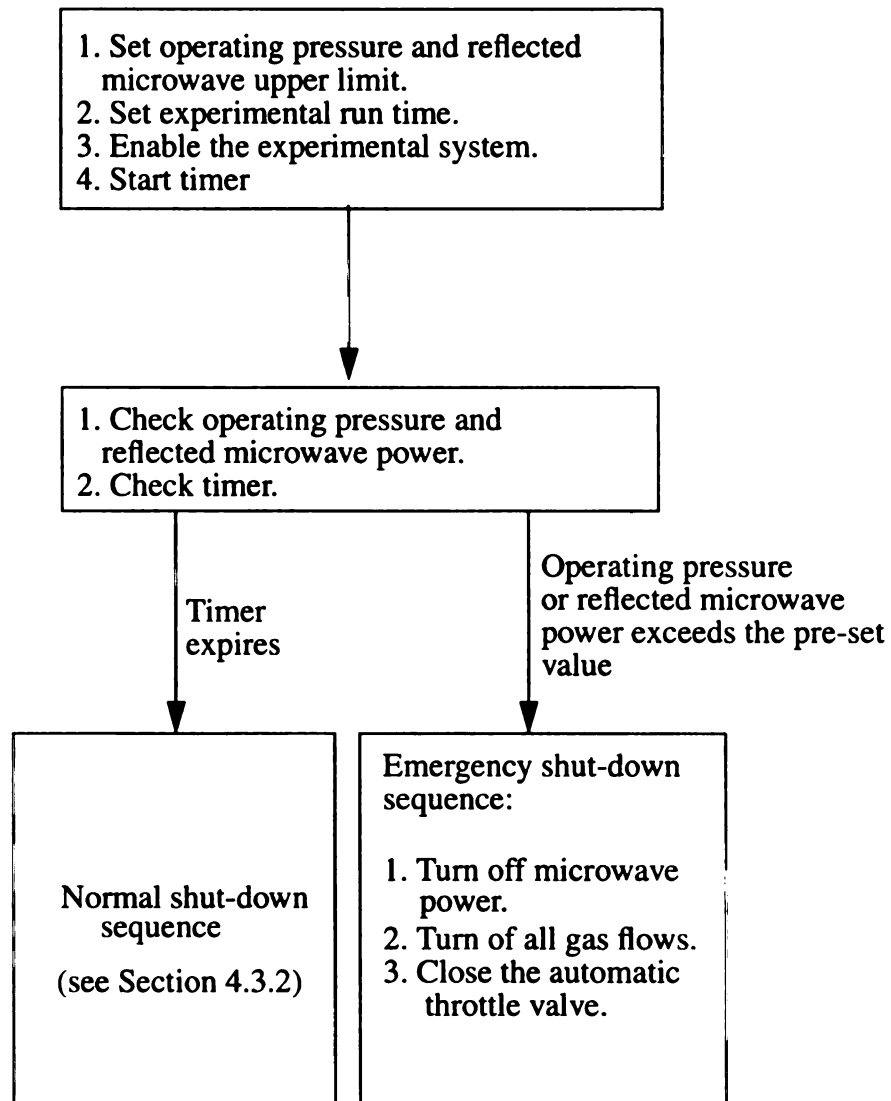


Figure 4.4. Computer monitor program flow chart for the MCPR [14].

lower absorbed microwave power limit is determined by the minimum power required to generate a discharge volume $(V_d)_{\min}$ that covers a 3" diameter substrate. Below $(V_d)_{\min}$ the discharge volume is too small to fully cover the substrate surface. The upper limit of the absorbed microwave power is determined by the maximum power that can be used to generate a discharge volume $(V_d)_{\max}$ that is not too big to touch the quartz dome walls. The upper limit of the absorbed microwave power is the maximum power that can be used to operate the reactor safely without over heating the quartz dome.

Total gas flow rate and CH_4/H_2 gas chemistry have also been shown to have insignificant influence on the pressure-substrate temperature relationship as shown in Figure 4.6. Therefore, under the thermally floating configuration the substrate temperature is primarily set by the operating pressure.

The increase of substrate temperature with operating pressure is due to an increase in the intensity of the microwave discharge as the pressure increases. That is, as the pressure increases the amount of power per volume (i.e., absorbed volume power density) increases due to a larger volume recombination of radicals and charged species. This results in an increase in the species flow to and recombination on the substrate and causes the substrate temperature to increase.

The increase in the volume recombination of radicals and charged species as pressure increases causes the discharge volume to decrease. Therefore, in order to make the plasma cover the entire substrate area, the microwave power needs to be increased with pressure.

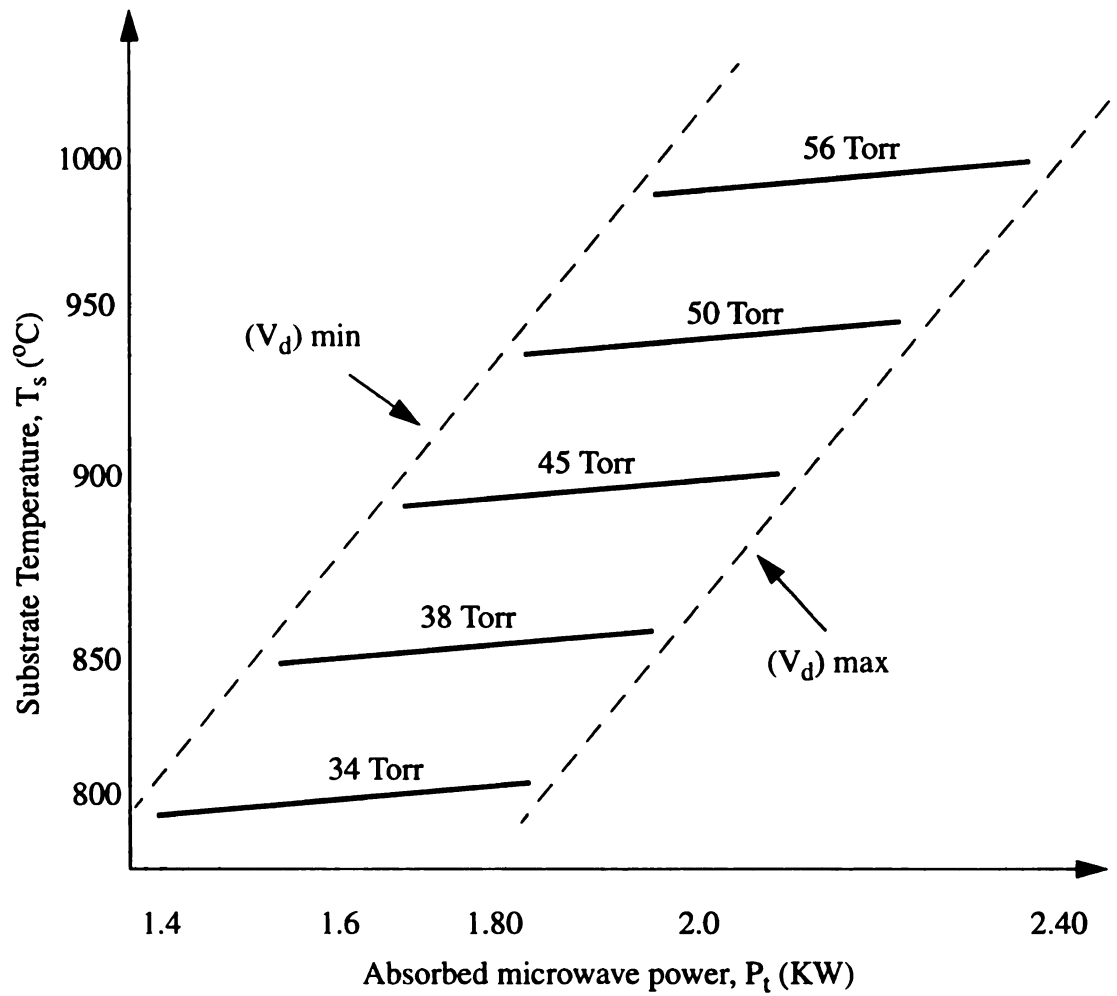


Figure 4.5. Reactor operating field map under thermally floating configuration For 5" quartz dome/3" substrate reactor configuration.

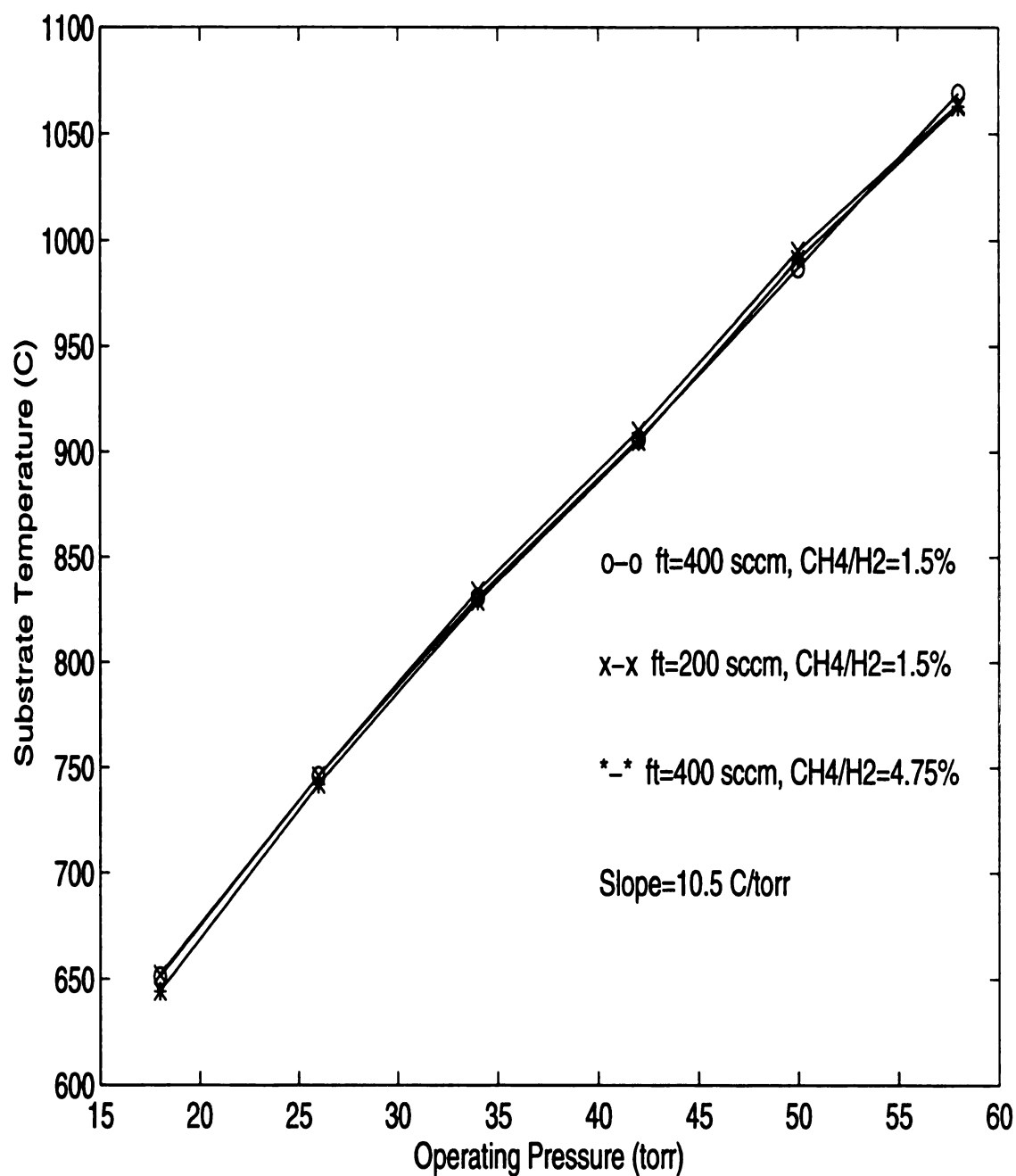


Figure 4.6. Pressure-substrate temperature relationship for various total gas flow rates and CH₄/H₂ chemistry under thermally floating configuration.

4.2.5 Repeatability of the diamond CVD experiments

Provided that the quartz dome was clean, CVD diamond films with almost identical properties (Y_1) were deposited even when the experiments were carried out almost 3 years apart. As an example, Figure 4.7 show SEM pictures of samples SK10 and SK203 which were deposited approximately three years apart. The two diamond films displayed similar morphologies. They also displayed similar structural quality. With respect to the reactor performance variables (Y_2), the growth rate of SK10 was $0.275 \mu\text{m/hr}$ and that of SK203 was $0.324 \mu\text{m/hr}$. As another example, Figure 4.8 illustrates SEM pictures of SK62 and SK64 samples which were deposited one week apart. The films displayed almost identical morphologies. They also displayed similar structural quality. With respect to the reactor performance variables (Y_2), the growth rates of SK62 and SK64 samples were $0.394 \mu\text{m/hr}$ and $0.38 \mu\text{m/hr}$, respectively.

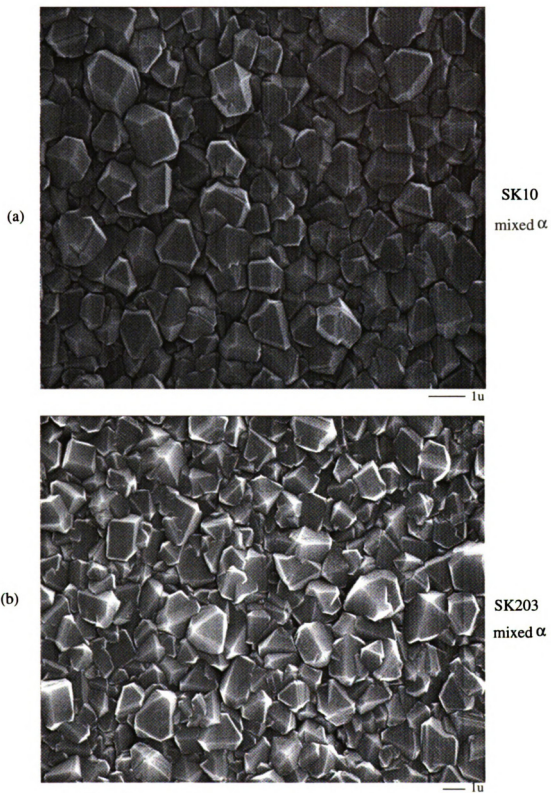


Figure 4.7. SEM pictures of samples deposited at $f_t=400$ sccm, $T_s=1000^\circ\text{C}$, and $\text{CH}_4/\text{H}_2=0.60\%$ deposited approximately three years apart.

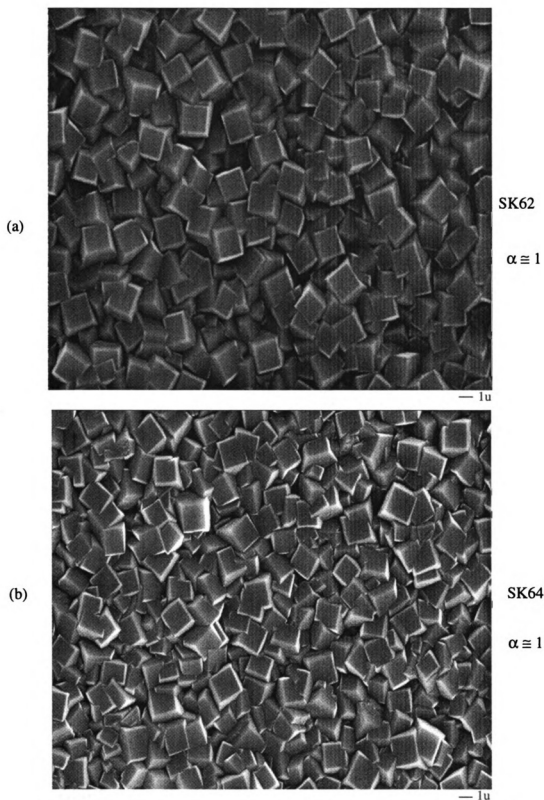


Figure 4.8. SEM pictures of samples deposited at $f_t=60$ sccm, $T_s=850^\circ\text{C}$, and $\text{CH}_4/\text{H}_2=1.50\%$ deposited one week apart.

4.3 Experimental procedures

4.3.1 Substrate seeding and seeding density

Silicon substrates used for diamond deposition are seeded prior to film deposition. A mixture of 0.1 μm diamond powder and photoresist solution (i.e., seeding solution) is used for substrate seeding [18]. The seeding is done using a spinner. The photoresist utilized is Shipley 1470 type photoresist along with type A Shipley photoresist thinner. Shipley 1813 type photoresist along with type P Shipley photoresist thinner have also been utilized and have also shown to give a good result. The latter type has less hazardous vapor and therefore is safer to use. Seeding solution preparation and seeding procedures are as follow:

- (i) Measure 916 mg. of 0.1 μm diamond powder into a bottle.
- (ii) Partly cover the bottle with aluminum foil and place it on a hot plate or in an oven (100°C) for 1 hour. This helps extract moisture from the diamond powder and prevent clumping of the powder.
- (iii) Add 34 ml of photoresist thinner into the bottle. Place a magnetic stirrer in the bottle and place the bottle on a stirring plate for 1 hour.
- (iv) Place the bottle in an ultrasonic bath for at least 1 hour.
- (v) Add 90 ml of photoresist to the solution and place it on an stirrer for 1 hour.
- (vi) Place the bottle in an ultrasonic bath for at least 1 hour.
- (vii) Set the spinner to 2500 rpm. Using a dropper dispense the diamond powder/photoresist solution on the substrate and spin it for 30 seconds.
- (viii) To harden the seeding solution on the substrate, place the seeded wafer in an oven for ~ 20 minutes at ~ 100 °C or store it in room temperature for few

hours.

The seeding density associated with the above procedure was $\sim 5 \times 10^8 \text{ cm}^{-2}$. The seeding density was determined via the following procedure: (i) A silicon wafer was spin seeded. (ii) The photoresist covering the seeds was removed by placing the seeded wafer in the deposition chamber and by subjecting the seeded wafer to a hydrogen plasma at approximately 700°C . (iii) SEM pictures were taken from several locations of the wafer and the number of seeds were counted on each photo. (iv) The average of the seed counts from the several locations was calculated. This number was considered as the seeding density associated with the wafer seeding procedure described above.

4.3.2 Reactor start-up and shut-down procedures

The start-up and shut-down procedures of the MCPR system are as follows:

1- Start-up procedure:

- (i) pump down the system to below 5 m Torr.
- (ii) turn on the microwave power supply and allow a few minutes for the microwave power supply to warm up.
- (iii) set the cavity length L_s to approximately 21.6 cm and the probe length L_p to approximately 3.2 cm.
- (iv) set the pressure to the desired value.
- (v) set the gas (i.e., H_2 , CH_4 , CO , etc.) concentrations to desired values and turn on the gas flows.
- (vi) turn on the microwave power when pressure reaches 8 torr.
- (vii) gradually increase microwave power as pressure increases.

(viii) start the timer when pressure, substrate temperature, and microwave power reach desired values.

2- Shut-down procedure:

- (i) turn off CH_4 and other gases except H_2 ,
- (ii) wait for 3 to 5 minutes for process self cleaning,
- (iii) turn off microwave power,
- (iv) turn off H_2 gas,
- (v) evacuate (pump down) the system.

4.3.3 Quartz dome cleaning

The quartz dome was cleaned on a regular basis after every two experiments and also when ever a contamination was observed or was expected on its walls. Hydroflouric acid (HF) was used to remove any contamination from the quartz dome and de-ionized (DI) water was used to rinse off the acid from the dome. The dome was then N_2 (nitrogen) dried using a nitrogen gas gun.

4.4 Experimental parameter space

- (i) **Operating pressure p :** $p \in [20, 80]$ torr.
- (ii) **Microwave power P_t :** microwave power was set by the pressure and deposition area. The power was adjusted so that $3 \leq A_d \leq 4$ inches for 5" quartz dome/3" substrate geometry and $2 \leq A_d \leq 3$ for 4" quartz dome/2" substrate geometry.

(iii) Methane concentration CH_4/H_2 : The methane concentration, $\frac{\text{CH}_4}{\text{H}_2} \%$ was varied

from a low value where there was virtually no diamond deposition to a high value where the diamond peak determined by 1332 cm^{-1} Raman shift was no longer observed. The

methane concentration range of $\frac{\text{CH}_4}{\text{H}_2} \in [0.5, 5.0] \%$ was used for experiments reported in

this thesis.

(iv) Hydrogen total flow rate f_t : $f_t \in [30, 600] \text{ sccm}$.

(v) Substrate temperature T_s : $T_s \in [650, 1100] \text{ }^\circ\text{C}$.

(vi) Substrate (Si wafer) sizes: 3 and 2 inches in diameter.

(vii) Quartz dome sizes: 4 and 5 inches in inner base diameter.

(viii) Deposition time t : $t \geq 8$.

4.5 Measurement Methodologies

4.5.1 Surface morphology analysis

Surface morphology of the films were determined via Scanning Electron Microscopy (SEM). Figure 4.9 shows a basic schematic of an SEM [74]. A beam of electrons is produced by the electron gun. The beam is then attracted by the anode, condensed by the condenser lens, and finally focused as a very fine point on the specimen by the objective lens. When a beam of electrons strike the specimen, it produces secondary electrons from the sample, which are collected by the detector, converted to a voltage, amplified, and converted to SEM images by CRT.

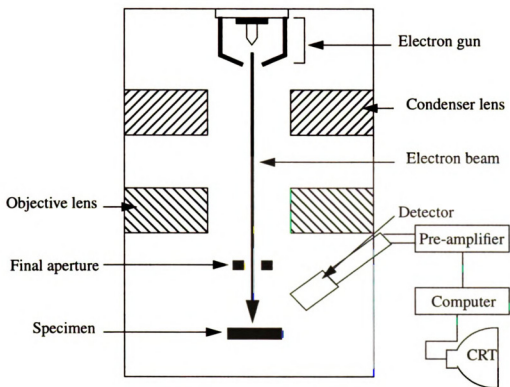


Figure 4.9. A basic schematic of an SEM [74].

4.5.2 Average grain size

For films with {100} morphology grain sizes were easily measured from SEM pictures since the crystals were almost of the same size and twin free. With {111} films, the method of linear intercept [75] was used since crystals were not of the same size and twinning persisted. In this method, the number of crystals are counted over a specific length (i.e., length of the SEM picture) and the average grain size is measured by dividing the length with the number of the crystals in that length.

4.5.3 Structural quality analysis

Among many methods such as AES (Auger Electron Spectroscopy), XPS (X-ray Photo electron Spectroscopy), Raman, etc. Raman spectroscopy is the most popular method to determine the structural quality of diamond films. The binding energy of core electrons in diamond differs by less than 1 eV from graphite and amorphous carbon [40]. This is too small to observe in most AES and XPS systems which means that these systems are not capable of differentiating between different forms of carbon structures. Raman analysis, on the other hand, can easily make the distinction between the different forms of carbon bonds. The Raman analysis, however suffers from the fact that it is approximately 50 times more sensitive to graphite than to diamond ([76], [77], [78], [79]). A small amount of graphite component appears as a broad peak in the Raman spectra. This means that the Raman spectrum is a very sensitive tool for detection of the graphitic carbon phase in diamond films but not conversely. Due to a relatively large amount of graphite component, a films proven to be predominantly diamond by other methods may only show a broad peak around 1580 cm^{-1} with no indication of 1332 cm^{-1} peak. A brief description of the Raman effect is provided in the following section.

4.5.3.1 The Raman effect

The backscattered light of an intense monochromatic light beam (i.e., a laser beam) of frequency f_0 shining on a sample contains three components: (i) Rayleigh scatter, (ii) Anti-Stoke scatter, and (iii) Stoke scatter. The Rayleigh scatter is elastic and has the frequency f_0 . The anti-Stoke and Stoke scatters are inelastic and have frequencies f_0+f_{vib} and f_0-f_{vib} , respectively, where f_{vib} is the vibrational frequency of the sample molecules

which undergo a vibration as a result of the excitation caused by the beam. The inelastic anti-Stoke and Stoke scatters are named after Raman. These scatters are typically about 0.10% of the Rayleigh scatter [80].

The diamond bonding structure is sp^3 hybridization as opposed to the graphite and amorphous carbon structure which show sp^2 and sp bondings, respectively [78]. For diamond, the anti-Stoke and Stoke Raman bands are shifted by 1332 cm^{-1} from the excitation frequency. Raman shifts for the sp^2 graphitic and disordered carbon phases are broad and occur around 1580 cm^{-1} and 1355 cm^{-1} , respectively ([78], [79]). Diamond Like Carbon (DLC) shows a Raman shift at $\sim 1510\text{ cm}^{-1}$ [78]. Micro and macro Raman analysis are carried out to study very fine (i.e., one or a small number of grains) and relatively larger (i.e., a collection of grains) structures, respectively. The depth resolution of the Raman measurement depends on many factors such as optical absorption, scattering and reflection by the polycrystalline films. The depth resolution is in the range of 5 - 20 microns for such samples [78]. Therefore, the contribution from the Raman scattering of the substrate materials may often be evident.

The laser used for the Raman analysis in this thesis was an Argon laser with the wavelength of 514.5 nm and power of 300 mW. The spot size of the laser beam on the sample was approximately $25\text{ }\mu\text{m}$ (diameter). The typical grain size of the diamond films used for Raman analysis was about $2\text{ }\mu\text{m}$. Hence, the laser beam spot size encompassed a collection of grains including grain boundaries for each Raman analysis carried out in this thesis. Thus the structural analysis of the diamond films carried out in this thesis did not correspond to a single diamond grain but to a collection of grains including the grain

boundaries.

Full Width at Half Maximum (FWHM) of Raman spectra is a measure of the structural quality of diamond films. Natural diamond shows a sharp Raman shift at 1332 cm^{-1} with FWHM in the range of 2 cm^{-1} . Internal and external stresses in a diamond film cause the FWHM of the film to widen. Grain boundaries, impurities, and crystal defects (i.e., twinning, etc.) create internal stresses in a film. At grain boundaries the adjacent crystals exert a force on each other creating a huge stress in those regions. Non-diamond carbon (i.e., graphite) components which are abundant in grain boundaries are among the impurities that create internal stress in polycrystalline diamond films. Crystal defects such as twinning produce internal stresses due to the distortion in the bond length and bond angle between the twin and parent crystals. Lattice mismatch between diamond and the substrate material and difference in the thermal expansion coefficients between diamond and the substrate material create external stresses in the film ([81], [82]) particularly at elevated temperatures.

In this thesis the FWHM measurements were done through careful measurements of the height and width of diamond peaks. The diamond peaks for most of the Raman spectra of the samples showed different leading and trailing points. For instance, from Figure 4.10 it is seen that the diamond peak begins at ~ 8200 counts per second (point A) and ends at ~ 8400 counts per second (point B). Throughout this dissertation whenever this situation was encountered, the middle point (point C at ~ 8300 counts per second) was calculated and used for FWHM measurements. This was in agreement with the technique utilized by S. Stuart [83].

The least square curve fitting technique was also applied to obtain FWHM. The

results were close to values obtained by measurement of height and width as previously discussed. Figure 4.11 shows a typical curve fitting of a Raman spectrum.

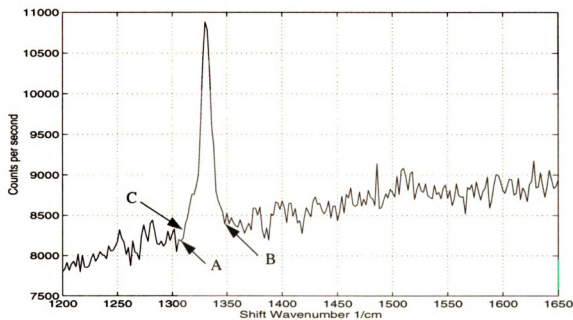


Figure 4.10. A typical Raman spectrum with a diamond peak with different leading and trailing points.

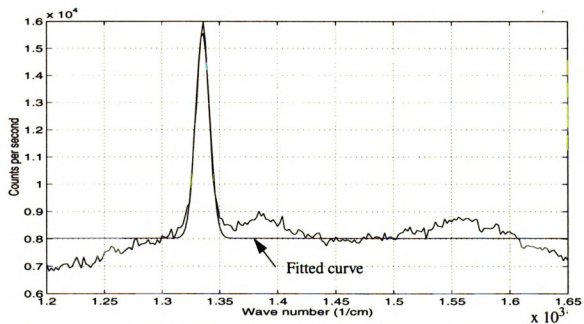


Figure 4.11. A fit for FWHM measurement for a typical Raman spectrum.

4.5.4 Film linear growth rate

Film linear growth rate determines the average film growth rate over the substrate surface. Film linear growth rate is calculated from the following equation:

$$d = \frac{W}{A \times D} \quad (\text{eq. 4.1})$$

where d is the average film thickness in cm, W (in grams) is total weight gain after deposition (i.e., diamond added to the substrate), A (in cm²) is the substrate area, and D = 3.515 g/cm³ is the diamond density.

4.5.5 Carbon conversion efficiency

Carbon conversion efficiency is the ratio of the carbon added to the film to the total amount of carbon supplied by the input gas. If A grams/hour of carbon is added to the film (i.e., weight gain) and B sccm of carbon (i.e., CH₄ gas) is supplied by the input gas, then the carbon conversion efficiency is calculated as follows:

$$\begin{aligned} \text{Carbon atoms/hour supplied} &= (B \text{ cc/min}) \times (60 \text{ min/hour}) \times \left(\frac{6.024 \times 10^{23} \text{ atoms}}{22400 \text{ cc}} \right) \\ &= 1.6136 \times 10^{21} \times B \quad (\text{gas phase}) \quad (\text{eq. 4.2}) \end{aligned}$$

$$\begin{aligned} \text{Carbon atoms/hour added to the film} &= (A \text{ grams/hour}) \times \left(\frac{\text{cm}^3}{3.515 \text{ gram}} \right) \times \\ &\left(\frac{1.79 \times 10^{23} \text{ atoms}}{\text{cm}^3} \right) = 5.0925 \times 10^{22} \times A \quad (\text{solid phase}) \quad (\text{eq. 4.3}) \end{aligned}$$

$$\begin{aligned} \% \text{ Carbon conversion efficiency} &= ((\text{carbon added to the film}) / (\text{carbon supplied by the} \\ &\text{gas})) \times 100 = ((5.0925 \times 10^{22} \times A) / (1.6136 \times 10^{21} \times B)) \times 100 \end{aligned}$$

$$= 3156 \times \frac{A}{B} \% \quad (\text{eq. 4.4})$$

4.5.6 Gas residence time

The gas residence time is a measure of how long supplied gas species stay over the substrate before they are pumped out. The gas residence time is determined from the following equation [14].

$$\tau_r = \frac{pV_q}{f_t} \quad (\text{sec}) \quad (\text{eq. 4.5})$$

where p (expressed in torr) is the pressure, V_q (in liters) is the quartz dome volume above the substrate, and f_t (in torr-liter/sec, 1 torr-liter/sec = 79.05) is the total flow rate.

4.5.7 Substrate temperature

A UX-10/20 ULTIMAX optical pyrometer is utilized for measurement of substrate temperature. When set to the emissivity value of the substrate (0.8 for polished silicon wafers), an optical pyrometer collects the infrared energy radiated by the substrate and converts the energy to an electrical signal proportional to the temperature being observed. Figure 4.12 shows a simplified substrate temperature measurement setup utilized in this research.

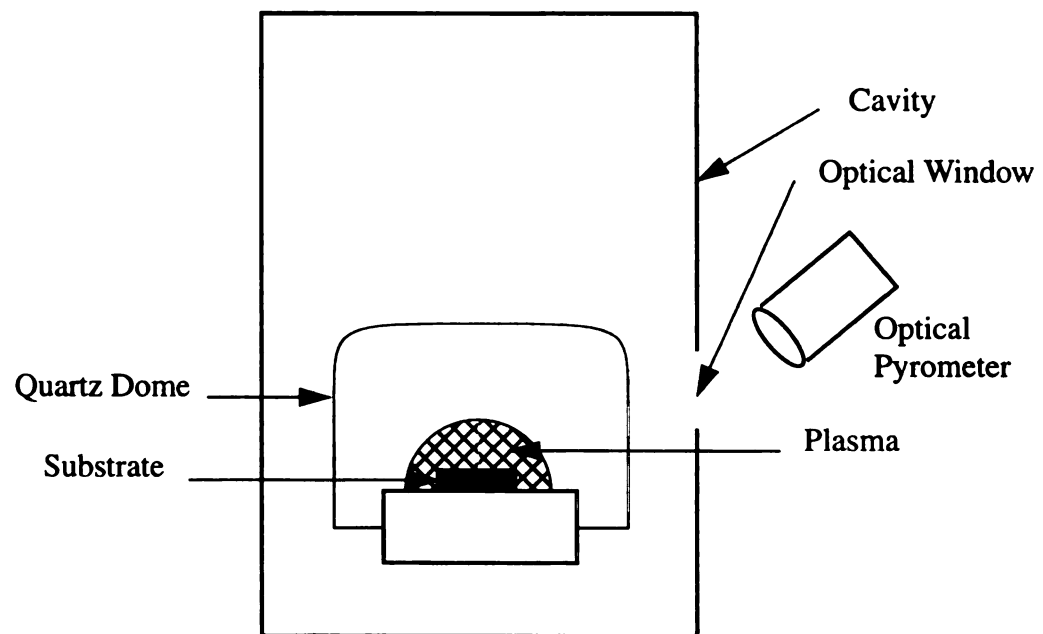


Figure 4.12. A simplified substrate temperature measurement setup.

CHAPTER 5

Reactor Field Map: 5" Quartz Dome/3" Substrate Reactor

5.1 Introduction

This Chapter and the Chapters that follow describe the results of a detailed experimental study of the output film properties (Y_1) and reactor performance (Y_2) of the most advanced MCPR design. The experimental data presented in this chapter resulted from about 250 experiments which represent over 2000 hours of reactor experimental operation.

In Section 1.3 (Figure 1.7) it was pointed out that the microwave plasma deposition process is very complex. It consists of a large number of input ($U = [U_1, U_2, U_3]$), internal (X), and output (Y) variables. The output variables are dependent upon the input and internal variables (i.e., $Y = g(U, X)$) and the internal variables are dependent upon the input variables ($X = f(U)$). In this chapter a subset of the parameter space shown in the block diagram of Figure 1.7 is investigated. In particular, the fixed reactor configuration consisting of a 5" quartz dome/3" substrate is experimentally studied. Figure 5.1 illustrates this subset and Table 5.1 summarizes the input (U), internal (X), and output (Y) variables considered in this chapter. The relationships between these output ($Y = [Y_1, Y_2]$) variables and the input (U_1, U_2, U_3) and internal (X) variables are experimentally investigated in

this chapter.

As shown in Figure 5.1 and Table 5.1 microwave power (P_t) - operating pressure (p), total gas flow rate (f_t), and methane concentration (CH_4/H_2) are the macroscopic controllable input variables (U_1). As indicated in Table 5.1 and by the dashed curve in Figure 5.1 and as discussed in Chapter 4 (Figure 4.5 and Figure 4.6) the reactor is operated in a thermally floating configuration and substrate temperature, operating pressure, and microwave power are directly related. Thus microwave power, operating pressure, and substrate temperature are not independent of each other and for the experiments presented in this chapter are referred to as a triad input variable, i.e., as the microwave power-operating pressure-substrate temperature (P_t - p - T_s) independent input variable. The reactor's geometry variables (U_2) are held constant at: (1) a cavity inner diameter of 17.78 cm, (2) a quartz dome with inner base diameter of 12.7 cm, (3) $p<100>$ oriented silicon substrates with a diameter of 7.62 cm, (4) electromagnetic excitation mode of TM_{013} , (5) discharge diameter of approximately 10 cm, and (6) a molybdenum thermally floating substrate holder (i.e., no external substrate heating or cooling arrangement). A variable deposition time (t), the substrate seeding procedure described in Section 4.3.1, and a fixed reactor start-up/shut-down procedure described in Section 4.3.2 are the deposition procedure variables (U_3). Output variables (Y) are comprised of the measured or observed film property variables (Y_1) which include surface morphology as expressed by the growth parameter α , grain size, and structural quality, and reactor performance variables (Y_2) which include linear growth rate, d and carbon conversion efficiency.

U = Input variables where $U = [U_1, U_2, U_3]$

U_1 : Macroscopic controllable variables

U_2 : Reactor geometry variables

U_3 : Deposition procedure and time variables

X = Internal variables

$Y = [Y_1, Y_2]$ Output variables (performances)

In general:

$$X = f(U)$$

$$Y = g(U, X)$$

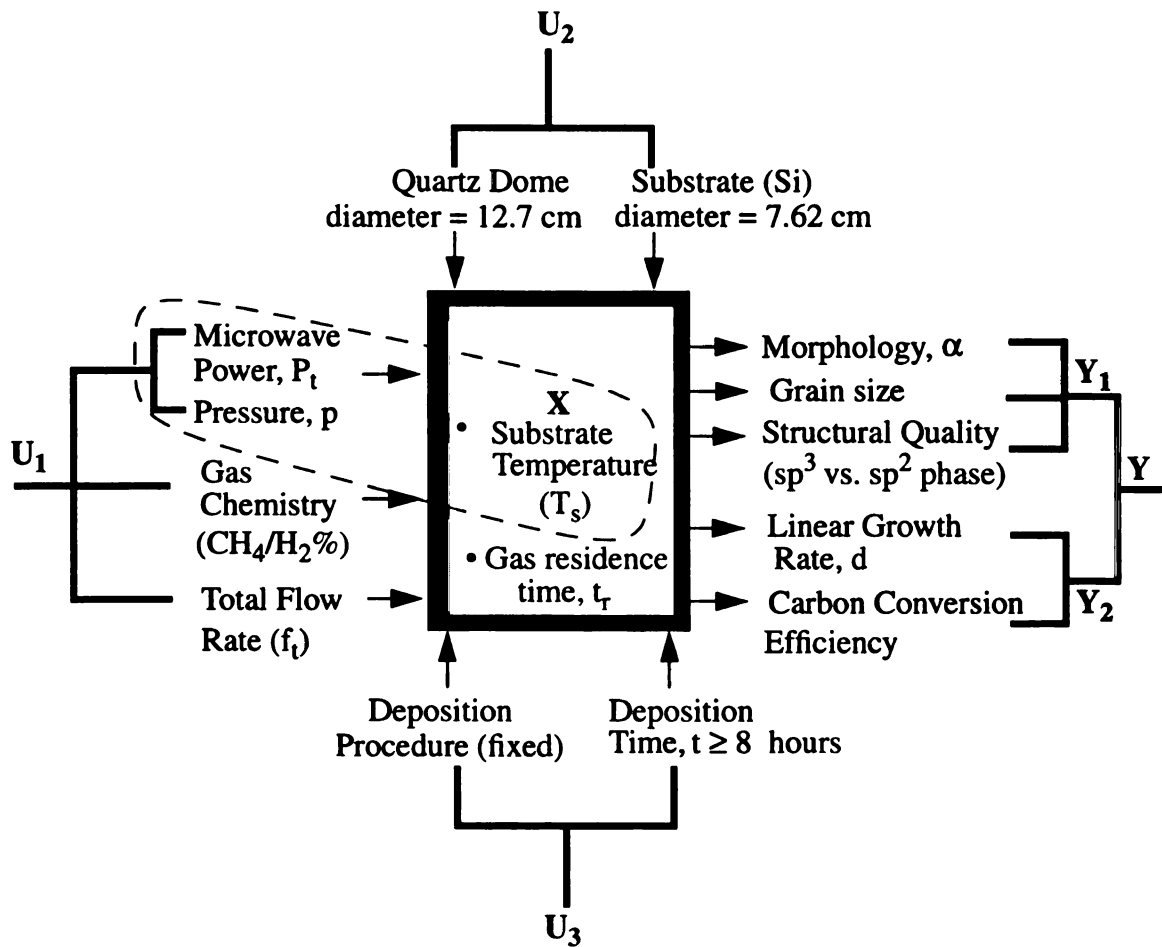


Figure 5.1. Microwave cavity plasma reactor block diagram for the experiments described in this chapter. The dashed curve encircles the T_s , p , and P_t variables indicating that this triad of variables can be considered as a single input variable for this investigation.

Table 5.1. Reactor input/internal/output variables studied in this chapter.

Input Variables, U	Macroscopic Controllable Variables, U_1	— Absorbed microwave power: $P_t = 1-3$ KW — Operating pressure: $p = 20-80$ torr - Total gas flow rate: $f_t = 30-600$ sccm - Gas chemistry: $CH_4/H_2 = 0.50-5.0\%$
	Reactor Geometry Variables, U_2	- Cavity inner diameter = 17.78 cm (fixed) - Quartz dome inner base dia. = 12.7 cm (fixed) - Excitation mode = TM_{013} (fixed) - Microwave frequency = 2.45 GHz (fixed) - Substrate Diameter = 7.62 cm (p<100>, Si) - Substrate holder = molybdenum under thermally floating configuration (fixed) - Discharge diameter ~ 10 cm (fixed)
	Deposition Procedure Variables, U_3	- Deposition Time, $t \geq 8$ hours - Substrate Seeding = A mixture of 0.1 micron diamond powder-photoresist solution (fixed) - Start-up and shut-down procedure (fixed)
Internal Variables, X		— -- Substrate temperature: $T_s = 650-1050$ °C - Gas residence time, t_r
Output Variables, Y		Y_1 — - Surface morphology and grain size — - Structural quality (Raman) Y_2 — - Linear growth rate, d — - Carbon conversion efficiency

The ra
concentrati
conditions

Operatin

The
power r
experim
deposit
the ab
exceed
There
subst
grow
whic
rate
temp

Meth

5.0%
cm⁻¹

The ranges of operating pressure, microwave power, substrate temperature, methane concentration CH_4/H_2 , and total gas flow rate were limited by a number of experimental conditions. These limiting conditions are described below.

Operating pressure and input microwave power

The pressure range of $p = 20 - 80$ Torr and the associated absorbed input microwave power range of $P_t = 1 - 3$ KW were experimentally studied. The choice of these experimental regimes was limited by substrate temperature limitations. Diamond film deposition is usually limited to the substrate temperatures between 600°C and 1100°C . In the absence of an external substrate cooling arrangement, the substrate temperature exceeds 1100°C for $p > 80$ Torr. Above 1100°C diamond deposition does not take place. Therefore, the upper limit of the operating pressure in this study was set to 80 Torr. The substrate temperature associated with $p = 20$ Torr was about 600°C (Figure 4.6). The growth rate associated with this substrate temperature was very small. Lower temperatures which are achieved at lower pressures result in even lower growth rates. Due to growth rate considerations, the lower boundaries for pressure and the associated substrate temperature, T_s , were chosen to be 20 Torr and 600°C , respectively.

Methane concentration, CH_4/H_2

The optimum range for the CH_4 to H_2 gas ratio was investigated. Above $\text{CH}_4/\text{H}_2 = 5.0\%$ the diamond quality as determined by the diamond film Raman signature at 1332 cm^{-1} was very poor (i.e., the diamond peak was non-existent). Below $\text{CH}_4/\text{H}_2 = 0.50\%$ the

growth rate was very small. Hence, the methane concentration was limited to $\text{CH}_4/\text{H}_2 = 0.50 - 5.0\%$. Thus as shown in Figure 5.2 the methane concentrations were within the well-defined diamond zone of the Bachmann diagram.

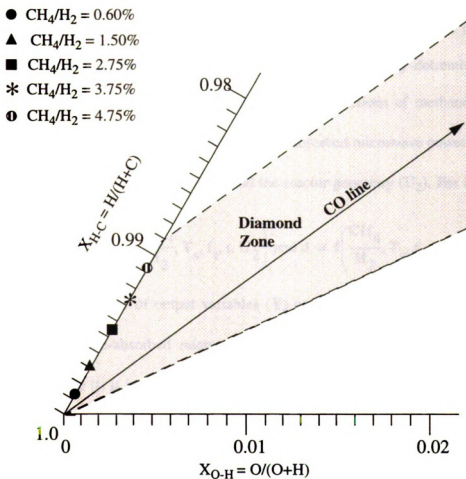


Figure 5.2. Locations of various methane gas concentrations investigated in this chapter on the C-H-O Bachmann phase diagram.

Total gas flow rate, f_t

A flow rate of 30 sccm was the lowest possible flow rate that could reliably be set with the available flow meter. At flow rates equal or larger than 600 sccm the morphology was predominantly cauliflower and the film structural quality was poor except when the methane concentration was limited to low values (i.e., $\text{CH}_4/\text{H}_2 \leq 0.6\%$). The growth rate associated with such low methane concentrations was low. Therefore, a flow rate range of $f_t = 30 - 600$ sccm was chosen in this investigation.

The problem of relating output variables to input variables turned out to be much more complex than originally anticipated. It was experimentally determined that output variables ($Y = [Y_1, Y_2]$) were complex non-linear functions of methane concentration (CH_4/H_2), triad of substrate-operating pressure-absorbed microwave power ($T_s\text{-p-P}_t$), total gas flow rate (f_t), deposition time (t), and the reactor geometry (U_2). For instance, it was

determined that $\alpha = f\left(\frac{\text{CH}_4}{\text{H}_2}, T_s, f_t, t, U_2\right)$ and $d = f\left(\frac{\text{CH}_4}{\text{H}_2}, T_s, f_t, t, U_2\right)$.

The dependence of output variables (Y) on CH_4/H_2 chemistry, triad of substrate-operating pressure-absorbed microwave power ($T_s\text{-p-P}_t$), total gas flow rate (f_t), and deposition time (t) is investigated in this chapter. The dependence of output variables (Y) on the reactor geometry (U_2) is described in Chapter 6.

The experimental data presented in this chapter are grouped into the data sets as described pictorially in Figure 5.3. An investigation of diamond deposition vs. input and internal variables for a fixed deposition time is described in Section 5.2. In this section,

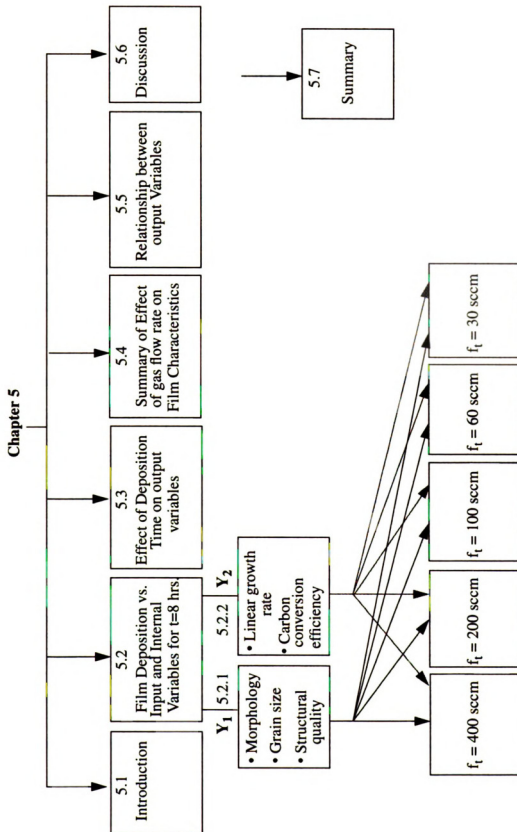


Figure 5.3. Outline of Chapter 5.

output film properties Y_1 which include morphology as expressed by the growth parameter α , grain size, and structural quality, and reactor performance output variables Y_2 which include linear growth rate, d and carbon conversion efficiency are presented vs. variations in the input variables CH_4/H_2 and the triad of substrate temperature-pressure-input absorbed microwave power for the constant total gas flow rates of 600, 400, 200, 100, 60, and 30 sccm. It is observed that in addition to methane concentration and the triad of substrate temperature-pressure-microwave power, the total gas flow rate plays an important role in determining film properties. The flow rates of 400, 200, and 60 sccms were considered as representative of high, intermediate, and low flow rates, respectively, and are examined in a greater detail than the other flow rates. Deposition time is held constant at eight hours for all experiments in this section. Deposition maps are constructed from the empirical data displaying the morphology (as expressed by the growth parameter α) vs. methane concentration and the triad of substrate temperature-pressure-microwave power for each total gas flow rate. As will be seen in the subsequent sections, the growth parameter α does not precisely explain all details (i.e., twinning, etc.) about the film morphology but it is a useful tool to describe various crystal habits that are observed in the deposited polycrystalline films such as cubic, cubo-octahedron, octahedron, etc. in terms of the growth velocities in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions (see Chapter 3). For reader's reference, the various crystal shapes (habits) and their corresponding α values are shown in Figure 3.2 ([10], [31], [32]). The evaluation of α parameter for the diamond films in this Chapter is done by comparing the film crystals as observed by SEM with the individual crystals shown in Figure 3.2.

Many experiments were conducted with a flow rate of 400 sccm. The incentive for selecting this flow rate was the work of Jie Zhang [14] which showed that among flow rates of 50, 100, 200, 300, and 400 sccm, the growth rate was maximum at 400 sccm. Therefore, it was decided to extensively investigate this flow rate.

Throughout this chapter whenever morphology (i.e., α) vs. substrate temperature is discussed, for the sake of brevity, only one methane concentration is selected for SEM picture illustrations. Likewise, to illustrate the dependence of film morphology on methane concentration, only one substrate temperature is selected for SEM picture illustrations. A fixed methane concentration of 1.50% and a fixed substrate temperature of 850°C are chosen for SEM picture illustration for every flow rate discussed. In each case the choice of the methane concentration and/or the substrate temperature are only representative. Choosing one fixed methane concentration and substrate temperature for each of the flow rates discussed in this Chapter gives the reader the opportunity to visually compare the SEM pictures and observe changes in Y_1 and Y_2 as the total gas flow rate changes.

However if one methane concentration did not produce a representative film crystallite morphology variation, a second methane concentration axis was chosen for SEM illustration. For instance, as will be seen in the subsequent section, with the flow rate fixed at 400 sccm, $CH_4/H_2 = 1.50\%$ did not result in both $\{111\}$ and $\{100\}$ morphologies but $CH_4/H_2 = 0.60\%$ did. Therefore, for $f_t = 400$ sccm, both methane concentrations are selected for SEM picture illustration of morphology vs. substrate temperature. The same principle applies to the illustration of Raman spectra (i.e., structural quality) vs. substrate temperature and methane concentration. For the reader's convenience the data points

chosen for SEM and Raman spectra are specified by the symbol + on the morphology field summary maps.

In Section 5.3, the influence of deposition time on output variables (Y_1 and Y_2) is investigated. It is shown that this input variable had a significant influence on output variables, particularly on the film morphology (i.e., α). In order to maintain the desired film surface morphology but vary the deposition time, a two-step growth process is experimentally investigated and the results are presented. A summary of the effects of total gas flow rate on various film properties is provided in Section 5.4. The relationships between various output film properties are examined in Section 5.5. Section 5.6 provides a discussion of the results. Finally, a summary of the results of the experiments discussed in this chapter is presented in Sections 5.7.

5.2 Film deposition vs. input and internal variables for a fixed deposition time of eight hours

5.2.1 Film properties (Y_1) vs. various input variables

In what follows, morphology (expressed by the growth parameter α), grain size, and structural quality of the CVD diamond films vs. methane concentration and substrate temperature for various flow rates are investigated.

5.2.1.1 Morphology and grain size

5.2.1.1.1 Total gas flow rate, $f_t = 400$ sccm

Using the MCPR, films with various morphologies were deposited over the entire 3 inch in diameter substrates. Figure 5.4 shows SEM pictures of films with {100} (i.e.,

$\alpha \cong 1 - 2.5$), $\{111\}$ ($\alpha \cong 3$), cauliflower, and small aggregates morphologies, respectively. Twins are the small crystals that protrude the parent crystals. Twinning occurs frequently on CVD diamond crystals. This phenomenon is more pronounced with respect to $\{111\}$ facets. Figure 5.4 (c) shows a twinned $\{111\}$ film.

A large number of experiments were carried out for the fixed flow rate, f_t , of 400 sccm and a fixed deposition time of 8 hours. The relationship between film morphology as expressed by α and various methane concentrations in hydrogen, CH_4/H_2 , and substrate temperatures, T_s , is shown in Figure 5.5 (a). This relationship is referred to as a morphology field map. It is seen that for a fixed flow rate, film morphology changes with substrate temperature (hence pressure and microwave power) and methane concentration in hydrogen. Figure 5.5 (b) summarizes the morphology field map for the 400 sccm flow rate. At this flow rate, the majority of the films showed $\{111\}$ facets with $\alpha \cong 3$ when CH_4/H_2 was kept below 1.75%. Beyond this methane concentration, films showed predominately cauliflower and small aggregates structures. Surface morphology consisted of mixed (i.e., $\{100\}$, $\{111\}$, etc.) facets when CH_4/H_2 was kept at or below 1.0% and T_s at or above 950°C. Because these films were comprised of crystals with different morphologies, it was not possible to assign a single α value to them. These films were denoted as having “mixed α ” value on the morphology field map. Figure 5.6 and Figure 5.7 show the variations of film morphology with the substrate temperature for the methane concentration fixed at $\text{CH}_4/\text{H}_2 = 0.60\%$ and $\text{CH}_4/\text{H}_2 = 1.50\%$, respectively. These Figures illustrate the SEM pictures of the films deposited at $\text{CH}_4/\text{H}_2 = 0.60\%$ and $\text{CH}_4/\text{H}_2 = 1.50\%$ with substrate temperature, $T_s \in [800, 1000]^\circ\text{C}$. The data points chosen for SEM

illustrations are specified by + on the morphology field map summary shown in Figure 5.5 (b). The reason for selecting $\text{CH}_4/\text{H}_2 = 0.60\%$ is that for $f_t = 400$ sccm, crystals with various morphologies (i.e., $\{111\}$ and $\{100\}$) were deposited at this methane concentration. Nevertheless, as seen in the morphology field map (Figure 5.5), film morphology was dependent upon the substrate temperature for other methane concentrations, as well.

Figure 5.8 illustrates the dependence of film morphology on methane concentration in hydrogen for the substrate temperature fixed at 850°C . Faceted crystals existed only for $\text{CH}_4/\text{H}_2 \leq 1.50\%$ and the α value was approximately equal to 3 (i.e., octahedron crystal habit) in this methane concentration range. Cauliflower and small aggregate structures became dominant at higher methane concentrations. The data points chosen for SEM illustrations are specified by + on the morphology field map summary in Figure 5.5 (b).

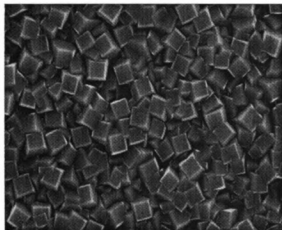
It should be noted that the $\{111\}$ films which were assigned $\alpha \cong 3$ did not look identical. Some were heavily twinned (i.e., Figure 5.7 (a), (b)), some were lightly twinned (i.e., Figure 5.7 (c)), and some were almost untwinned (i.e., Figure 5.7 (d)). This means that the α parameter though useful in describing various crystal habits in the crystal CVD process, did not precisely explain all details about the film morphology.

The method of linear intercept (Section 4.5.2) was used to determine the average grain size vs. substrate temperature and methane concentration. This method was utilized since crystals were not of the same size and twinning persisted. Grain size showed an increase with substrate temperature regardless of the film morphology. Figure 5.9 shows the plot of grain size vs. substrate temperature for CH_4/H_2 fixed at 1.50% . The plot shows

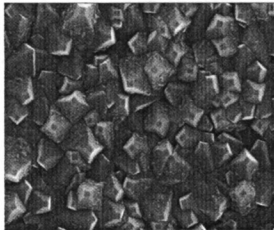
a monotonic increase of grain size with substrate temperature in its respected range (i.e., $T_s \in [800, 1000] \text{ } ^\circ\text{C}$). Figure 5.10 illustrates the plot of grain size vs. methane concentration in hydrogen for substrate temperature fixed at 1000°C . The grain size reached a maximum value of $\sim 2.50\mu\text{m}$ at $\text{CH}_4/\text{H}_2=1.0\%$.

Twin concentration was shown to be directly proportional to CH_4/H_2 and inversely proportional to T_s . At $\text{CH}_4/\text{H}_2=1.50\%$, crystals were heavily twinned when $T_s \leq 850^\circ\text{C}$ but showed clear (i.e., no significant twinning) facets beyond this substrate temperature. The crystals were less twinned at lower CH_4/H_2 values.

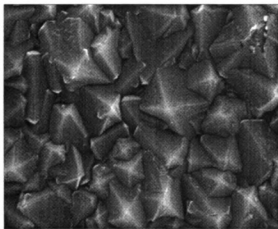
In summary, at the total flow rate, f_t , of 400 sccm, films with $\{111\}$ morphology (i.e., $\alpha \equiv 3$) were favored at low substrate temperatures ($T_s < 950^\circ\text{C}$) and a broad $\text{CH}_4/\text{H}_2\%$ range (i.e., $\text{CH}_4/\text{H}_2 \in [0.6, 1.50]\%$) while $\{100\}$ crystals appeared at relatively higher substrate temperatures ($T_s \geq 950^\circ\text{C}$) and a narrower $\text{CH}_4/\text{H}_2\%$ range ($\text{CH}_4/\text{H}_2 \leq 1.0\%$). Cauliflower and microcrystallites structures appeared at high $\text{CH}_4/\text{H}_2\%$ with small aggregates appearing at the high substrate temperature high $\text{CH}_4/\text{H}_2\%$ field map zone.



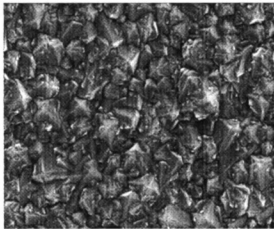
(a) $\{100\}$ $\alpha \approx 1$



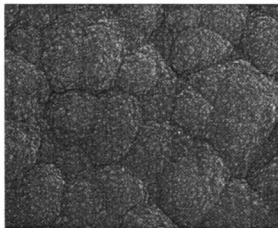
(b) $\{100\}$ $\alpha \approx 2.5$



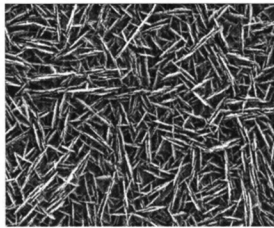
(c) Clear (untwinned) $\{111\}$ $\alpha \approx 3$



(d) Twinned $\{111\}$ $\alpha \approx 3$



(e) Cauliflower



(f) Small aggregated

Figure 5.4. CVD diamond films with various morphologies deposited using the MCPDR.

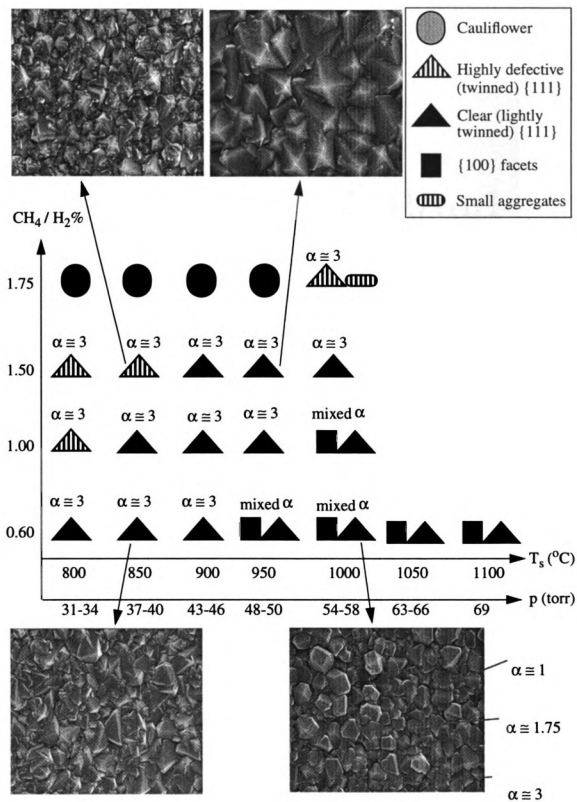


Figure 5.5 (a). Morphology field map for total flow rate $f_t = 400$ sccm.

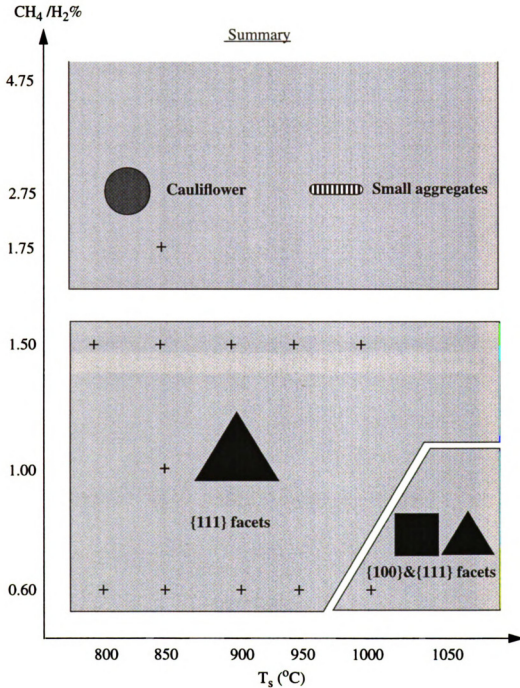


Figure 5.5 (b). Summary of morphology field map for $f_t = 400$ sccm. + represents the data points chosen for SEM illustration.

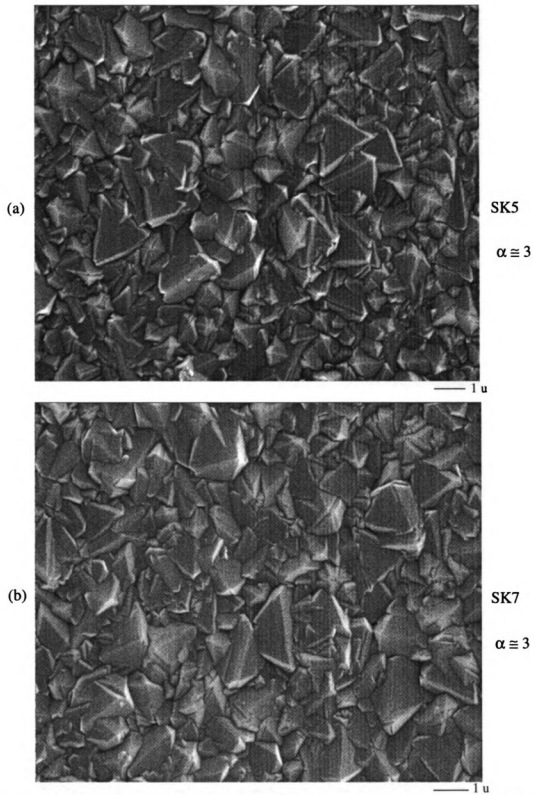


Figure 5.6. SEM pictures of the samples deposited at $f_l = 400$ sccm, $\text{CH}_4/\text{H}_2 = 0.60\%$, and (a) $T_s = 800^\circ\text{C}$, (b) $T_s = 850^\circ\text{C}$, (c) $T_s = 900^\circ\text{C}$, (d) $T_s = 950^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$.

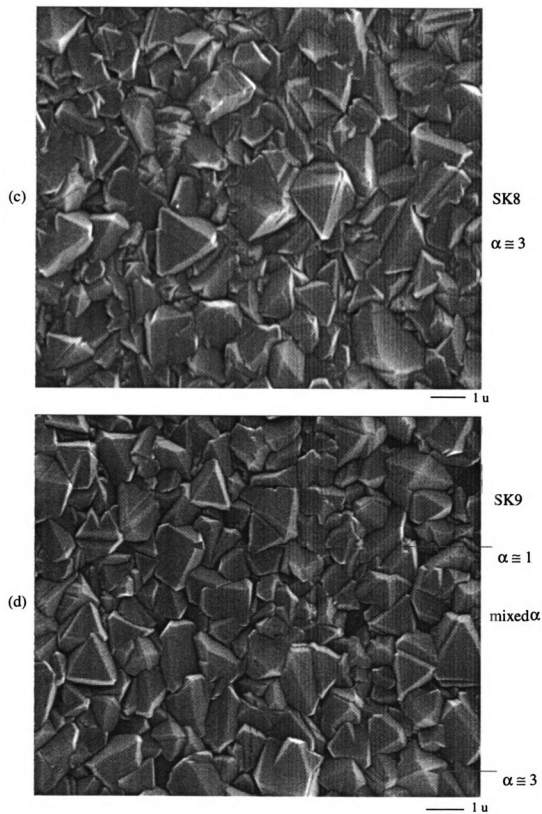


Figure 5.6. Continued.

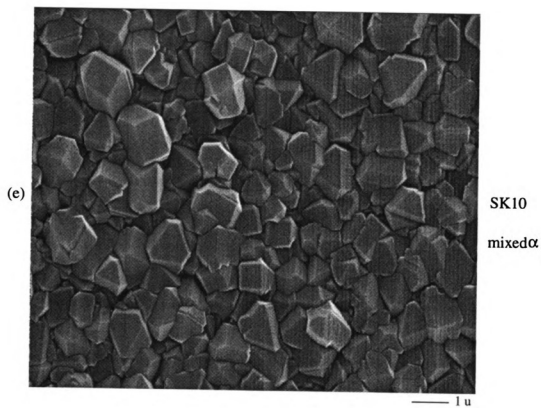


Figure 5.6. Continued.

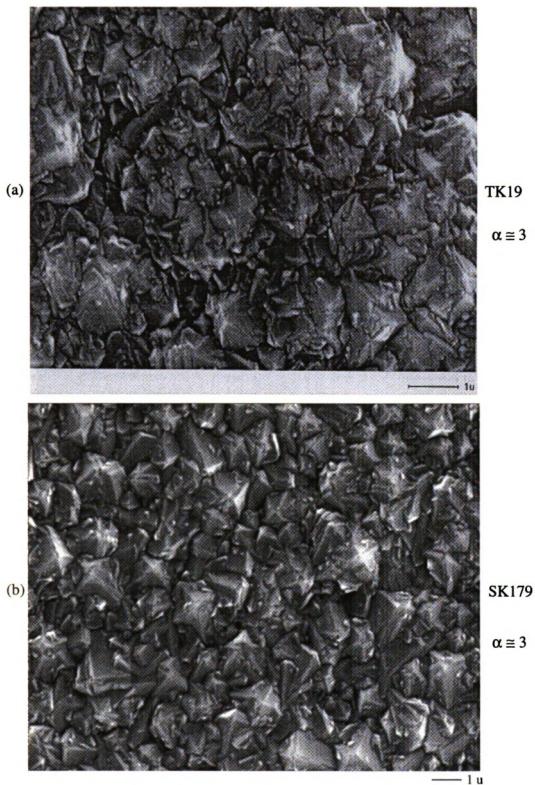


Figure 5.7. SEM pictures of the samples deposited at $f_t=400$ sccm, $\text{CH}_4/\text{H}_2=1.50\%$, and (a) $T_s=800^\circ\text{C}$, (b) $T_s=850^\circ\text{C}$, (c) $T_s=900^\circ\text{C}$, (d) $T_s=950^\circ\text{C}$, and (e) $T_s=1000^\circ\text{C}$.

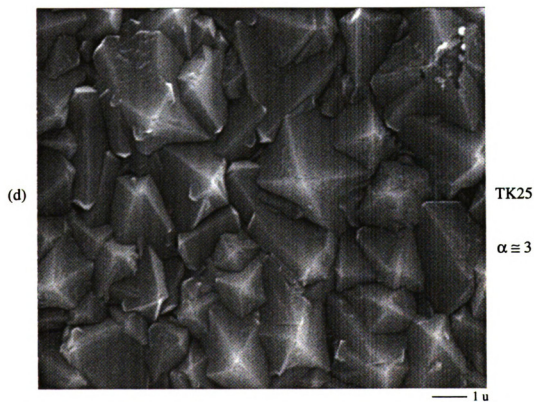
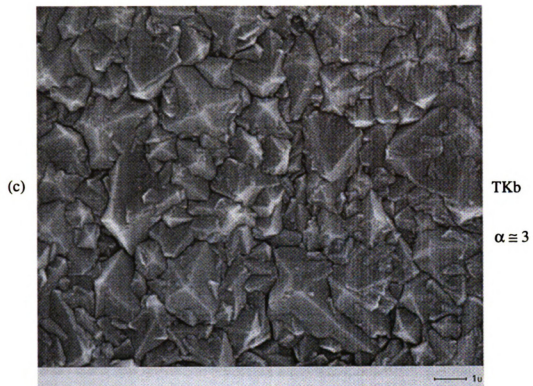


Figure 5.7. Continued.

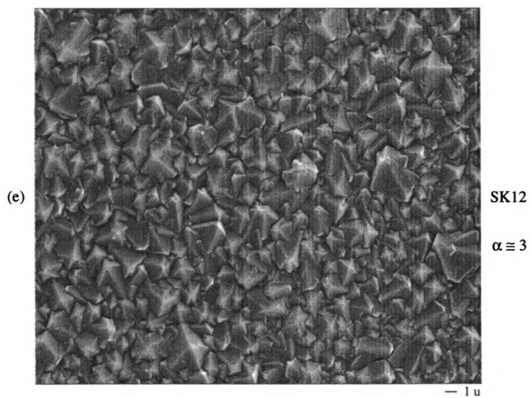


Figure 5.7. Continued.

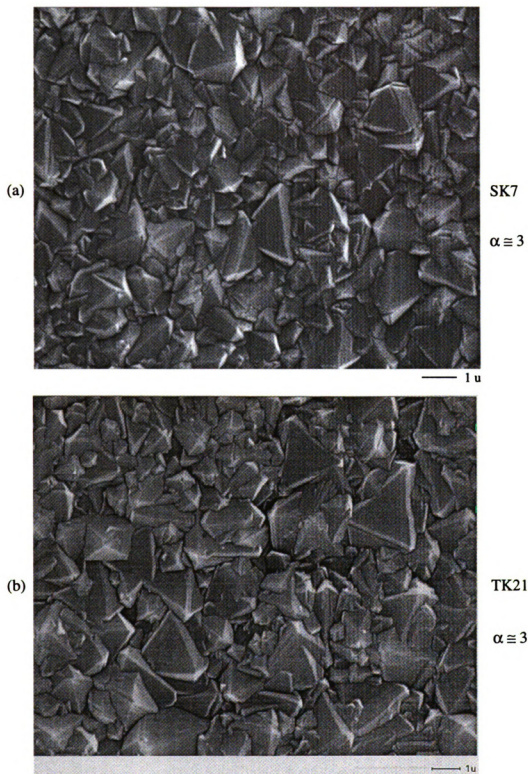
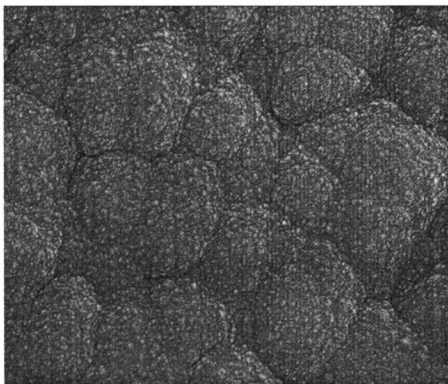


Figure 5.8. SEM pictures of the samples deposited at $f_t=400$ sccm, $T_s=850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2=0.6\%$, (b) $\text{CH}_4/\text{H}_2=1.0\%$, (c) $\text{CH}_4/\text{H}_2=1.50\%$, and (d) $\text{CH}_4/\text{H}_2=1.75\%$.

(c)



(d)



TK20

Figure 5.8. Continued.

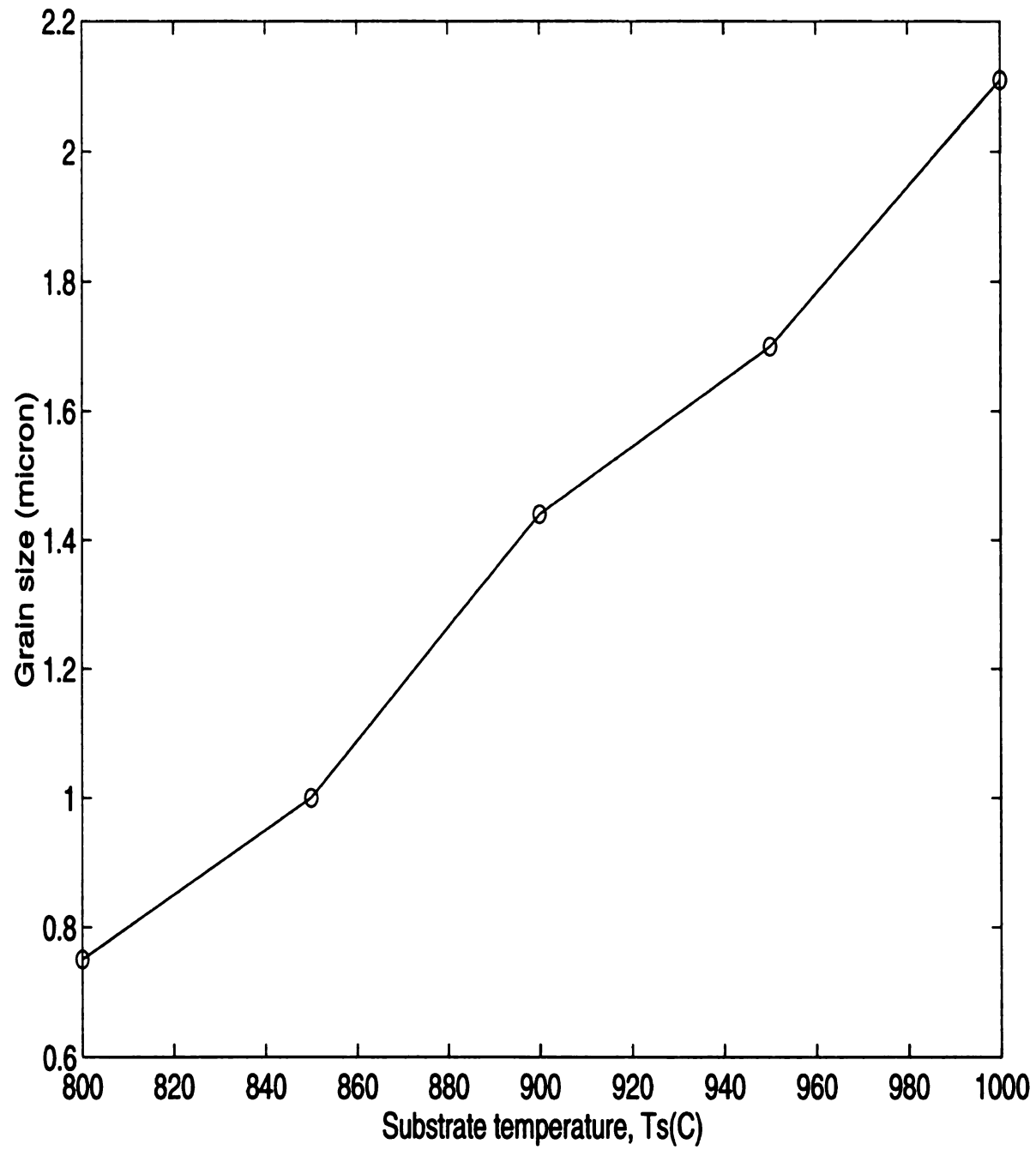


Figure 5.9. Plot of grain size vs. T_s for $f_t = 400$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

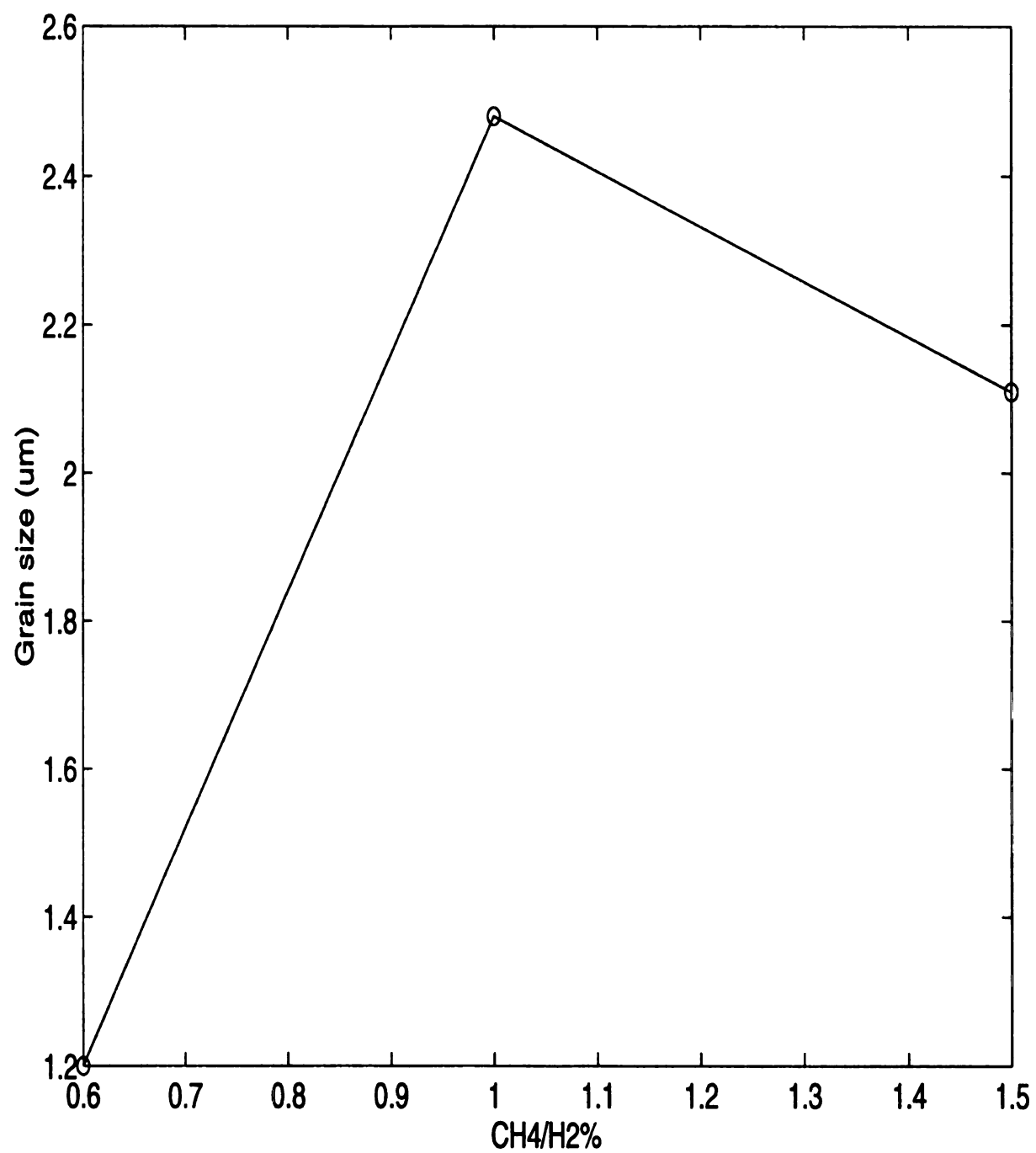


Figure 5.10. Plot of grain size vs. CH_4/H_2 for $f_t = 400$ sccm and $T_s = 1000^\circ\text{C}$.

5.2.1.1.2 Total gas flow rate, $f_t = 200$ sccm

Figure 5.11 (a) illustrates the morphology (expressed by α) field map developed for $f_t = 200$ sccm. It relates CVD diamond film surface morphology to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s for the total gas flow rate of 200 sccm. Figure 5.11 (b) summarizes the morphology field map at this total gas flow rate. At this flow rate, films displayed primarily $\{100\}$ ($\alpha \cong 1$ and $\alpha \cong 2$) and $\{111\}$ ($\alpha \cong 3$) facets when CH_4/H_2 did not exceed 2.0%. Beyond $\text{CH}_4/\text{H}_2 = 2.0\%$, films showed predominately cauliflower structure. Films with $\{100\}$ morphology were deposited at low substrate temperatures ($T_s \leq 850^\circ\text{C}$) and mainly in $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ regime. Films with $\{111\}$ morphology grew at the same methane concentration range (i.e., $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$) but at a higher substrate temperature regime ($T_s > 850^\circ\text{C}$). At a low methane concentration of 0.60%, predominantly $\{111\}$ films were deposited.

Figure 5.12 shows SEM pictures of film surface morphology vs. T_s for CH_4/H_2 fixed at 1.50%. For $T_s \in [675, 850]^\circ\text{C}$ the surface morphology of the films was $\{100\}$ ($\alpha \cong 1$ and $\alpha \cong 2$) and no twinning was observed on the crystals. As shown in Figure 3.2, $\alpha \cong 1$ corresponds to crystals with cubic shape such as the one shown in Figure 5.12 (d) while $\alpha \cong 2$ corresponds to crystals with $\{100\}$ top face and sloped side faces similar to the one shown in Figure 5.12 (b). The growth parameter α experienced an abrupt change from $\alpha \cong 1$ ($\{100\}$ morphology) to $\alpha \cong 3$ ($\{111\}$ morphology) as the substrate temperature was increased from 850°C to 900°C . Beyond $T_s = 900^\circ\text{C}$, $\{111\}$ morphology ($\alpha \cong 3$) persisted and the crystals were twinned with twin concentration being inversely

proportion

the substrate

this flow

{100} cry

Fig

hydroge

for CH₄

It

2.0% h

(i.e., α

from F

H₂ = 2

showe

facets

betwe

The

twinn

mean

CVD

F

1.50%

proportional to the substrate temperature, T_s . The variation of the growth parameter α with the substrate temperature for $\text{CH}_4/\text{H}_2=1.50\%$ is illustrated in Figure 5.13. It is seen that this flow rate favored the deposition of $\{100\}$ facets and substrates fully covered with $\{100\}$ crystals were grown in this flow rate.

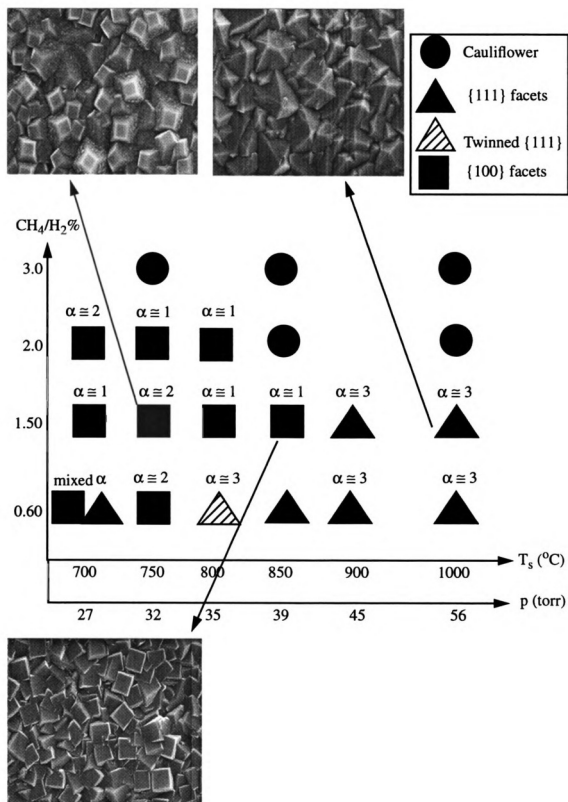
Figure 5.14 shows diamond film surface morphology vs. methane concentration in hydrogen, CH_4/H_2 , with T_s fixed at 850°C . The surface morphology changed from $\{111\}$ for $\text{CH}_4/\text{H}_2 = 0.60\%$ to $\{100\}$ for $\text{CH}_4/\text{H}_2 = 1.50\%$ to cauliflower for $\text{CH}_4/\text{H}_2 \geq 2.0$.

It should be noted that the $\{100\}$ (i.e., $\alpha \cong 1$) films that grew with the $\text{CH}_4/\text{H}_2 = 2.0\%$ had rough (jagged) edges and were twinned. They were not identical to the $\{100\}$ (i.e., $\alpha \cong 1$) films that were grown with the $\text{CH}_4/\text{H}_2 = 1.50\%$ condition. This is evident from Figure 5.15 which shows SEM pictures of two diamond films deposited under $\text{CH}_4/\text{H}_2 = 2.0\%$ with $T_s = 750^\circ\text{C}$ and $T_s = 800^\circ\text{C}$, respectively. The first film (i.e., $T_s = 750^\circ\text{C}$) showed $\{100\}$ facets with rough (jagged) edges while the second film showed $\{100\}$ facets with twinning on side and top faces. Also some $\{100\}$ films did not have voids between crystals (i.e., Figure 5.12 (d)) and some $\{100\}$ films did (i.e., Figure 5.12 (c)). The $\{111\}$ films which were assigned $\alpha \cong 3$ did not look identical, either. Some were twinned (i.e., Figure 5.12 (e)) and some were almost untwinned (i.e., Figure 5.12 (f)). This means that the α parameter though useful in describing various crystal habits in the crystal CVD process, does not precisely explain all details about the film morphology.

Figure 5.16 shows the plot of grain size vs. substrate temperature for CH_4/H_2 fixed at 1.50% . The plot shows a monotonic increase of grain size with the substrate temperature

in its respected range (i.e., $T_s \in [700, 1000] \text{ }^\circ\text{C}$). For films with $\{100\}$ morphology, the grain sizes were easily measured from SEM pictures since the crystals were almost of the same size and were twin free. For $\{111\}$ films, the method of linear intercept (Section 4.5.2) was used since crystals were not of the same size and twinning persisted.

With respect to CH_4/H_2 , the grain size experienced an increase from $\sim 1.25 \text{ }\mu\text{m}$ for the sample with $\text{CH}_4/\text{H}_2 = 0.60\%$ to $\sim 2.5 \text{ }\mu\text{m}$ for the sample with $\text{CH}_4/\text{H}_2 = 1.50\%$. It then decreased sharply as cauliflower crystal morphology became dominant. As expected (see Chapter 3), twinning occurred on the sample with $\{111\}$ morphology, not on the samples with $\{100\}$ morphology.

Figure 5.11 (a). Morphology field map for $f_t = 200$ sccm.

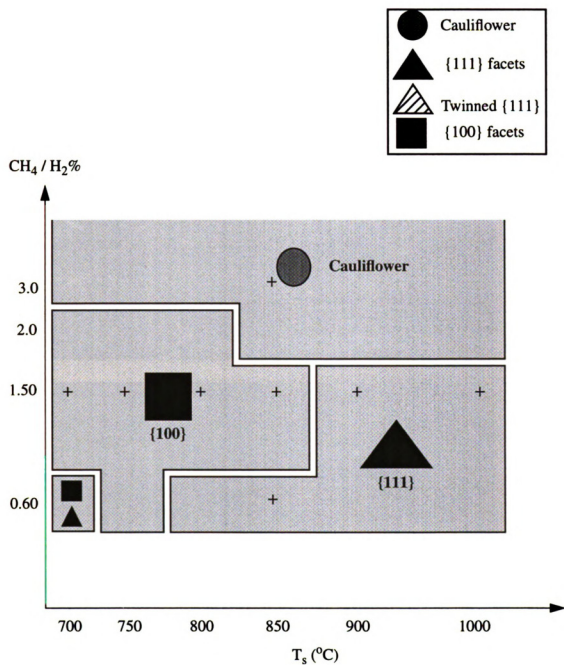


Figure 5.11 (b). Summary of morphology field map for $f_t = 200$ sccm.

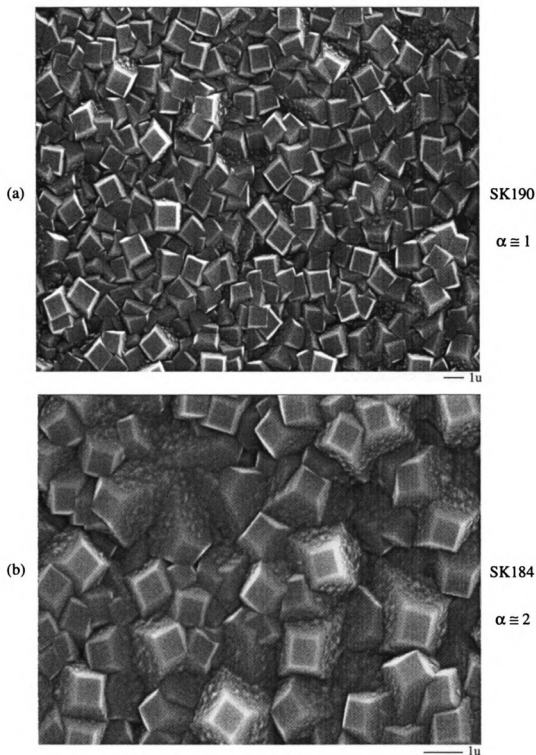
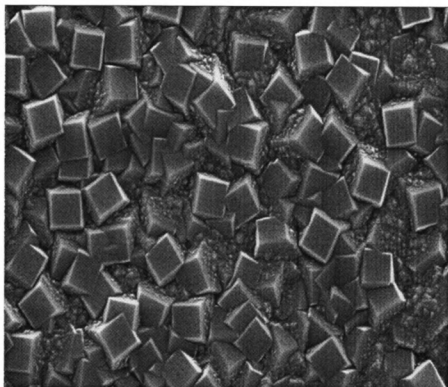


Figure 5.12. SEM pictures of the samples deposited at $f_t = 200$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 750^\circ\text{C}$, (c) $T_s = 800^\circ\text{C}$, (d) $T_s = 850^\circ\text{C}$, (e) $T_s = 900^\circ\text{C}$, and (f) $T_s = 1000^\circ\text{C}$

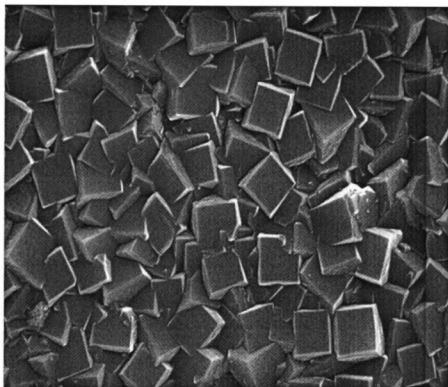
(c)



SK185

 $\alpha \cong 1$ — 1 μ

(d)



SK177

 $\alpha \cong 1$ — 1 μ

Figure 5.12. Continued.

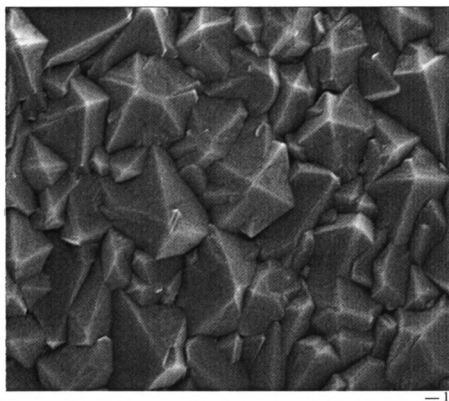
(e)



SK183

 $\alpha \cong 3$

(f)



SK209r

 $\alpha \cong 3$

Figure 5.12. Continued.

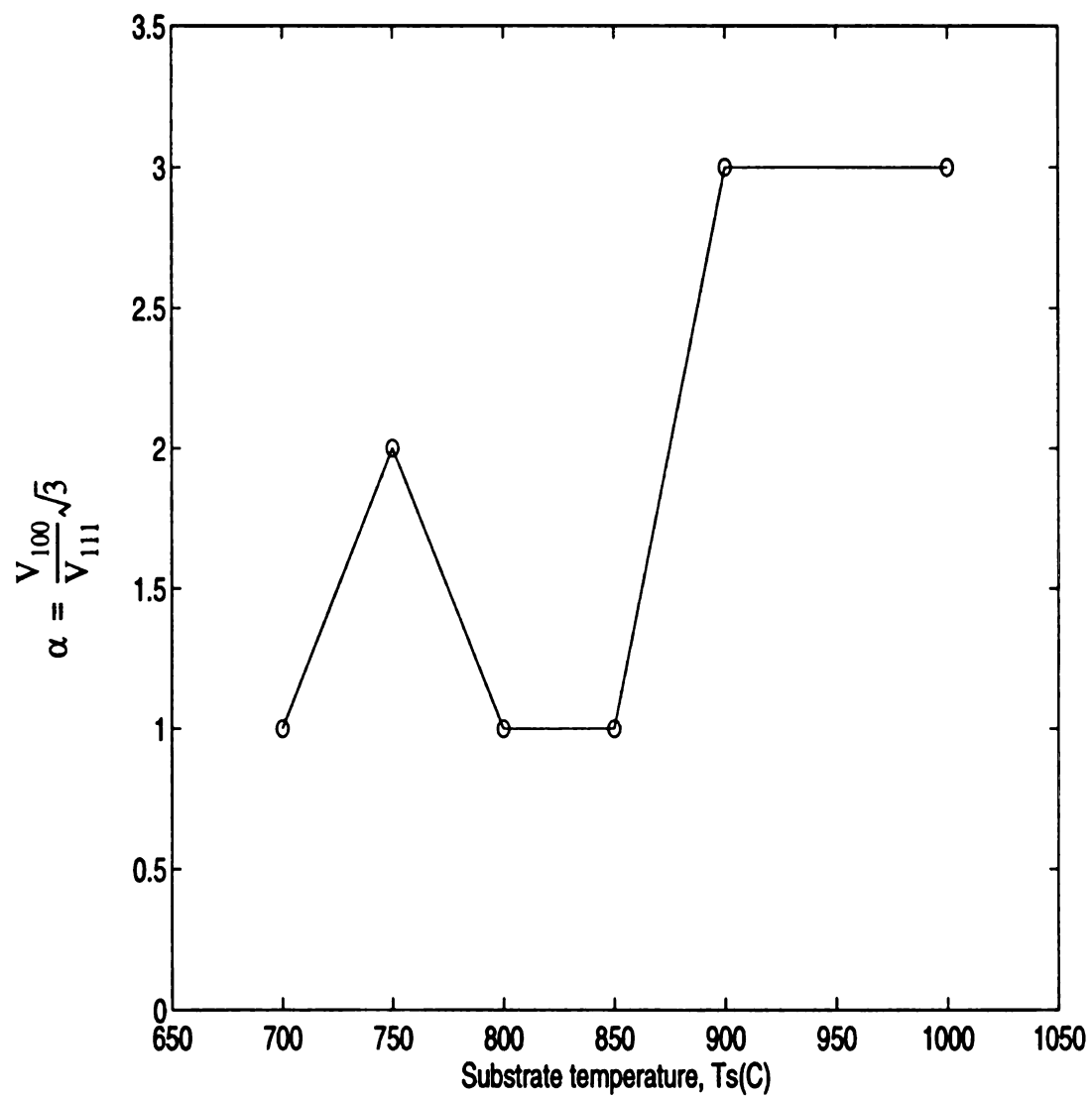


Figure 5.13. Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

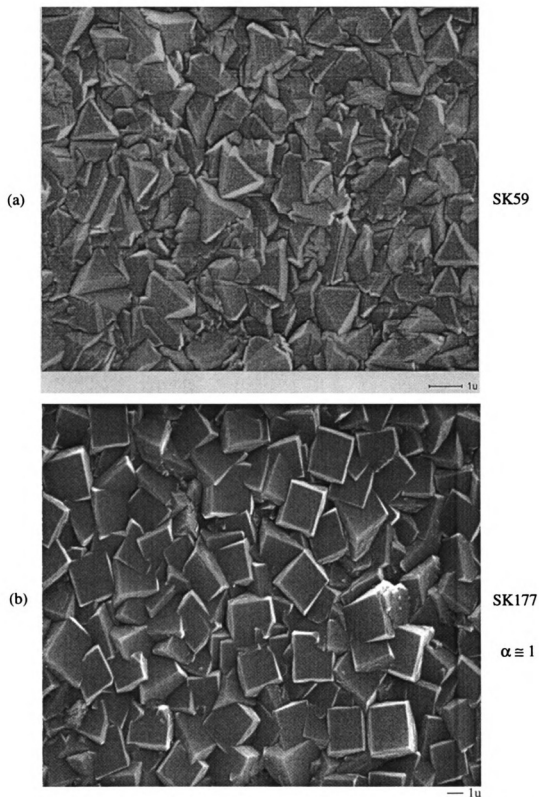


Figure 5.14. SEM pictures of the samples deposited at $f_l = 200$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 0.60\%$, (b) $\text{CH}_4/\text{H}_2 = 1.50\%$, (c) $\text{CH}_4/\text{H}_2 = 3.0\%$

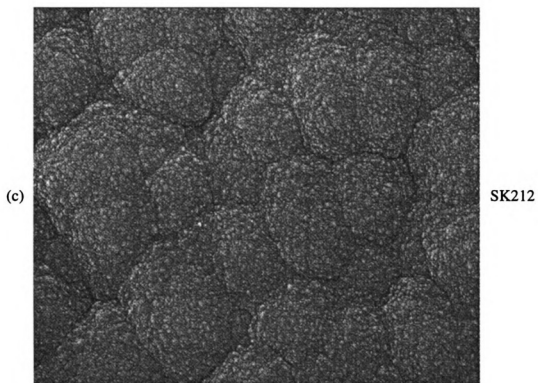


Figure 5.14. Continued.

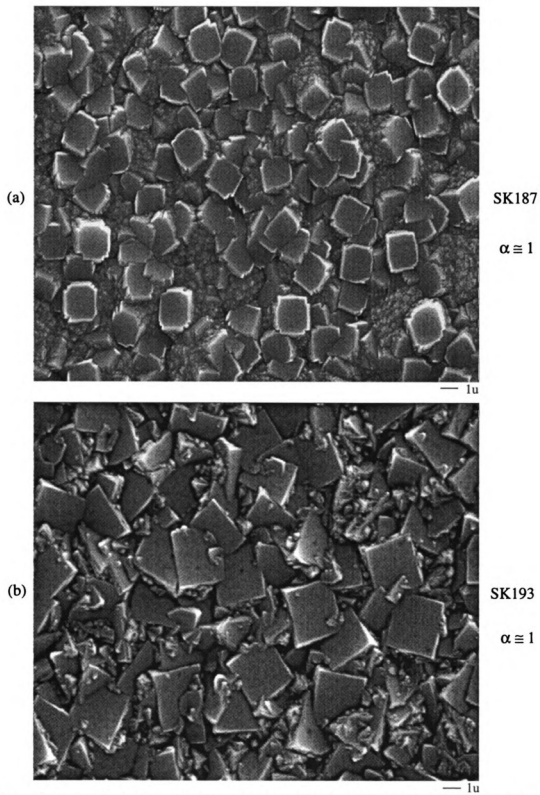


Figure 5.15. SEM pictures of samples deposited at $f_t = 200$ sccm, $\text{CH}_4/\text{H}_2 = 2.0\%$, and (a) $T_s = 750^\circ\text{C}$ and (b) $T_s = 800^\circ\text{C}$.

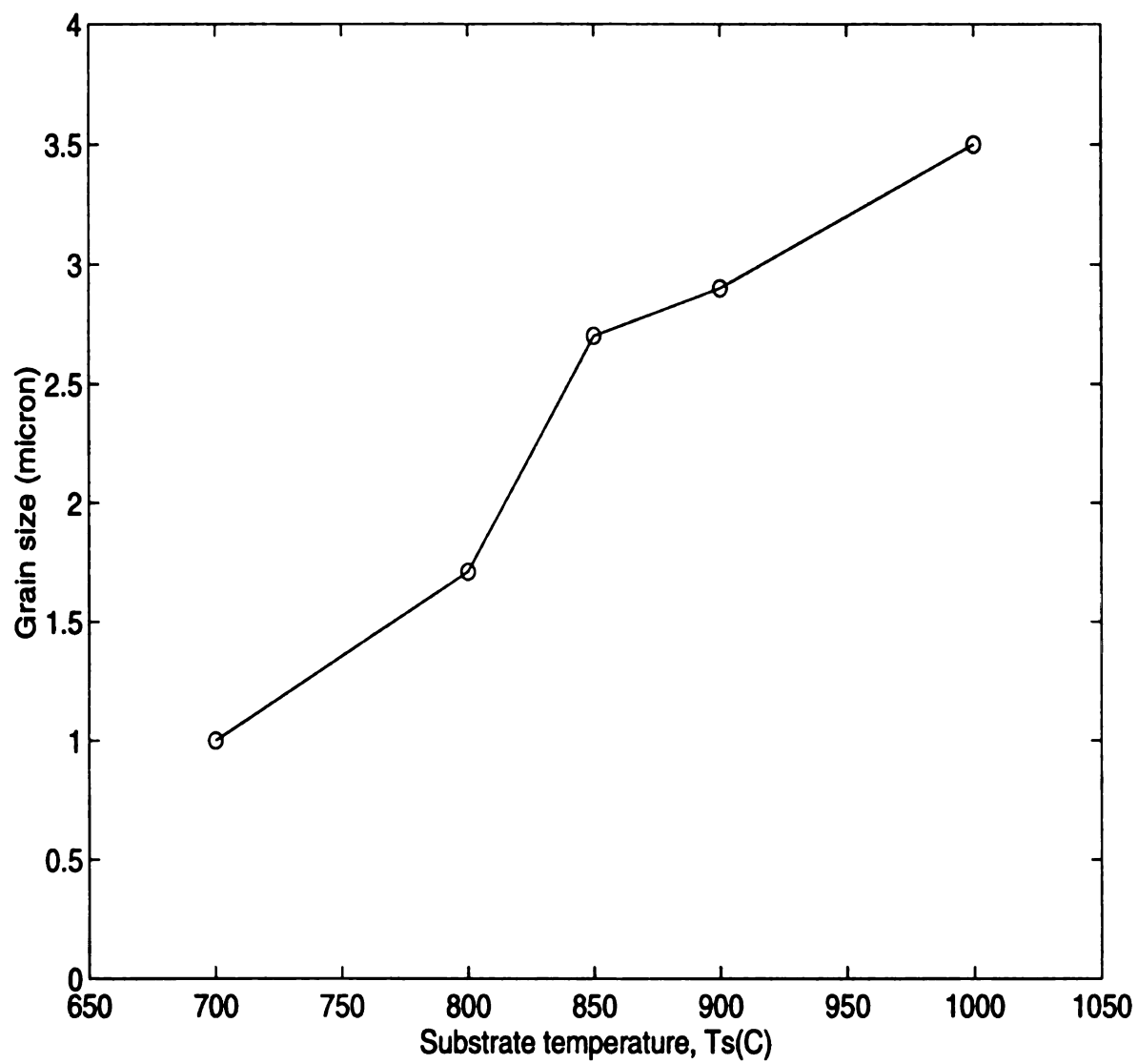
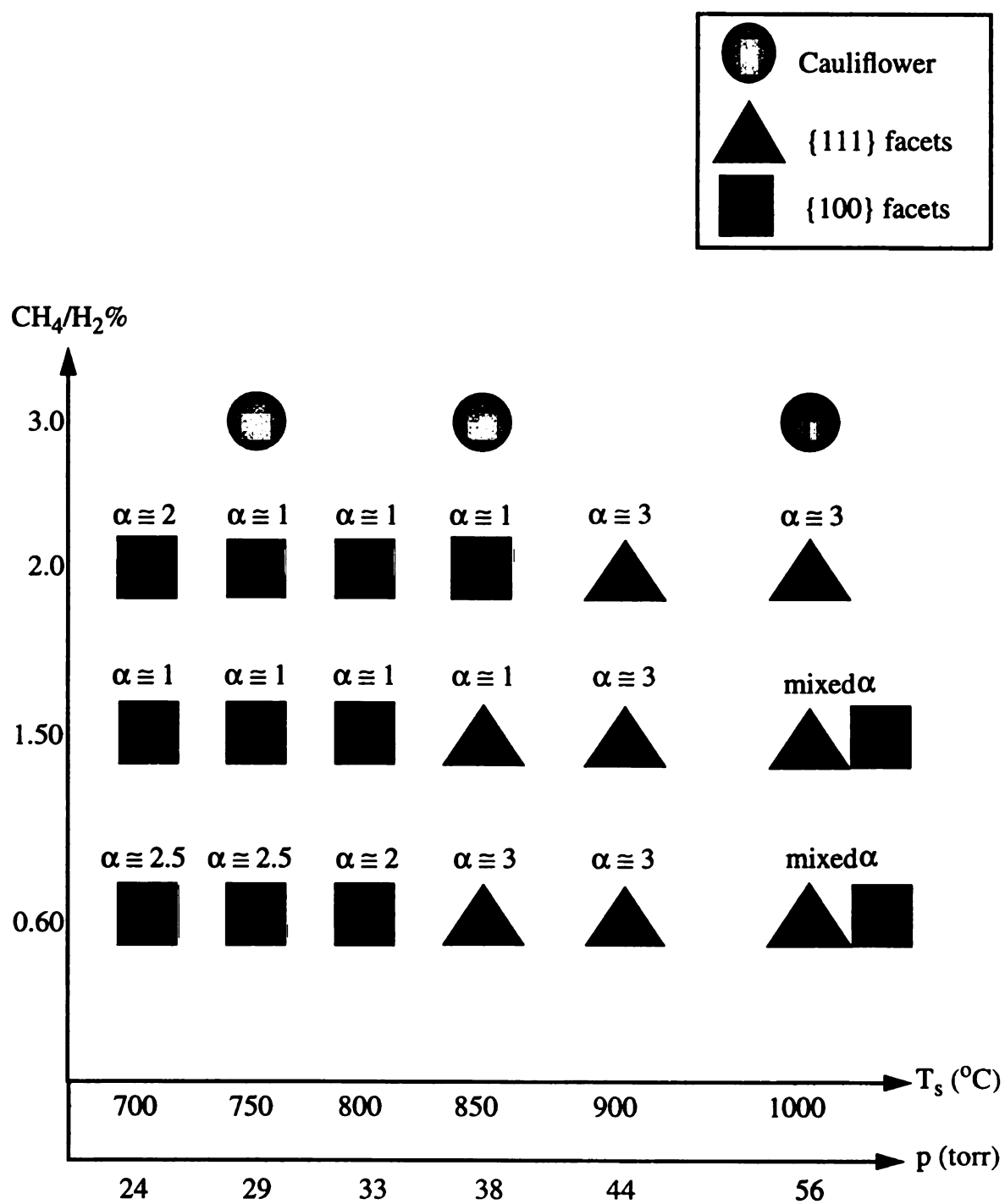


Figure 5.16. Plot of grain size vs. substrate temperature for $f_t = 200$ sccm with CH_4/H_2 fixed at 1.50%.

5.2.1.1.3 Total gas flow rate, $f_t = 100$ sccm

The Film properties under the total gas flow rate of 100 sccm was studied carefully but for the sake of brevity, the detailed discussion of the film properties under this flow rate is not presented in this dissertation. The flow rate of 60 sccm is discussed in detail in Section 5.2.1.1.4 as the representative of small flow rates.

For total gas flow rate of 100 sccm, a field map that related surface morphology (expressed by the growth parameter α) to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s , was developed as shown in Figure 5.17 (a). Figure 5.17 (b) summarizes the morphology field map at this total gas flow rate. Films with $\{100\}$ morphology ($\alpha \equiv 1 - 2.5$) appeared at $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ when $T_s \leq 850^\circ\text{C}$. The $\{111\}$ morphology ($\alpha \equiv 3$) was favored at $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ when $T_s \geq 850^\circ\text{C}$. For $\text{CH}_4/\text{H}_2 > 2.0\%$, predominantly cauliflower structure was favored for all substrate temperatures in the $T_s \in [700, 1000]^\circ\text{C}$ range. Figure 5.18 and Figure 5.19 show sample SEM pictures of the CVD diamond films deposited at this flow rate which have $\{100\}$ or $\{111\}$ morphologies. It is seen that films with $\{100\}$ facets were deposited at this flow rate, as well.

Figure 5.17 (a). Morphology field map for $f_t = 100$ sccm.

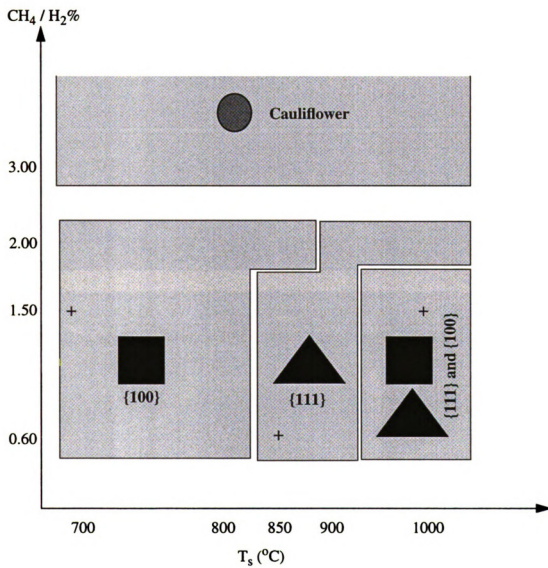


Figure 5.17 (b). Summary of morphology field map for $f_l = 100$ sccm.

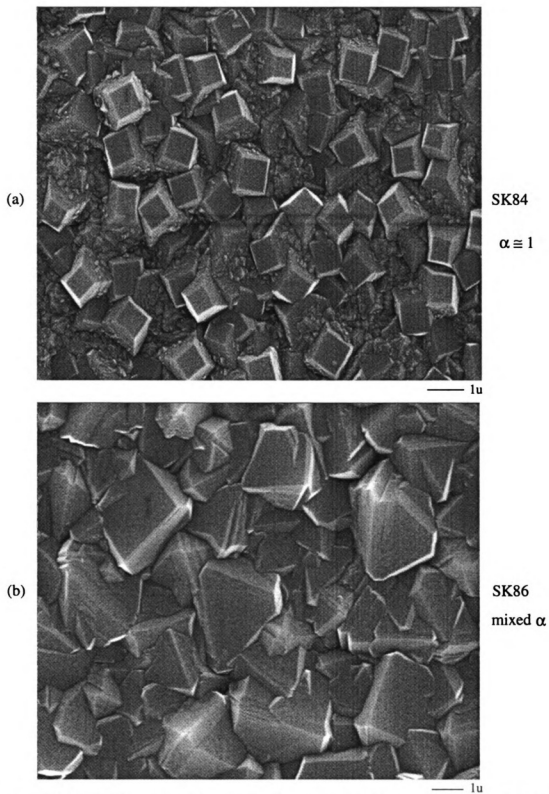


Figure 5.18. SEM pictures of the samples deposited at $f_t=100$ sccm, $\text{CH}_4/\text{H}_2=1.50\%$, and (a) $T_s=700^\circ\text{C}$, and (b) $T_s=1000^\circ\text{C}$.

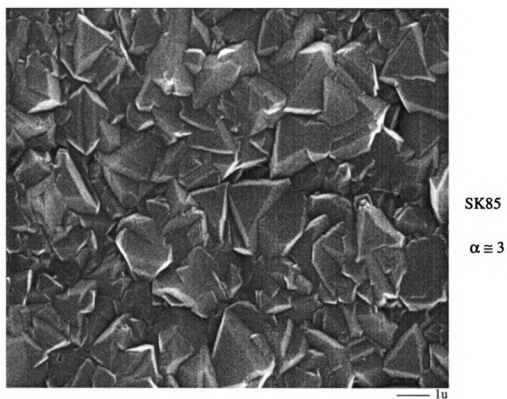


Figure 5.19. SEM picture a sample deposited at $f_t = 100$ sccm, $\text{CH}_4/\text{H}_2=0.60\%$ and $T_s = 850^\circ\text{C}$.

5.2.1.1.4 Total gas flow rate, $f_t = 60$ sccm

A large number of diamond films were deposited at the flow rate of 60 sccm. This flow rate was carefully studied in order to understand deposition at the low total gas flow rates.

For the total gas flow rate fixed at 60 sccm, a field map that related surface morphology (expressed by the growth parameter α) to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s , was developed. It is shown in Figure 5.20 (a). Figure 5.20 (b) summarizes the morphology field map at this total gas flow rate. At this flow rate, films displayed $\{100\}$ and $\{111\}$ facets when CH_4/H_2 did not exceed 2.0%. Higher methane concentrations yielded films with predominately cauliflower structure. Films with $\{100\}$ morphology (i.e., $\alpha \cong 1 - 2.5$) were deposited at low substrate temperatures ($T_s \leq 850^\circ\text{C}$) and $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. Films with $\{111\}$ morphology (i.e., $\alpha \cong 3$) grew at a higher substrate temperature regime of ($T_s > 850^\circ\text{C}$) when $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. At a low methane concentration of 0.50% only $\{111\}$ films (i.e., $\alpha \cong 3$) were deposited at all substrate temperatures in the range of $T_s \in [700, 1000]^\circ\text{C}$. At $T_s = 1000^\circ\text{C}$, for $\text{CH}_4/\text{H}_2 < 2.0\%$ some $\{110\}$ (i.e., roof like morphology) and $\{100\}$ crystal facets grew in addition to $\{111\}$ crystals. Therefore, it was not possible to assign a single α value to these films. These films were denoted as having “mixed α ” value on the morphology field map. Furthermore, it seems that secondary nucleation which resulted in the appearance of small crystals between large crystals occurred at this substrate temperature.

Figure 5.21 shows the variation of film surface morphology with T_s for CH_4/H_2 fixed at 1.50%. At $T_s=700^\circ\text{C}$ the diamond film was comprised of crystals that looked like truncated octahedra with $\{100\}$ top face and sloped side faces (i.e., $\alpha \cong 2.5$). The $\{100\}$ facets became more and more columnar (i.e., α decreased to 1) as T_s was increased to 850°C . At $T_s = 900^\circ\text{C}$, $\{111\}$ morphology (i.e., $\alpha \cong 3$) became predominant and at $T_s = 1000^\circ\text{C}$ a combination of $\{110\}$, $\{100\}$ and $\{111\}$ faceted crystals appeared on the film surface. Figure 5.22 illustrates the variation of α parameter with substrate temperature for the methane concentration fixed at 1.50%. The value of α parameter decreased from $\alpha \cong 2.5$ to $\alpha \cong 1$ (i.e., cubic crystals) when the substrate temperature was increased from 700°C to 850°C and experienced an abrupt increase from $\alpha \cong 1$ to $\alpha \cong 3$ (i.e., octahedron crystal habit with $\{111\}$ facets) when the substrate temperature was further increased to 900°C .

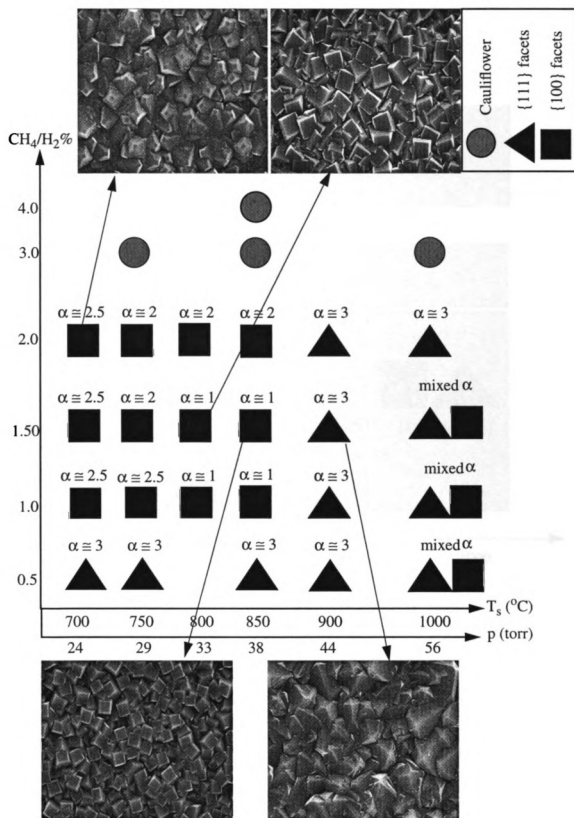
Figure 5.23 shows the variation of film surface morphology with CH_4/H_2 for T_s fixed at 850°C . The morphology changed from $\{111\}$ ($\alpha \cong 3$) to $\{100\}$ ($\alpha \cong 1 - 2$) to cauliflower as methane concentration in hydrogen increased from 0.50% to 4.0%.

It should be noted that the $\{100\}$ films that were assigned the same α value were not identical in appearance. Some were twinned (i.e., Figure 5.23 (b)) and some were not twinned (i.e., Figure 5.21 (d)). Also some $\{100\}$ films did not have voids between crystals (i.e., Figure 5.21 (d)) and some $\{100\}$ films did (i.e., Figure 5.21 (c)). The $\{111\}$ films which were assigned $\alpha \cong 3$ did not look identical, either. Some were twinned (i.e., Figure 5.23 (a)) and some did not have a significant twinning population (i.e., Figure 5.21 (e)).

Furthermore, some {111} films had rough faces and some had smooth faces as shown in Figure 5.24. This means that the α parameter though useful in describing various crystal habits in the crystal CVD process, did not precisely explain all details about the film morphology.

Figure 5.25 illustrates the grain size vs. T_s for CH_4/H_2 fixed at 1.50%. The grain size increased monotonically from $\sim 1/3 \mu\text{m}$ for $T_s=700^\circ\text{C}$ to $\sim 3.50 \mu\text{m}$ for $T_s=1000^\circ\text{C}$. The plot of grain size vs. $\text{CH}_4/\text{H}_2\%$ for T_s fixed at 850°C is illustrated in Figure 5.26. For this substrate temperature the maximum grain size of $\sim 2.70 \mu\text{m}$ was obtained for $\text{CH}_4/\text{H}_2 = 1.0\%$.

As evident from Figure 5.21 and Figure 5.23 twinning occurred on the crystals with {111} morphology and did not take place on {100}-faceted crystals. Furthermore, it is seen that substrates fully covered with {100} crystals were grown at this flow rate, as well.

Figure 5.20 (a). Morphology field map for $f_t = 60$ sccm.

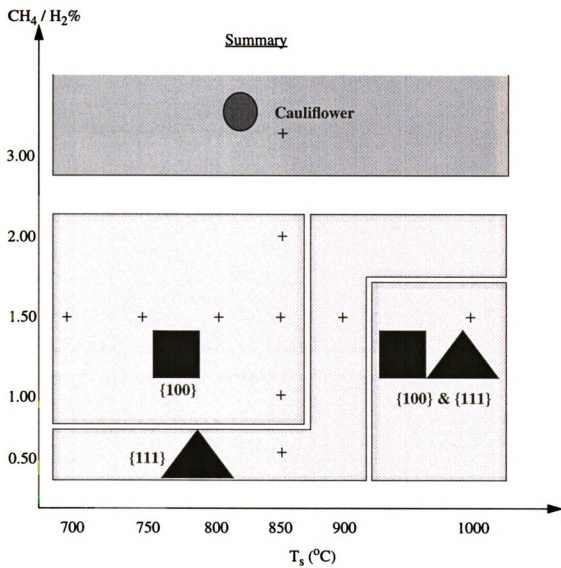


Figure 5.20 (b). Summary of morphology field map for $f_t = 60$ sccm.

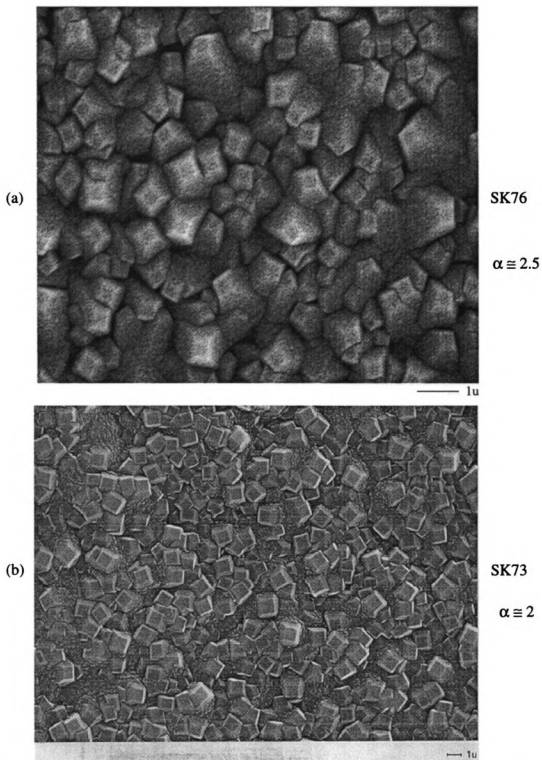
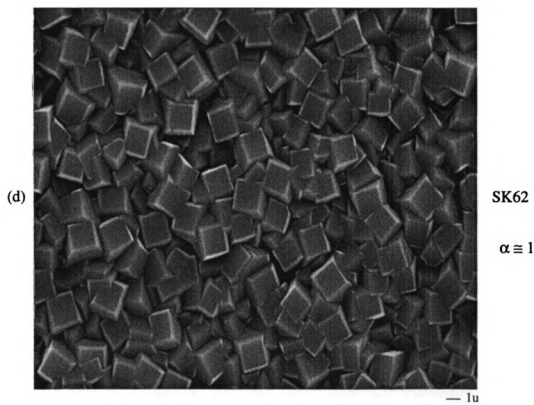
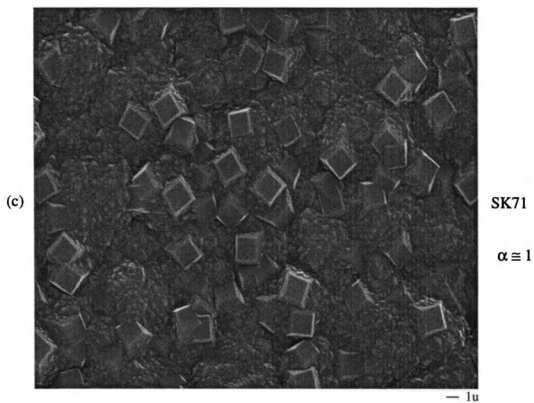
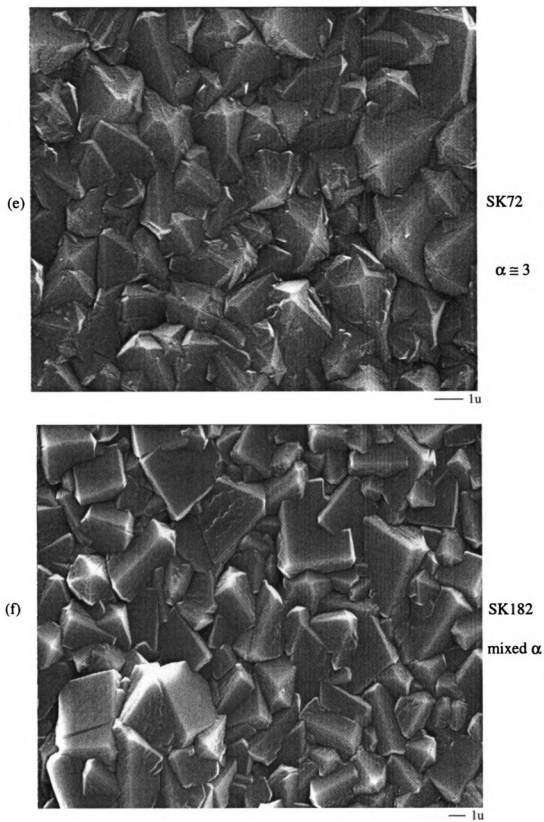


Figure 5.21. SEM pictures of the samples deposited at $f_t=60$ sccm, $\text{CH}_4/\text{H}_2=1.50\%$, and (a) $T_s=700^\circ\text{C}$, (b) $T_s=750^\circ\text{C}$, (c) $T_s=800^\circ\text{C}$, (d) $T_s=850^\circ\text{C}$, (e) $T_s=900^\circ\text{C}$, and (f) $T_s=1000^\circ\text{C}$.



Figures 5.21. Continued.



Figures 5.21. Continued.

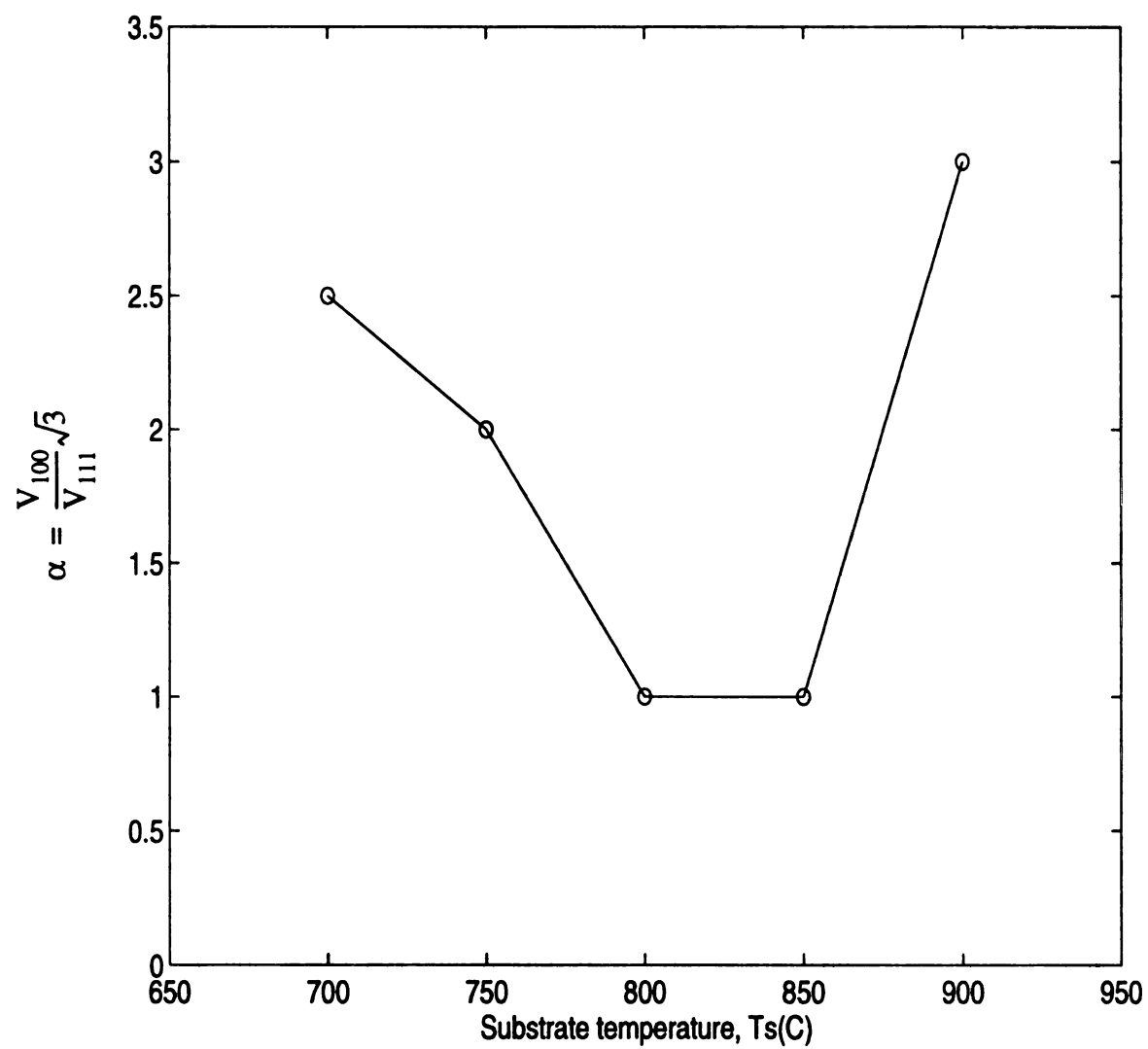


Figure 5.22. Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 60$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

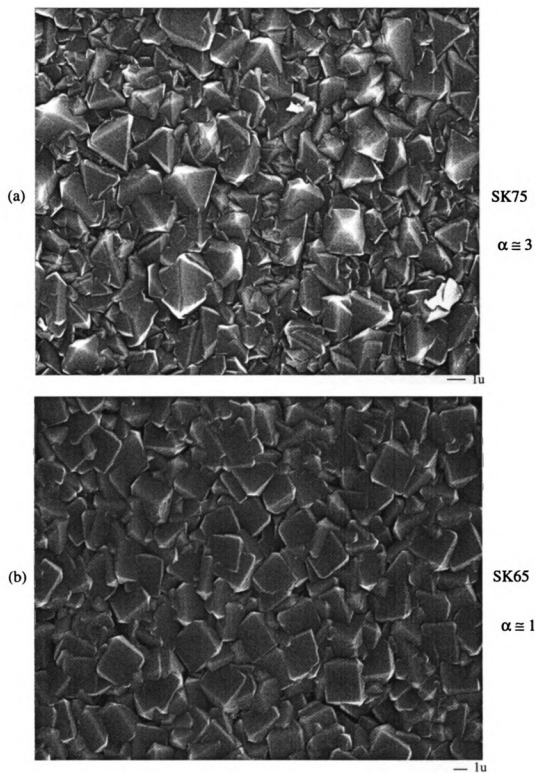


Figure 5.23. SEM pictures of the samples deposited at $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 0.50\%$, (b) $\text{CH}_4/\text{H}_2 = 1.0\%$, (c) $\text{CH}_4/\text{H}_2 = 1.50\%$, (d) $\text{CH}_4/\text{H}_2 = 2.0\%$, and (e) $\text{CH}_4/\text{H}_2 = 3.0\%$.

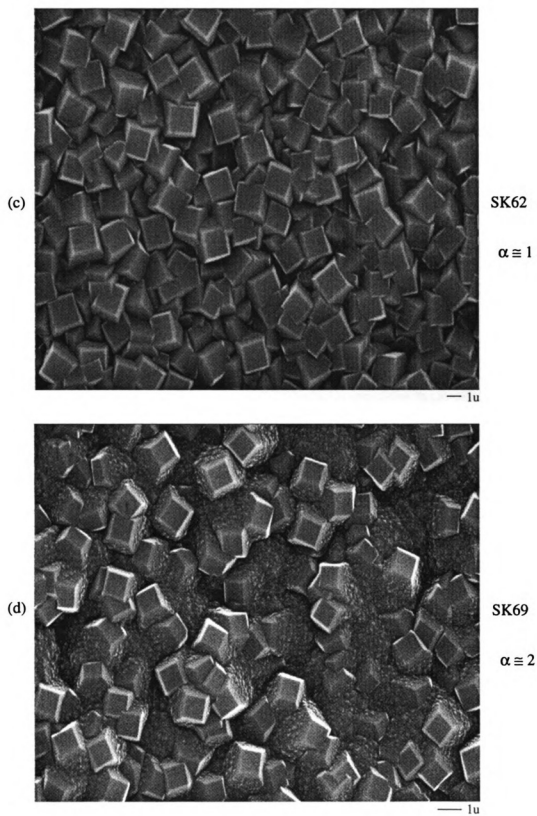


Figure 5.23. Continued.

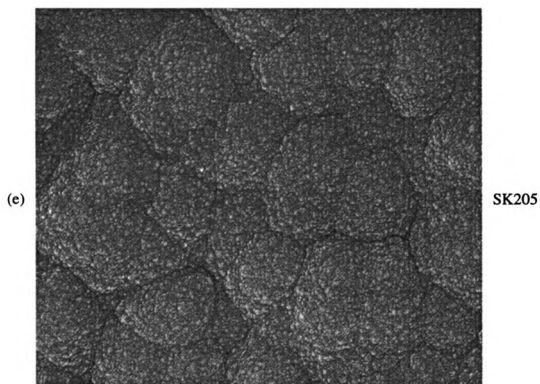


Figure 5.23. Continued.

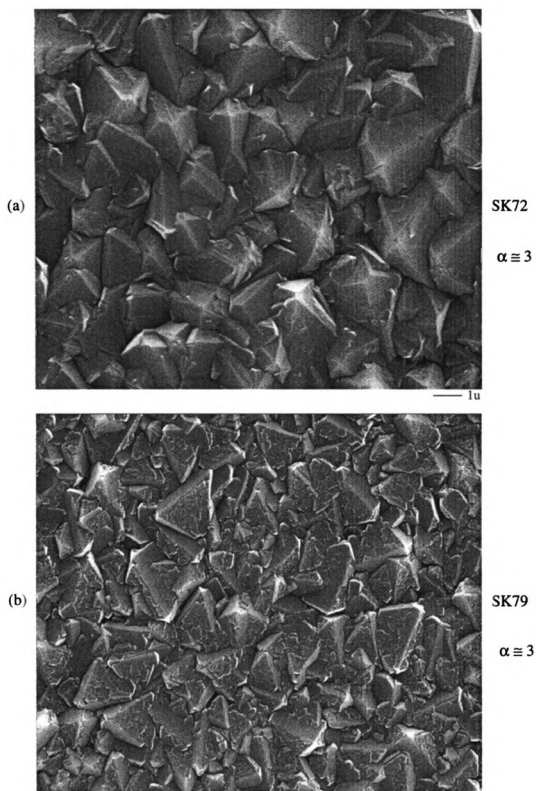


Figure 5.24. SEM pictures of $\{111\}$ films with (a) smooth faces and (b) rough faces.

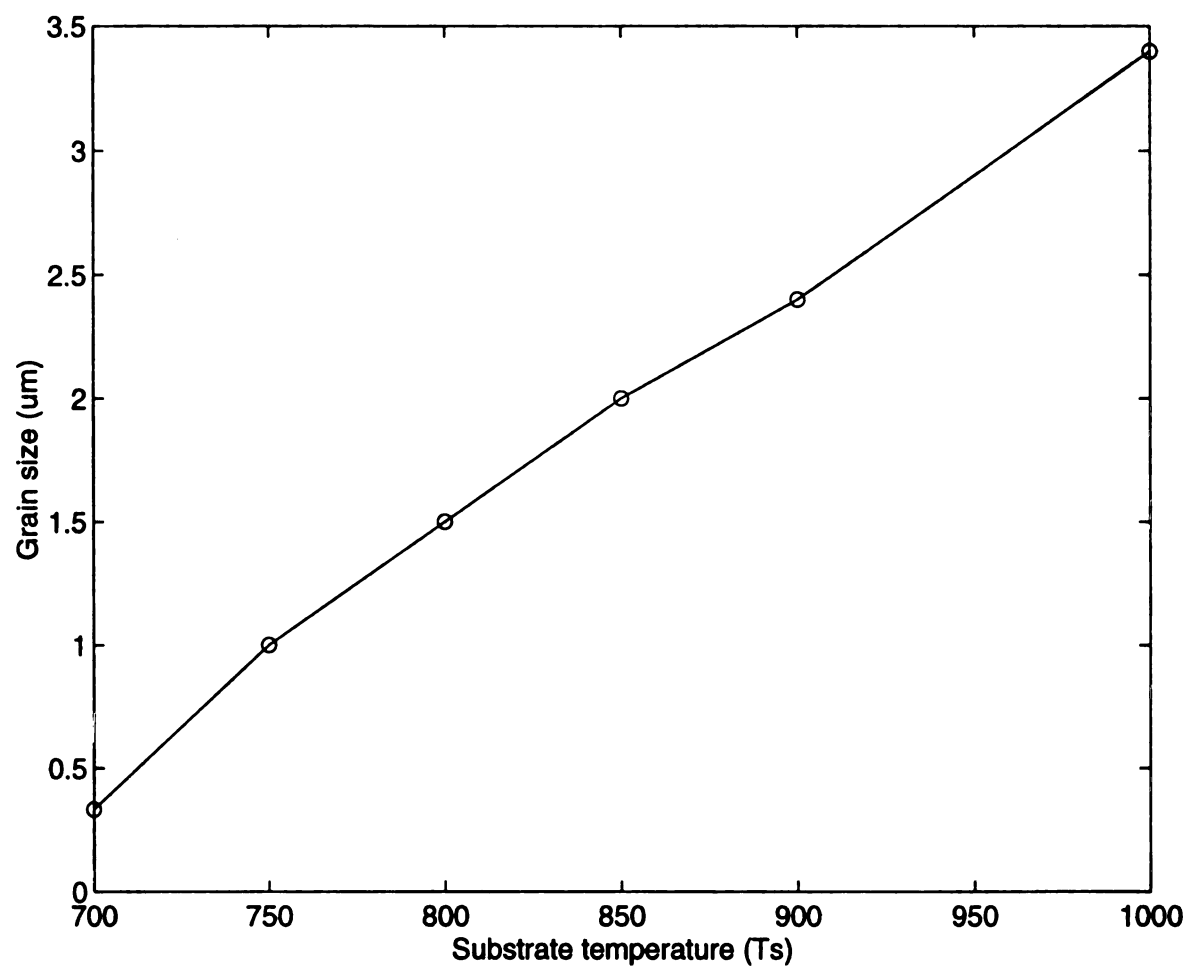


Figure 5.25. Grain size vs. T_s for $f_1 = 60$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

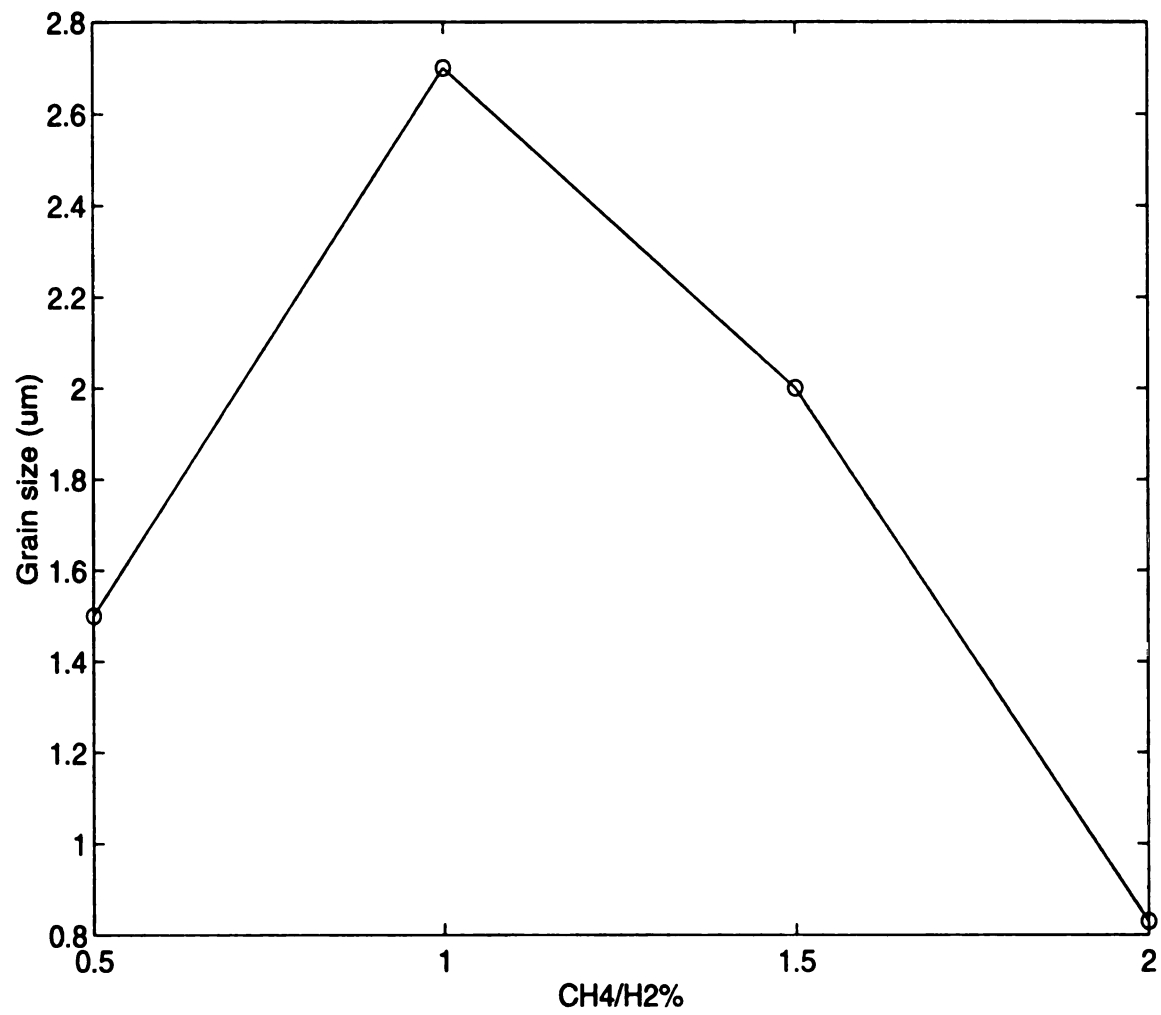


Figure 5.26. Grain size vs. $\text{CH}_4/\text{H}_2\%$ for $f_1 = 60$ sccm and $T_s = 850^\circ\text{C}$.

5.2.1.1.5 Total gas flow rate, $f_t = 30$ sccm

The 30 sccm was the lowest possible flow rate that could reliably be set with the available flow meter. Therefore only a small number of experiments were conducted at this flow rate.

For the total gas flow rate fixed at 30 sccm, a field map that related surface morphology (expressed by the growth parameter α) to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s , was developed as shown in Figure 5.27. Diamond films with various morphologies such as $\{100\}$, $\{111\}$, and cauliflower were deposited at this flow rate. Figure 5.28 shows the variation of film surface morphology with T_s for CH_4/H_2 fixed at 1.50%. As seen from the SEM pictures, low substrate temperature (i.e., $T_s = 700^\circ\text{C}$) resulted in diamond film with cauliflower structure whereas higher substrate temperatures yielded well-faceted crystals, predominantly $\{100\}$ (i.e., $\alpha \cong 1 - 2.5$). At $T_s = 750^\circ\text{C}$, crystals with $\alpha \cong 2.5$ which corresponds to crystals that look like truncated octahedra with small $\{100\}$ top face and sloped side faces appeared on the film surface. The $\{100\}$ top facets grew bigger and became more columnar (closer to cubic crystal habit with $\alpha \cong 1$) as the substrate temperatures was increased to $T_s = 850^\circ\text{C}$.

With substrate temperature fixed at 850°C , the film morphology changed from $\{111\}$ ($\alpha \cong 3$) to $\{100\}$ ($\alpha \cong 1$) as CH_4/H_2 was changed from 0.60% to 1.50%. The growth parameter α then increased to $\alpha \cong 2.5$ as CH_4/H_2 was further increased to 2.0%. Figure 5.29 illustrates the variation of the film morphology (i.e., α) with methane concentration for the substrate temperature fixed at 850°C .

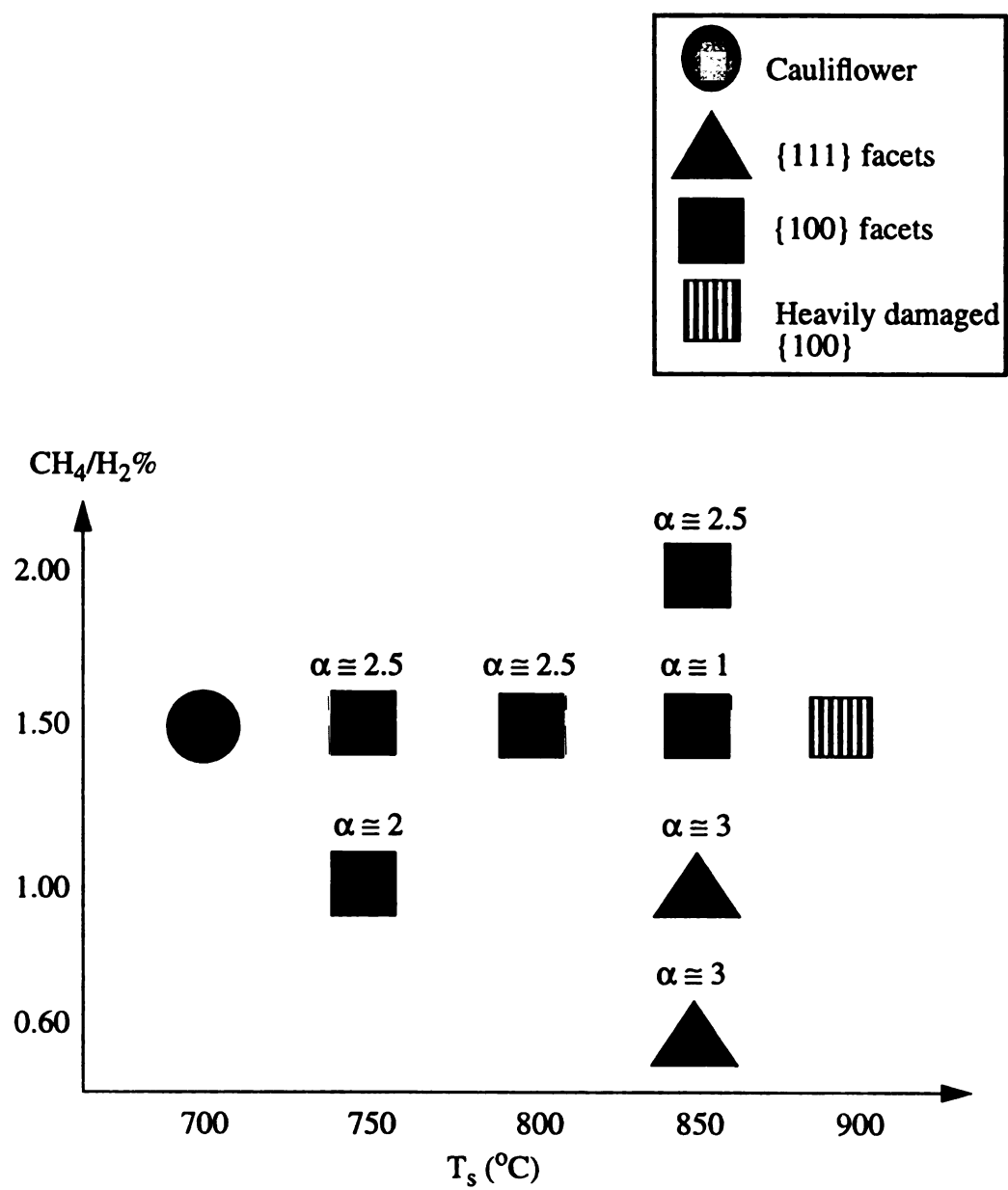


Figure 5.27. Morphology field map for $f_t = 30$ sccm.

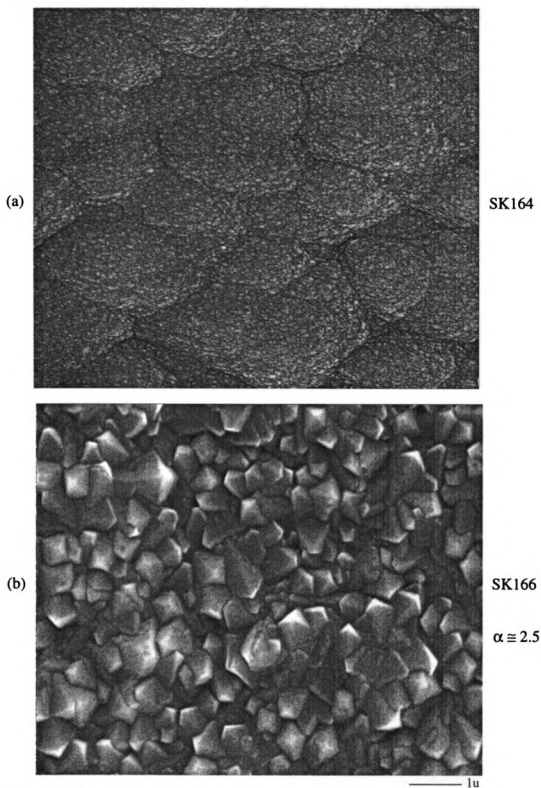
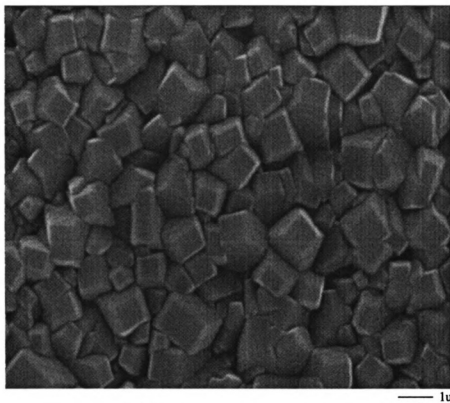


Figure 5.28. SEM pictures of sample deposited at $f_t = 30$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 750^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, and (d) $T_s = 900^\circ\text{C}$.

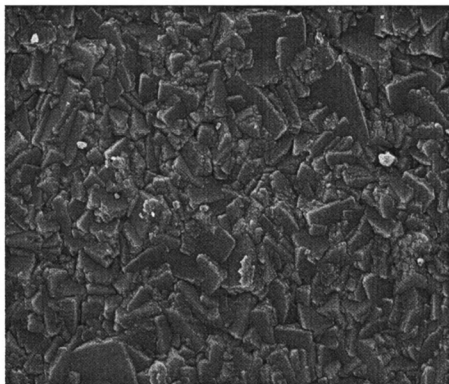
(c)



SK155

 $\alpha \cong 1$

(d)



SK165

Figure 5.28. Continued.

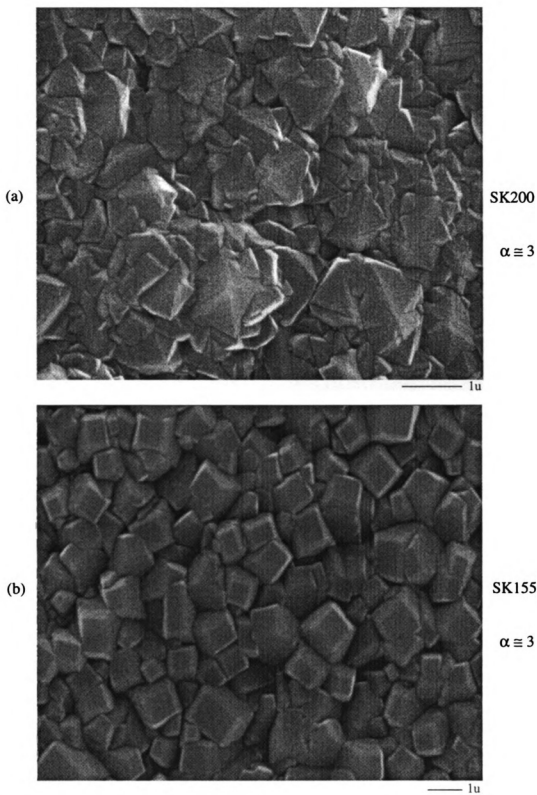


Figure 5.29. SEM pictures of samples deposited at $f_t = 30$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 0.60\%$, (b) $\text{CH}_4/\text{H}_2 = 1.50\%$, and (c) $\text{CH}_4/\text{H}_2 = 2.0\%$.

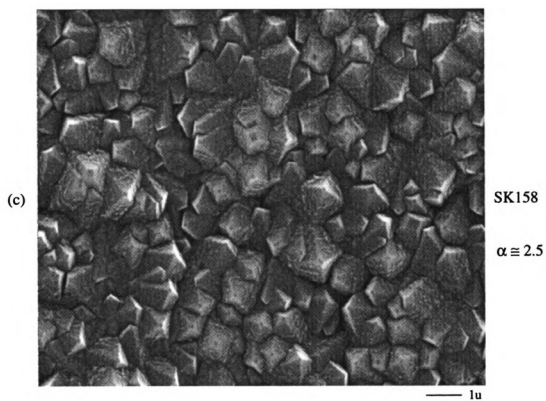


Figure 5.29. Continued.

5.2.1.2 Structural quality

5.2.1.2.1 Total gas flow rate, $f_t = 400$ sccm

Raman spectroscopy technique was utilized to determine structural quality (sp^3 peak vs. sp^2 peak) of the CVD diamond films deposited by the MCPR. Diamond phase (i.e., sp^3 bonding) represents a Raman peak at or around 1332 cm^{-1} line while graphite phase (i.e., sp^2 bonding) shows a broad peak around 1550 cm^{-1} line.

Figure 5.30 shows the variation of the Raman spectra of the samples with substrate temperature for a fixed methane concentration of $\text{CH}_4/\text{H}_2 = 1.50\%$. The plot of FWHM vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ is shown in Figure 5.31. As shown in the Figure, the FWHM decreased as T_s increased.

Due to incorporation of noise, it was difficult to distinguish the graphite peak from the background luminescence. But by visual inspection it was seen that the graphite peaks and their ratio to the diamond peaks decreased with the substrate temperature in its respected range (i.e., $T_s \in [800, 1000]^\circ\text{C}$).

Basically the same trend was observed for a different methane concentration in hydrogen. Figure 5.32 shows Raman spectra vs. T_s of the films deposited at $\text{CH}_4/\text{H}_2 = 0.60\%$. They correspond to diamond films of Figure 5.6. The plot of FWHM vs. T_s of these films is shown in Figure 5.33 which shows that the FWHM decreased with T_s in its respected range. It is seen that in the substrate temperature range of $T_s \in [800, 1000]^\circ\text{C}$ where the Raman analysis were carried out, FWHM did not change significantly. For this methane concentration, the crystals were well-faceted (no cauliflower or microcrystallites/small aggregates).

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is apparent from Figure 5.34 which shows Raman spectra of the diamond films deposited at a fixed substrate temperature of 850°C with CH_4/H_2 varying between 0.60% and 3.75%. The Raman spectra show strong diamond peaks associated with $\text{CH}_4/\text{H}_2 \leq 1.75\%$. The diamond peak diminished as methane concentration was further increased. The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ of these diamond films is illustrated in Figure 5.35 which shows that the FWHM increased sharply with methane concentration in hydrogen. By visual inspection of the Raman spectra of Figure 5.34 it is seen that the noise level was also increased with methane concentration in hydrogen. At $\text{CH}_4/\text{H}_2 \geq 2.75\%$ the Raman spectra were so noisy that the diamond peaks could not be easily distinguished from the noise as seen in Figure 5.34 (e) and (f). Furthermore, from Figure 5.34 and Figure 5.35, it is seen that methane concentration had a more pronounced effect on the film structural quality than the substrate temperature. FWHM increased sharply as crystals became ill-faceted (cauliflower, small aggregates, etc.) as methane concentration was increased beyond $\text{CH}_4/\text{H}_2 = 1.50\%$.

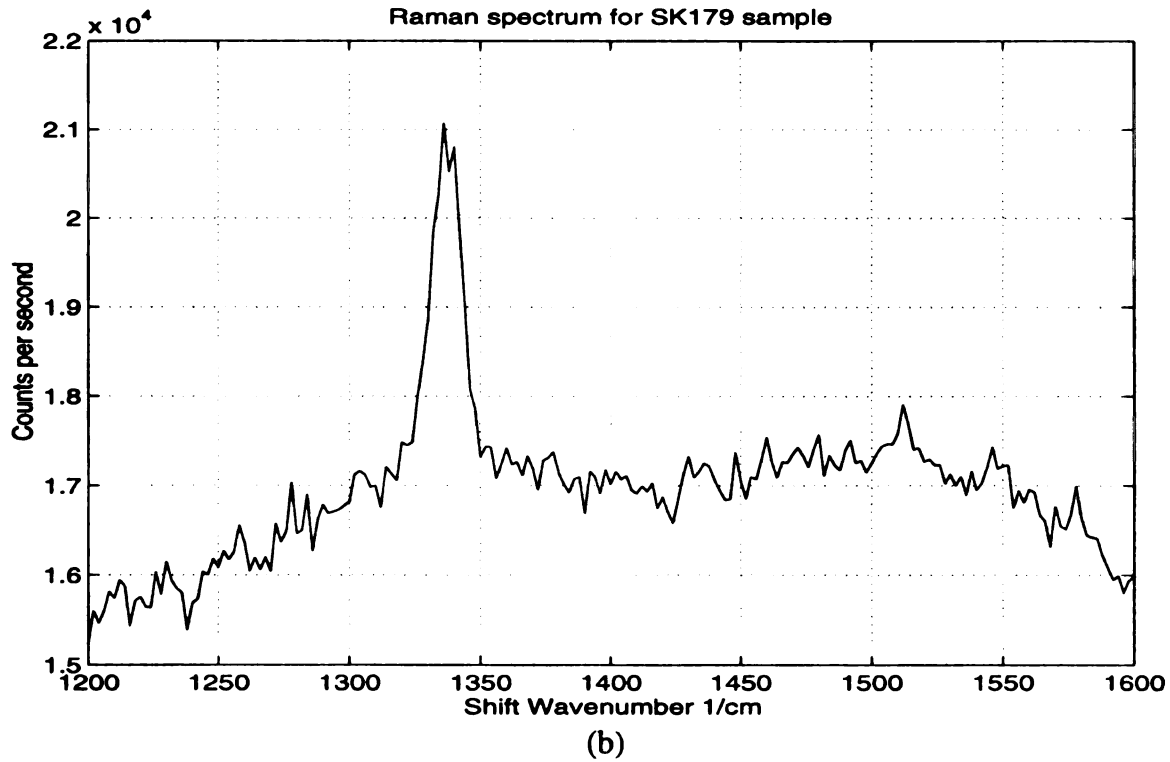
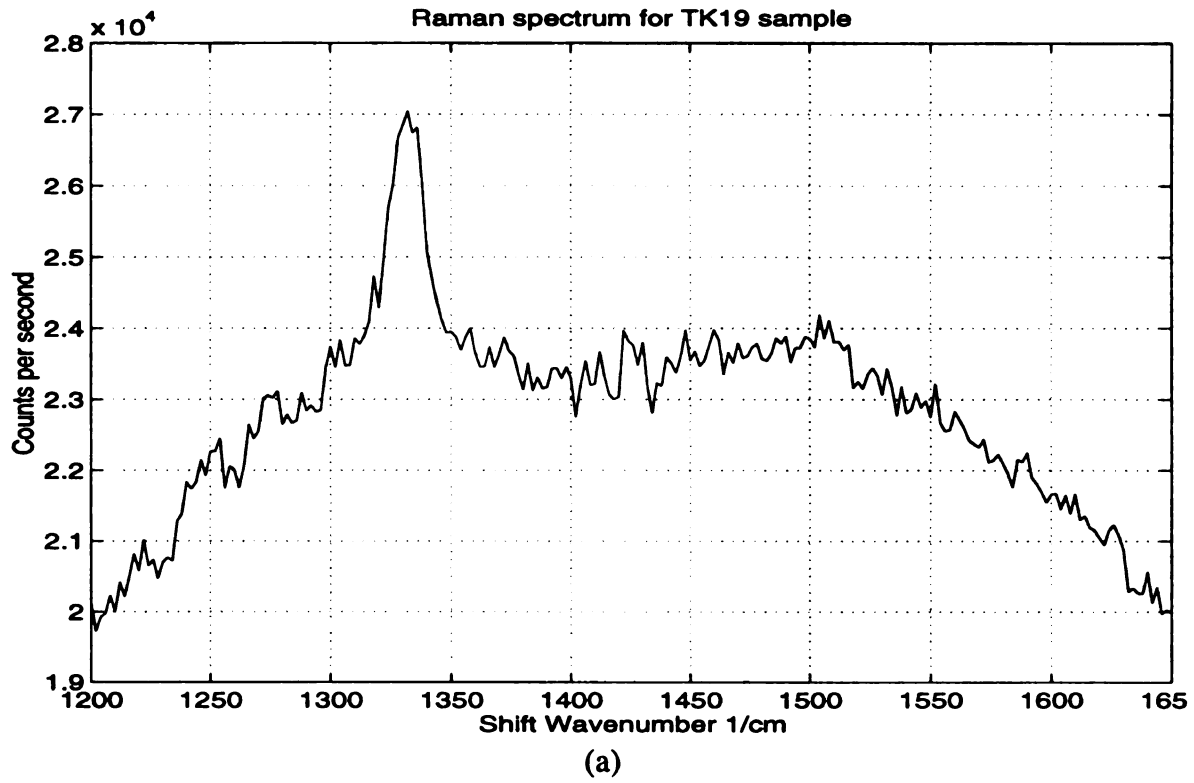


Figure 5.30. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2=1.50\%$ and $f_t=400$ sccm with $T_s =$ (a) 800°C , (b) 850°C , (c) 900°C , (d) 950°C , and (e) 1000°C .

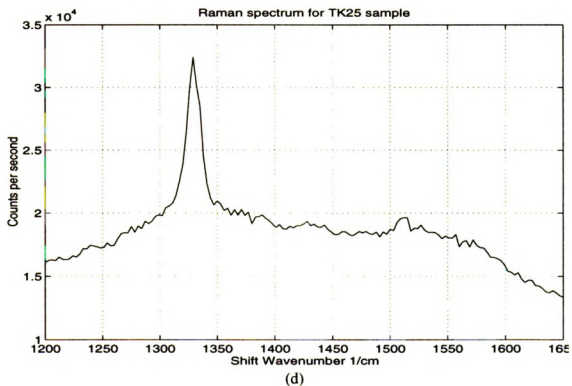
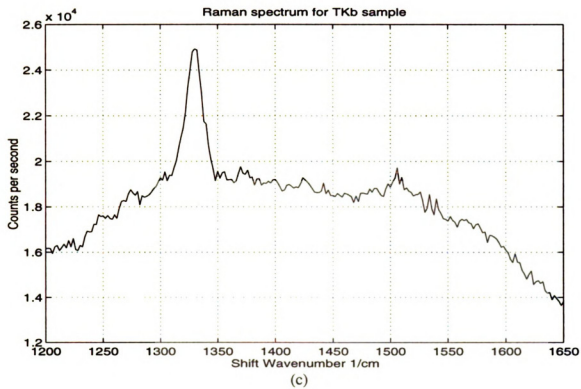


Figure 5.30. Continued.

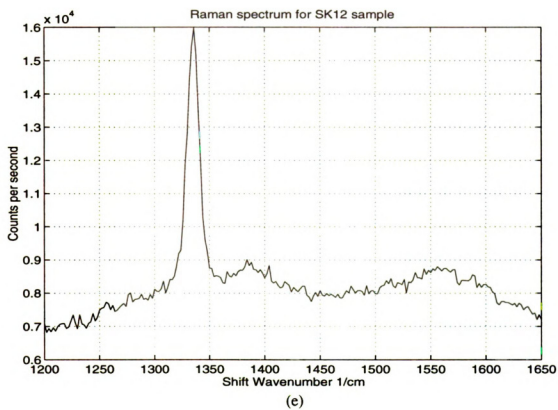
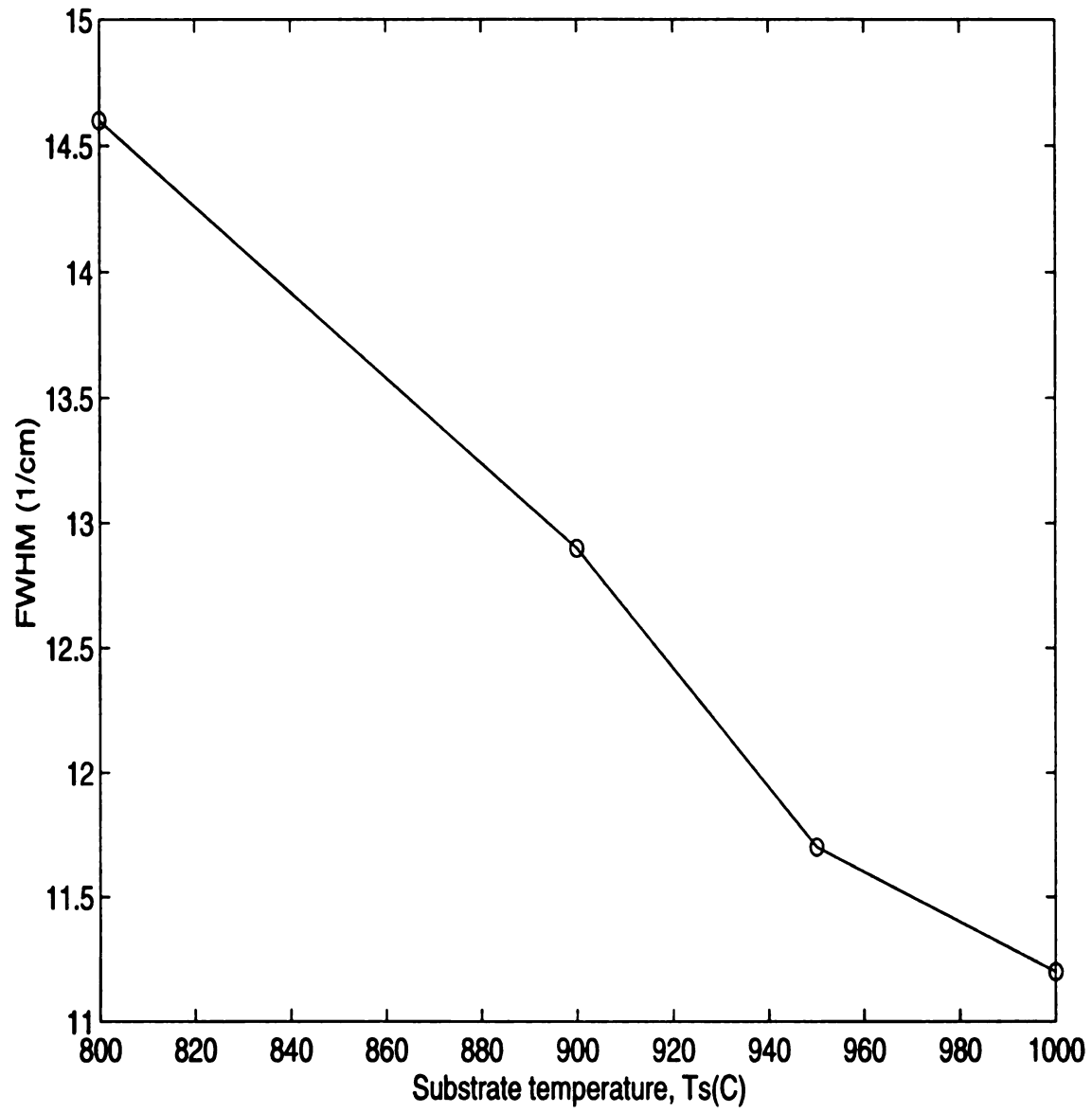


Figure 5.30. Continued.



Sample	T_s (°C)	FWHM (1/cm)
TK19	800	14.6
TKb	900	12.9
TK25	950	11.7
SK12	1000	11.2

Figure 5.31. FWHM vs. T_s for $\text{CH}_4/\text{H}_2 = 1.5\%$ and $f_t = 400$ sccm.

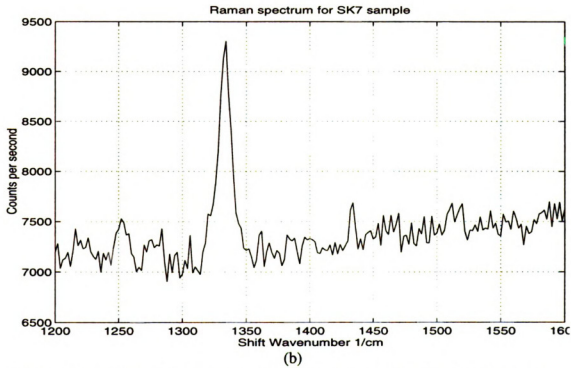
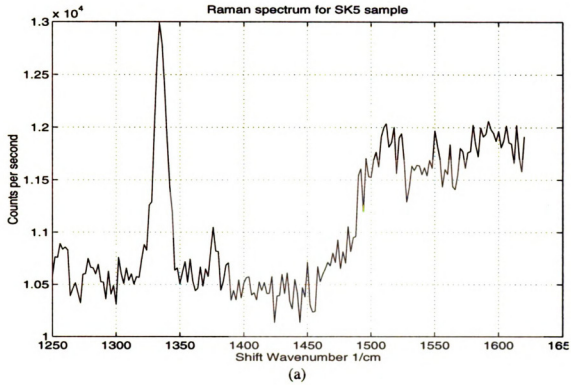


Figure 5.32. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2=0.60\%$ and $f_t = 400$ sccm with $T_s =$ (a) 800°C , (b) 850°C , (c) 900°C , (d) 950°C , and (e) 1000°C .

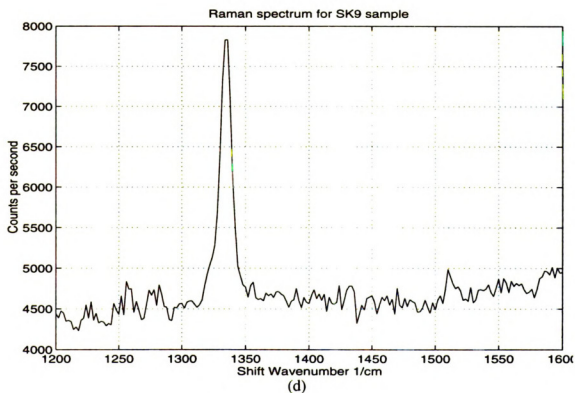
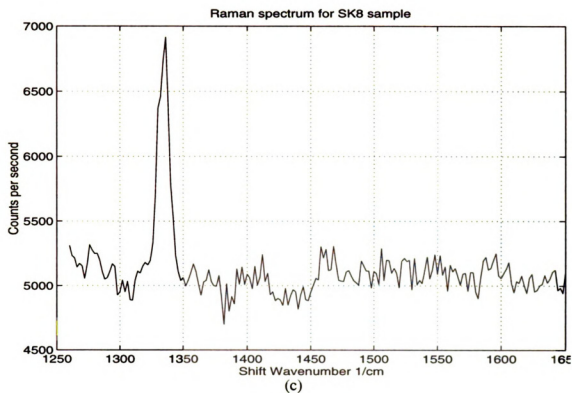


Figure 5.32. Continued.

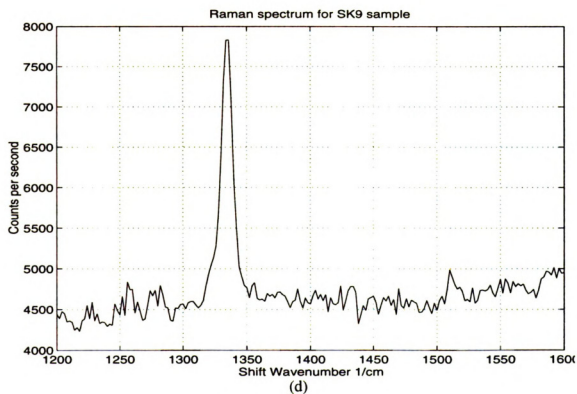
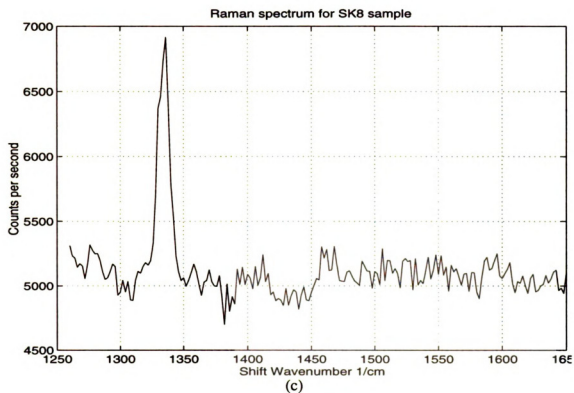


Figure 5.32. Continued.

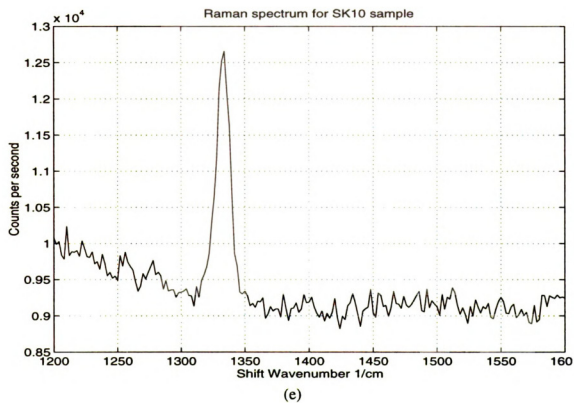
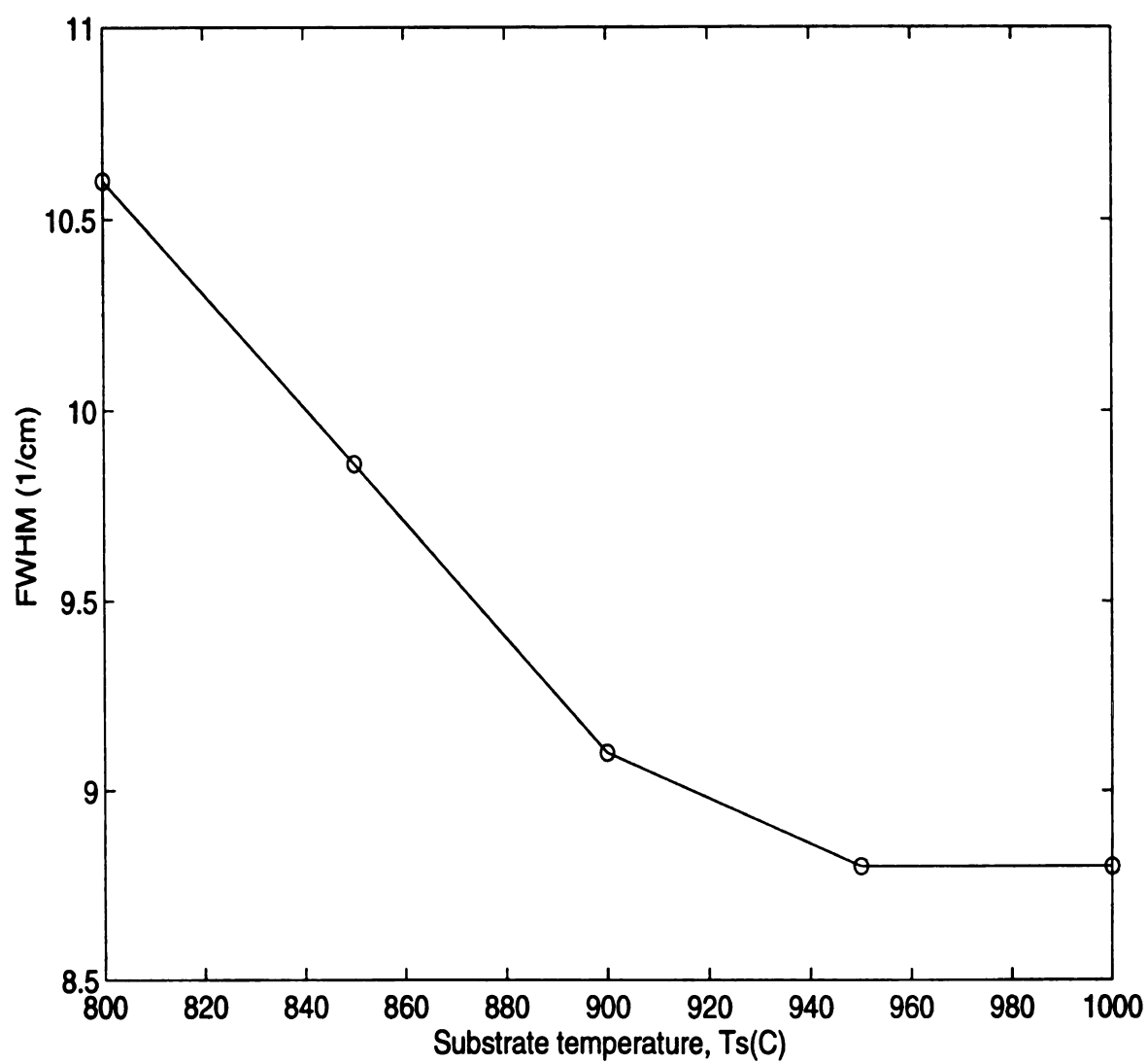


Figure 5.32. Continued.



Sample	T_s (°C)	FWHM (1/cm)
SK5	800	10.6
SK7	850	9.86
SK8	900	9.10
SK9	950	8.80
SK10	1000	8.80

Figure 5.33. FWHM vs. T_s for $\text{CH}_4/\text{H}_2=0.60\%$ and $f_t=400$ sccm.

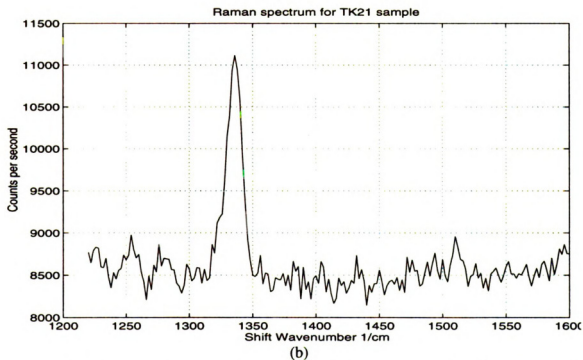
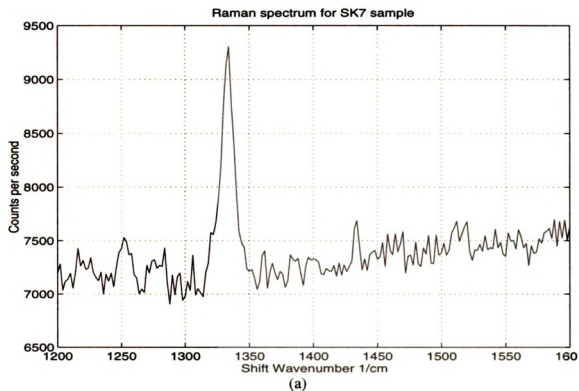
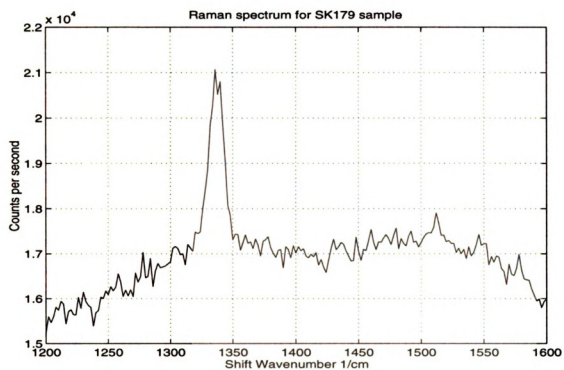
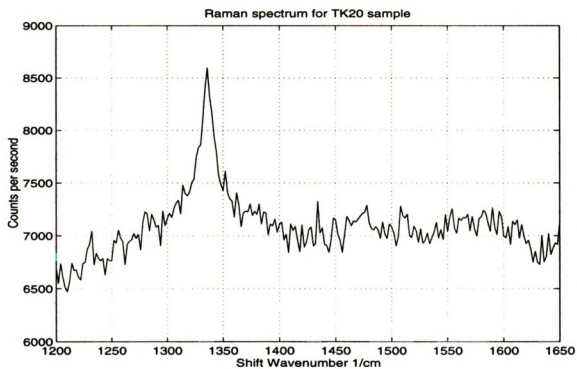


Figure 5.34. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_i = 400$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 0.60%, (b) 1.0%, (c) 1.50%, (d) 1.75%, (e) 2.75%, and (f) 3.75%



(c)



(d)

Figure 5.34. Continued.

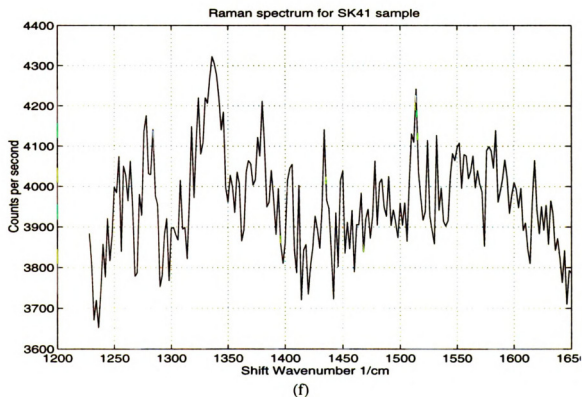
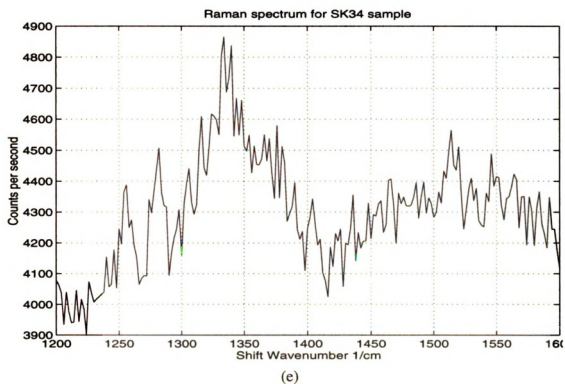
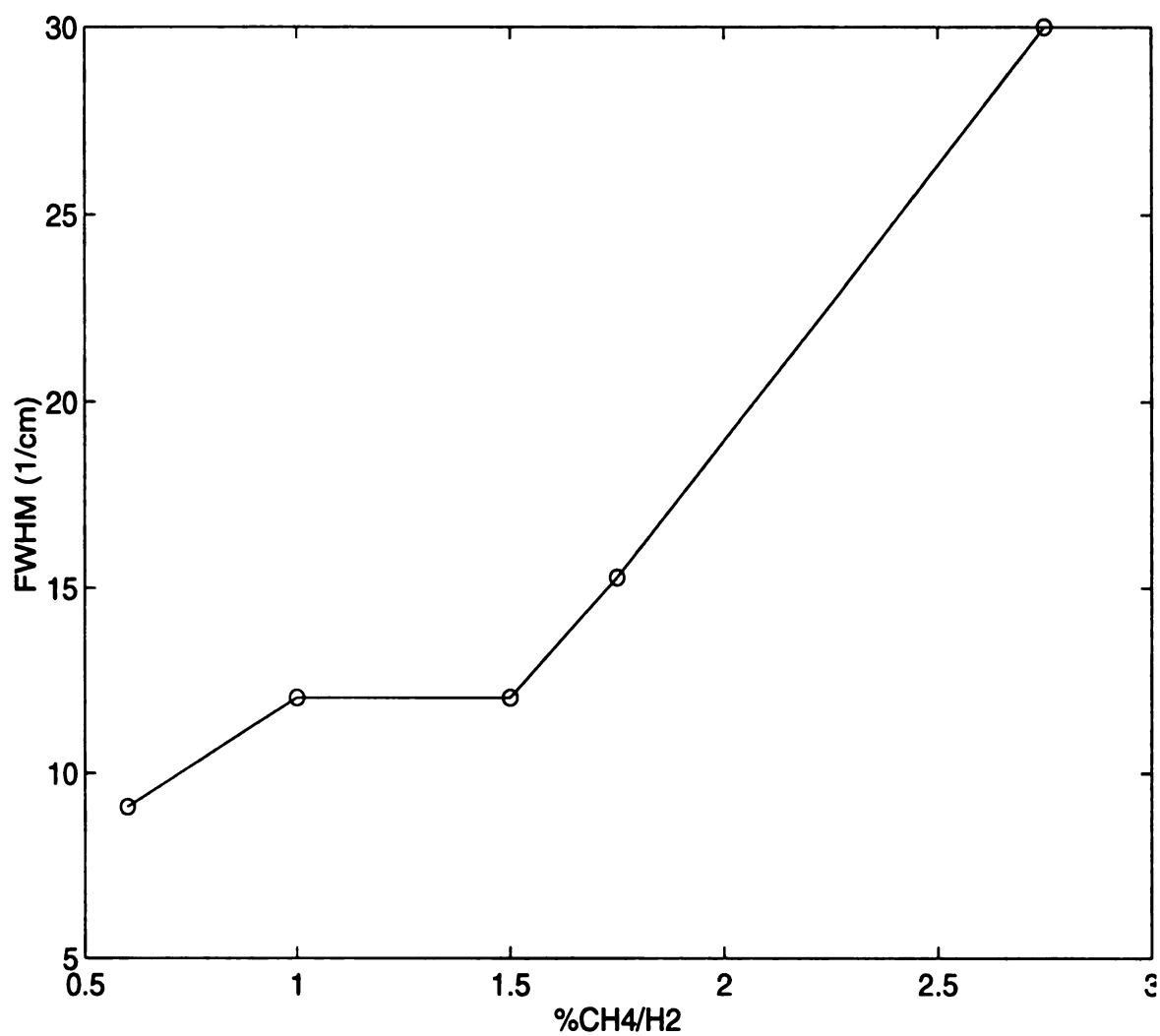


Figure 5.34. Continued.



Sample	CH ₄ /H ₂ %	FWHM (1/cm)
SK7	0.60	9.09
TK21	1.00	12.04
SK179	1.50	12.04
TK20	1.75	15.28
SK34	2.75	> 30
SK41	3.75	na

Figure 5.35. FWHM vs. CH₄/H₂% for diamond films deposited at $f_t=400$ sccm and $T_s=850^\circ\text{C}$.

5.2.1.2.2 Total gas flow rate, $f_t = 200$ sccm

Figure 5.36 shows the variation of the Raman spectra (i.e., structural quality) of the samples with the substrate temperature for a fixed methane concentration of $\text{CH}_4/\text{H}_2 = 1.50\%$. All Raman spectra show strong diamond peak (around 1332 cm^{-1}). By visual inspection of the Raman spectra it is seen that the graphite peak decreased with the substrate temperature in its respected range of (i.e., $T_s \in [700, 1000]^\circ\text{C}$).

The plot of FWHM vs. T_s for $\text{CH}_4/\text{H}_2=1.50\%$ is shown in Figure 5.37. The minimum FWHM of 7.05 cm^{-1} was associated with $T_s = 850^\circ\text{C}$ and $T_s = 1000^\circ\text{C}$. The FWHM was maximum (10.5 cm^{-1}) for the film deposited at $T_s = 900^\circ\text{C}$.

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is evident from Figure 5.38 which shows Raman spectra of the diamond films deposited at a fixed substrate temperature of 850°C with CH_4/H_2 varying between 0.60% and 3.0% . The Raman spectra show strong diamond peaks and low graphitic peaks for $\text{CH}_4/\text{H}_2 \leq 1.50\%$. The diamond peaks experienced a significant decrease and broadening and the graphitic peaks experienced a sharp increase when the methane concentration was increased to and beyond 2.0% (i.e., $\text{CH}_4/\text{H}_2 \geq 2.0\%$).

The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ for T_s fixed at 850°C is shown in Figure 5.39. As shown, the FWHM was low and did not change significantly for $\text{CH}_4/\text{H}_2 \leq 1.50$ but increased sharply for $\text{CH}_4/\text{H}_2 \geq 2.0\%$. From Figure 5.37 and Figure 5.39 it is seen that the film structural quality was heavily dependent upon $\text{CH}_4/\text{H}_2\%$ and only slightly dependent upon the substrate temperature (hence pressure and microwave power).

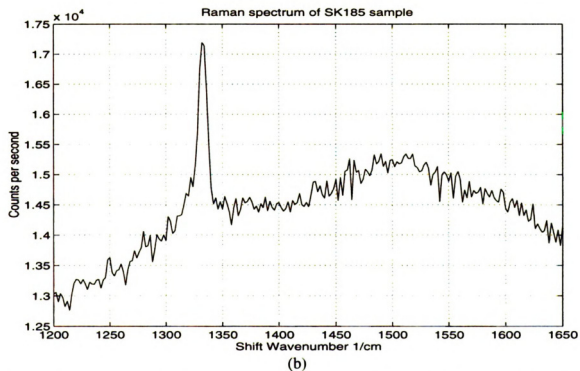
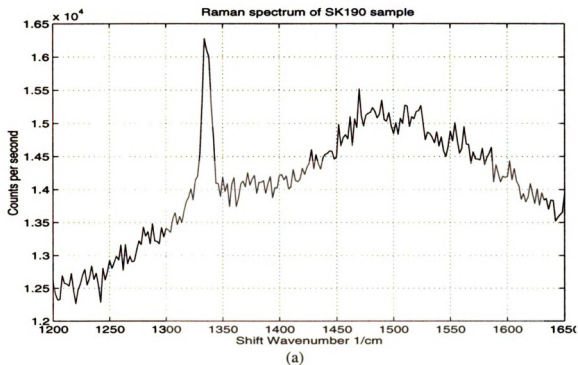


Figure 5.36. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 200$ sccm with $T_s =$ (a) 700°C , (b) 800°C , (c) 850°C , (d) 900°C , and (e) 1000°C .

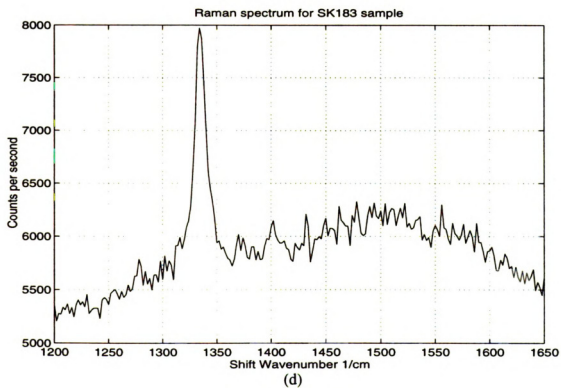
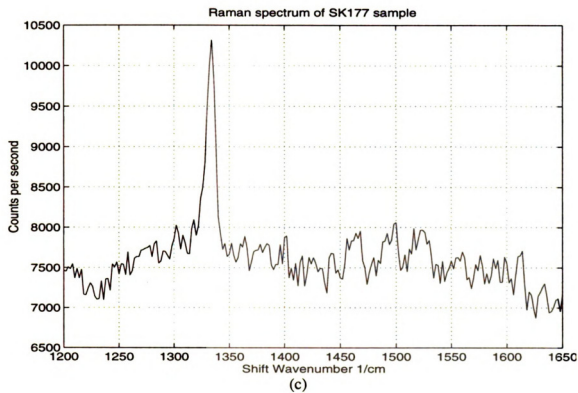


Figure 5.36. Continued.

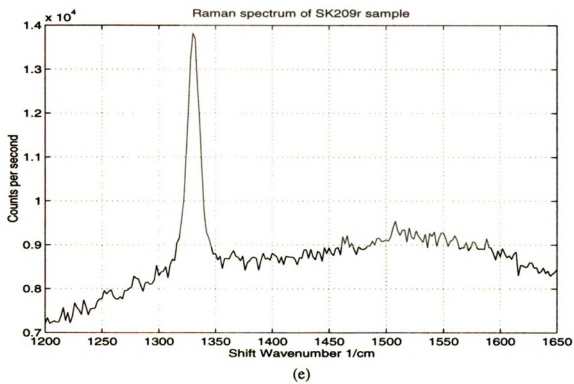
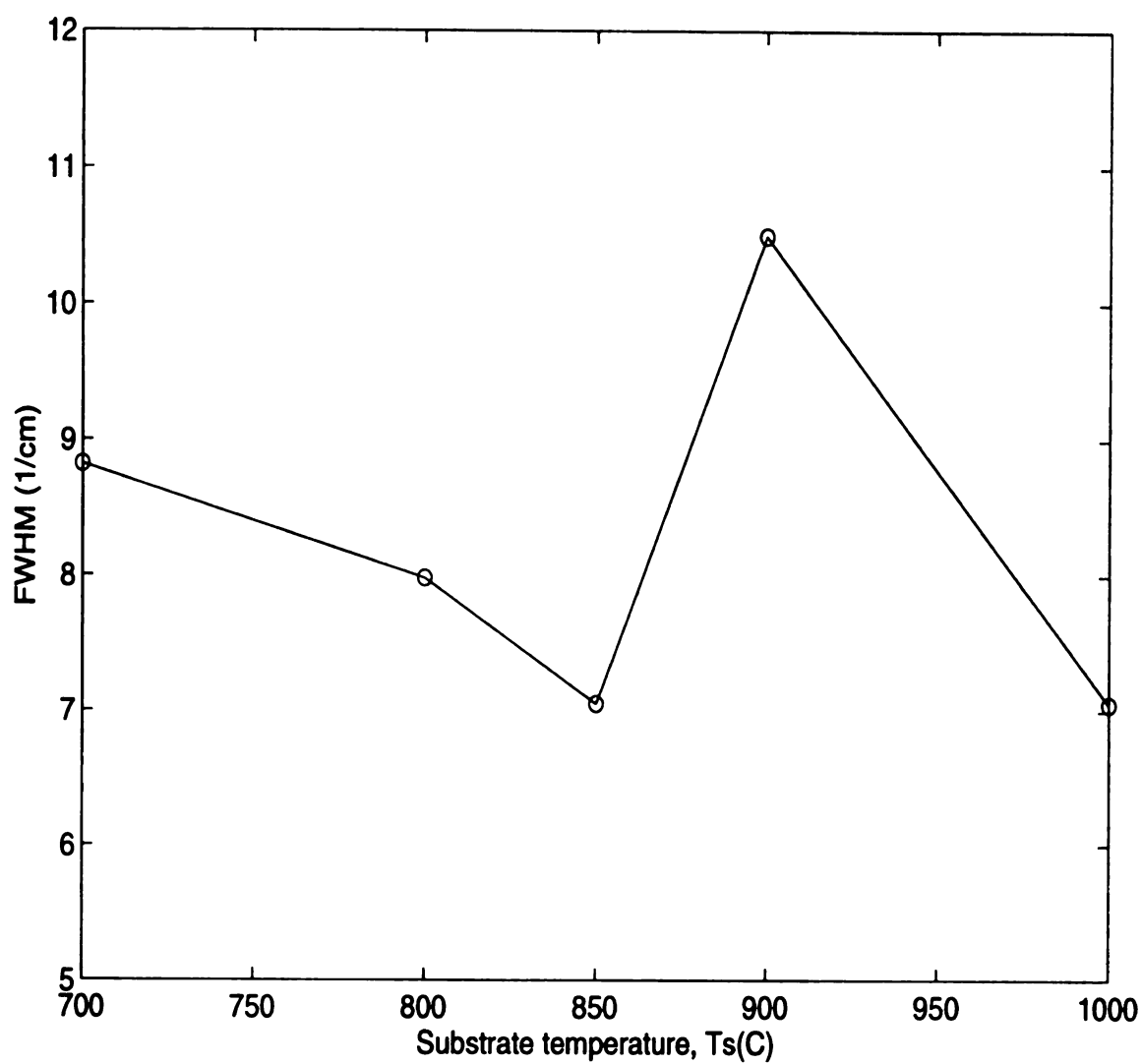


Figure 5.36. Continued.



Sample	T_s (°C)	FWHM (1/cm)
SK190	700	8.82
SK185	800	7.98
SK177	850	7.05
SK183	900	10.50
SK209r	1000	7.05

Figure 5.37. FWHM vs. substrate temperature for diamond films deposited at $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

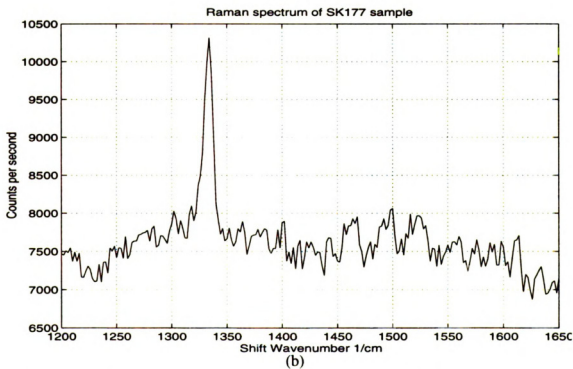
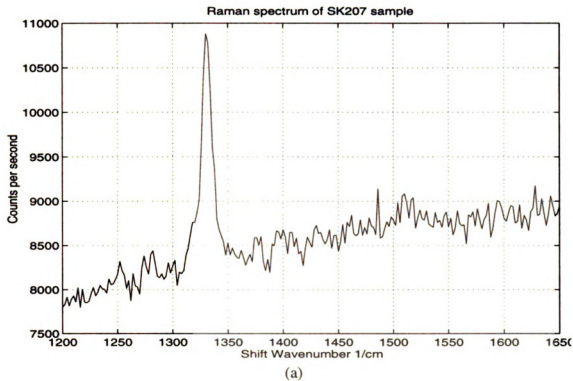


Figure 5.38. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 200$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 0.60%, (b) 1.50%, (c) 2.0%, (d) 3.0%.

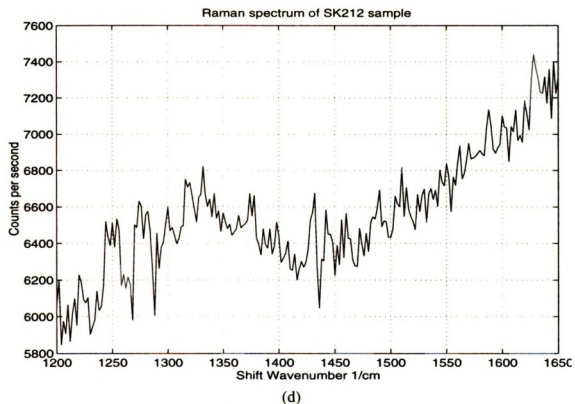
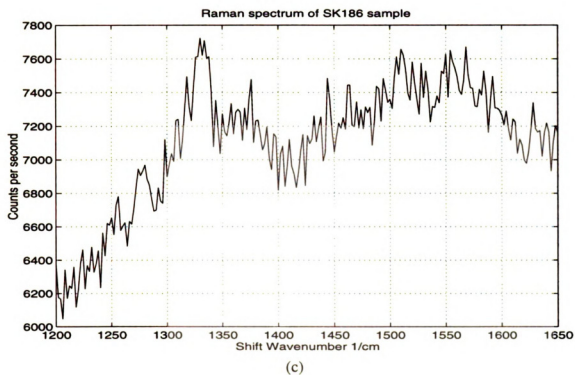
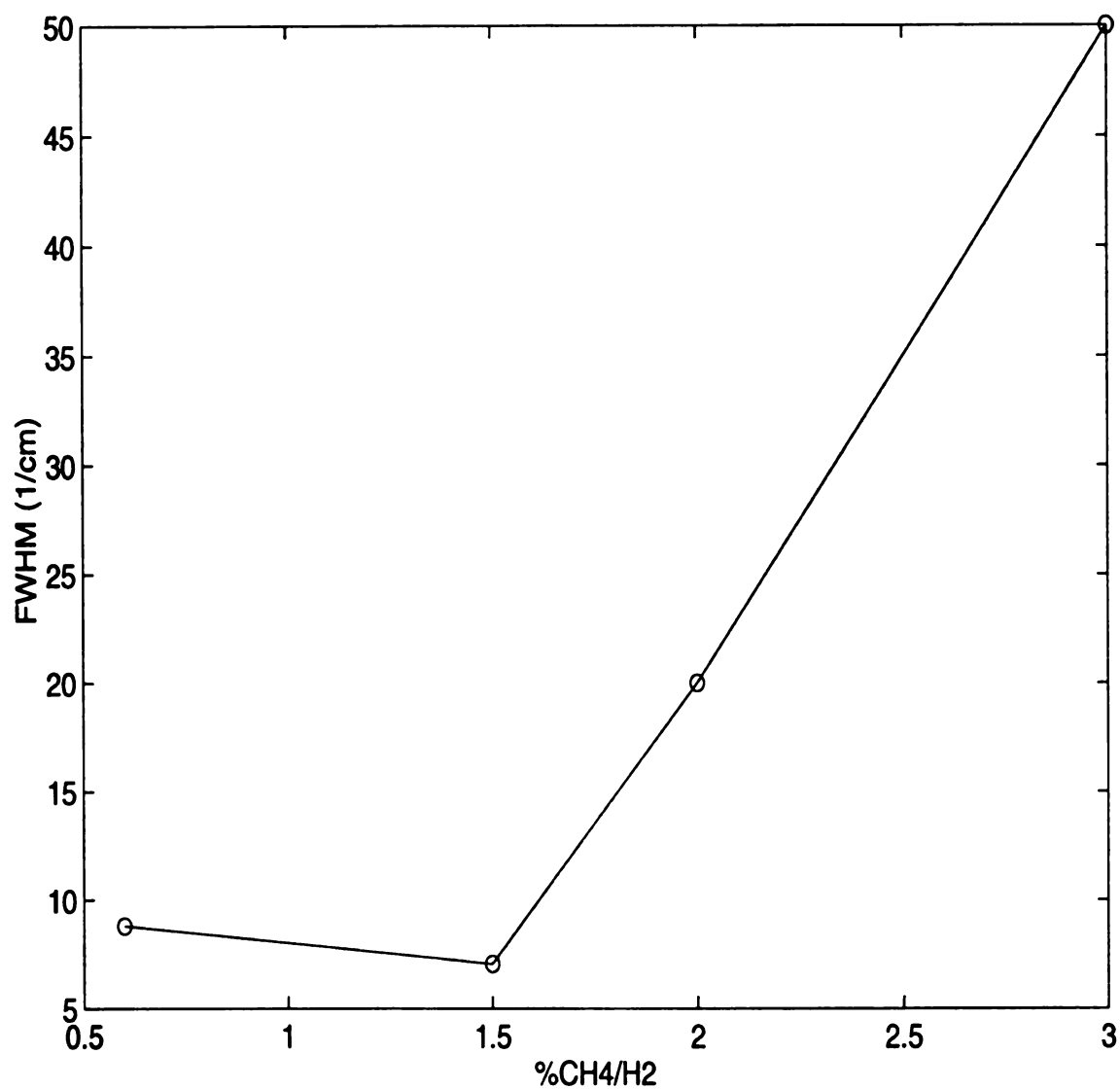


Figure 5.38. Continued.



Sample	CH ₄ /H ₂ %	FWHM (1/cm) for T _s =850°C
SK207	0.60	8.815
SK177	1.50	7.05
SK186	2.00	~ 20
SK212	3.00	>50

Figure 5.39. FWHM vs. %CH₄/H₂ for diamond films deposited at $f_t = 200$ sccm and $T_s = 850^\circ\text{C}$.

5.2.1.2.3 Total gas flow rate, $f_t = 100$ sccm

In general, substrate temperature only slightly affected the film quality as determined by FWHM of Raman spectra. Methane concentration in hydrogen had a greater influence on the structural quality of the films. At the methane concentrations where the films became morphologically structureless (i.e., cauliflower), FWHM experienced a large increase. Figure 5.40 shows a typical Raman spectra of a sample deposited at this flow rate. The FWHM associated with this diamond film was 12.12 cm^{-1} .

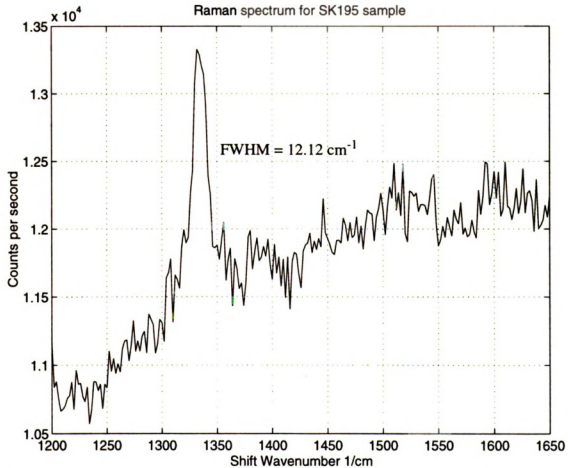


Figure 5.40. A typical Raman spectra of a sample deposited at $f_t = 100$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$.

5.2.1.2.4 Total gas flow rate, $f_t = 60$ sccm

Figure 5.41 shows the variation of the Raman spectra of the samples with substrate temperature for a fixed methane concentration of $\text{CH}_4/\text{H}_2 = 1.50\%$. By visual inspection of the Raman spectra it is seen that the graphite peak decreased with the substrate temperature in its respected range (i.e., $T_s \in [700, 1000]^\circ\text{C}$).

The plot of FWHM vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ is shown in Figure 5.42. The minimum FWHM of 9.09 cm^{-1} was associated with $T_s = 850^\circ\text{C}$. The FWHM was maximum (10.59 cm^{-1}) for the film deposited at $T_s = 800^\circ\text{C}$.

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is evident from Figure 5.43 which shows Raman spectra of the diamond films deposited at a fixed substrate temperature of 850°C with CH_4/H_2 varying between 0.50% and 4.0% . The Raman spectra show strong diamond peaks and low graphitic peaks for $\text{CH}_4/\text{H}_2 \leq 2.0\%$. The diamond peaks experienced a significant decrease and broadening and the graphitic peaks experienced a sharp increase when the methane concentration was increased to and beyond 3.0% (i.e., $\text{CH}_4/\text{H}_2 \geq 3.0\%$).

The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ for T_s fixed at 850°C is shown in Figure 5.44. As shown, the FWHM was small and did not change significantly for $\text{CH}_4/\text{H}_2 \leq 2.0$ but increased sharply for $\text{CH}_4/\text{H}_2 \geq 3.0\%$. From Figure 5.42 and Figure 5.44 it is seen that $\text{CH}_4/\text{H}_2\%$ had a stronger influence on the film structural quality than the substrate temperature.

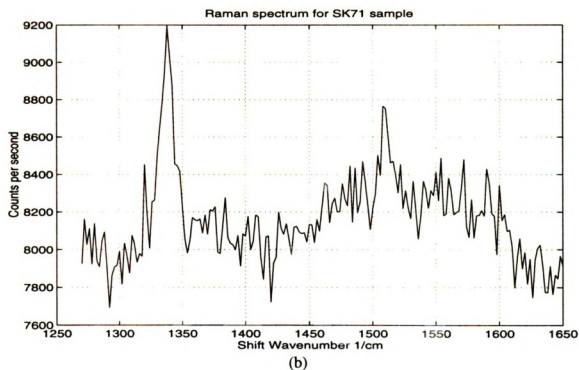
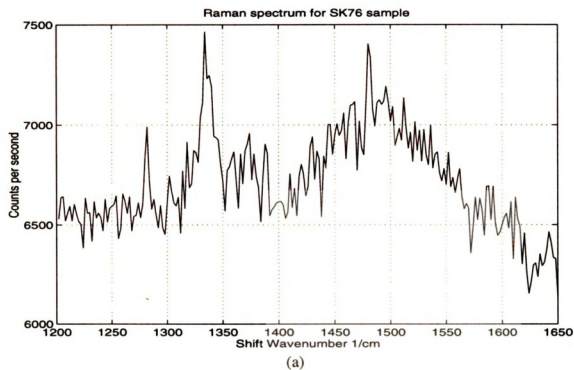


Figure 5.41. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 60$ sccm with $T_s =$ (a) 700°C , (b) 800°C , (c) 850°C , (d) 900°C , and (e) 1000°C .

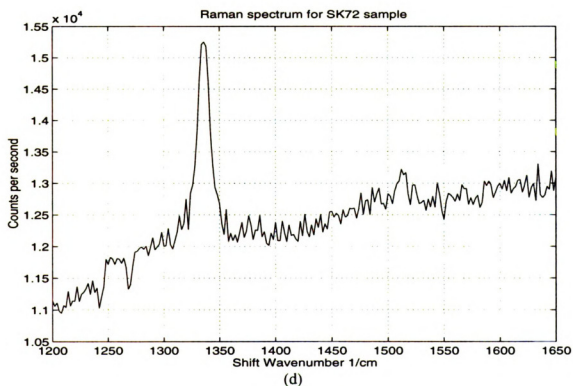
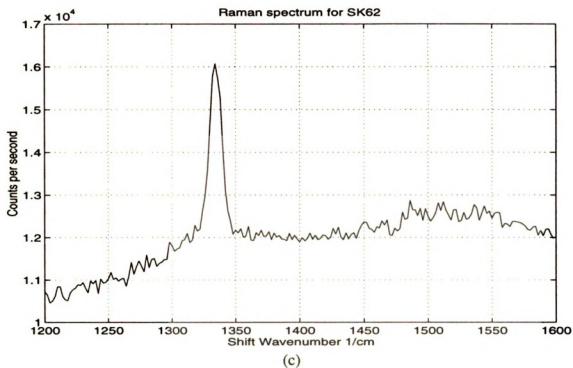


Figure 5.41. Continued.

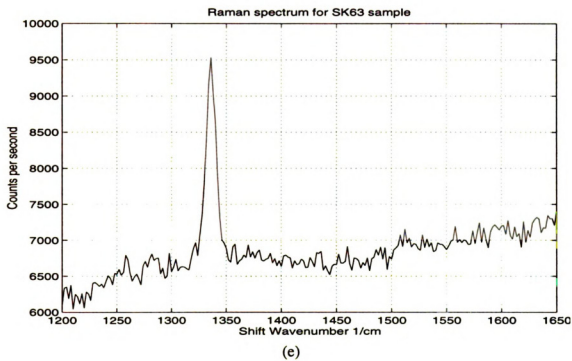
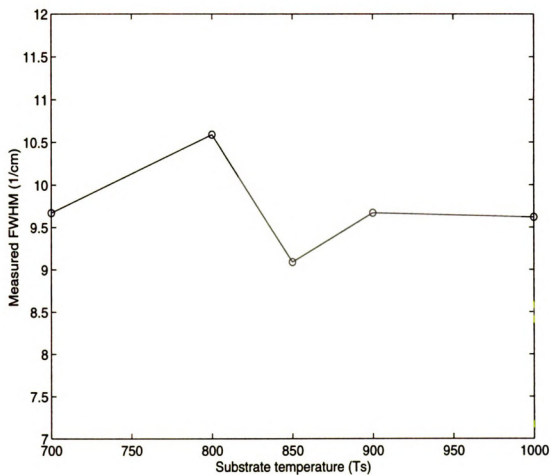


Figure 5.41. Continued.



Sample	T_s (°C)	FWHM (1/cm)
SK76	700	9.67
SK71	800	10.59
SK62	850	9.09
SK72	900	9.67
SK63	1000	9.62

Figure 5.42. The plot of FWHM vs. T_s for diamond films deposited at $f_t = 60$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$

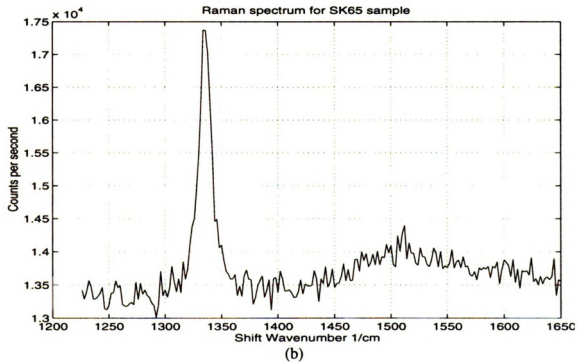
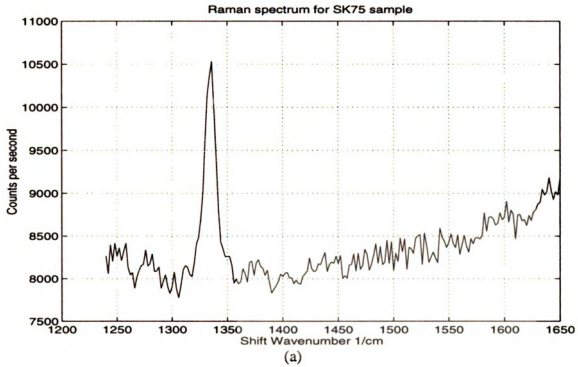


Figure 5.43. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 0.50%, (b) 1.0%, (c) 1.50%, (d) 2.0%, (e) 3.0%, and (f) 4.0%.

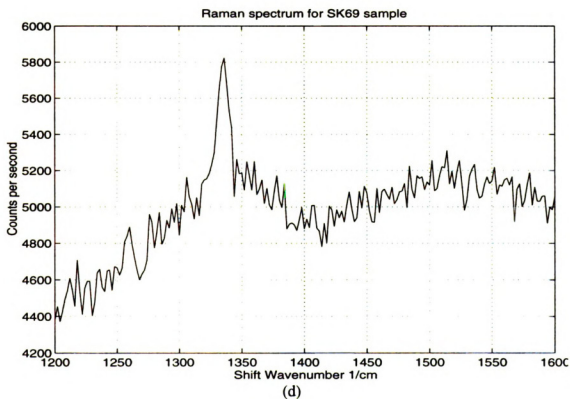
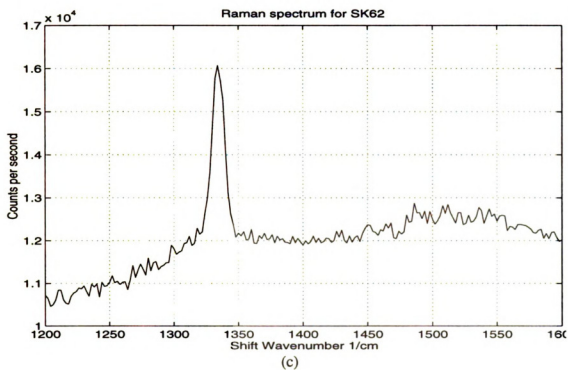
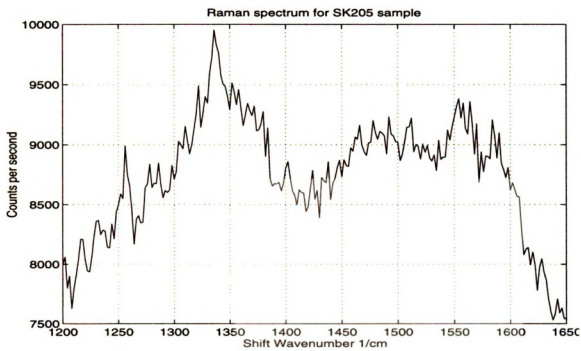
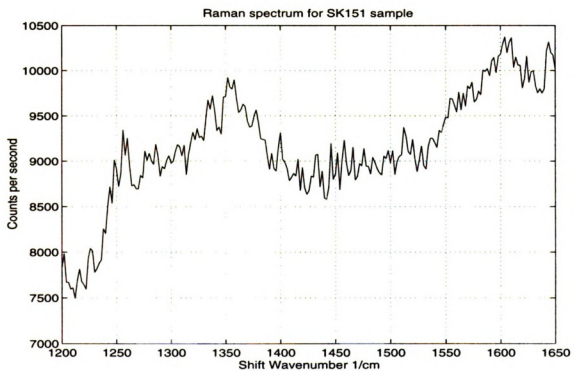


Figure 5.43. Continued.

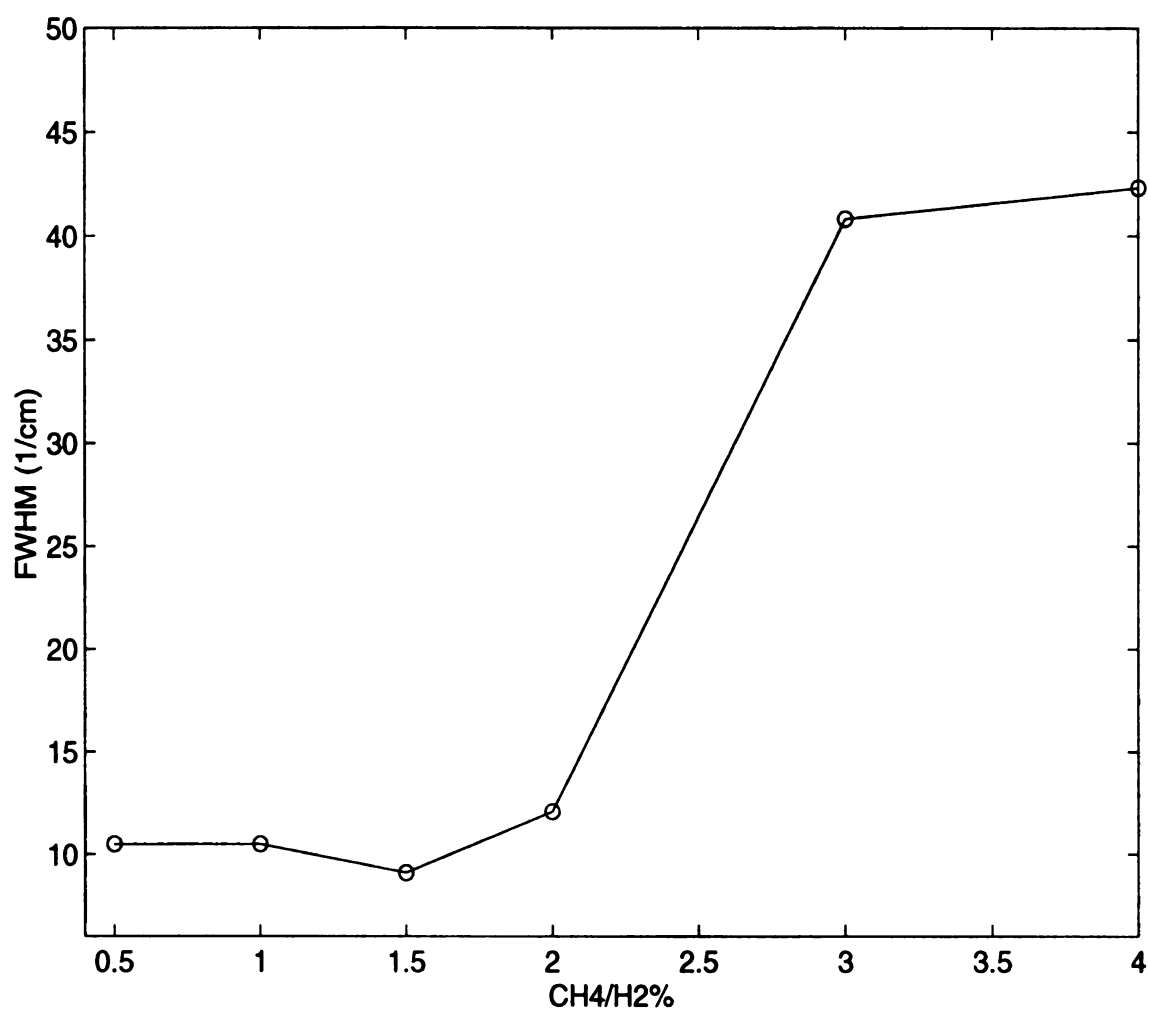


(e)



(f)

Figure 5.43. Continued.



Sample	CH ₄ /H ₂ %	FWHM (1/cm)
SK75	0.50	10.49
SK65	1.00	10.49
SK62	1.50	9.09
SK69	2.0	12.08
SK205	3.00	40.83
SK151	4.00	42.32

Figure 5.44. The plot of FWHM vs. CH₄/H₂ for diamond films deposited at $f_t = 60$ sccm and $T_s = 850^\circ\text{C}$.

5.2.1.2.5 Total gas flow rate, $f_t = 30$ sccm

Figure 5.45 shows a typical Raman spectrum of a diamond sample deposited at this flow rate. It shows a pronounced diamond peak and a very small graphitic peak. The FWHM associated with this diamond film was 11.1 cm^{-1} .

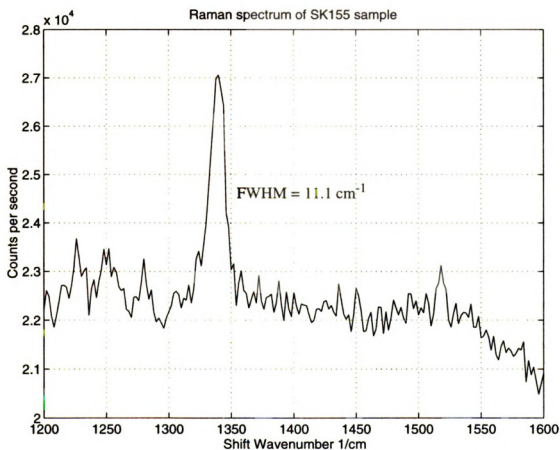


Figure 5.45. A typical Raman spectra of a sample deposited at $f_t = 30$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$.

5.2.2 Reactor performance (Y_2) vs. various input variables

In what follows, linear growth rate (d) and carbon conversion efficiency vs. methane concentration and substrate temperature for various fixed flow rates are investigated.

5.2.2.1 Linear growth rate

Film linear growth rates have been calculated via the method described in Section 4.5.4 (eq. 4.1.). This measurement method determines the average film growth rate over the substrate surface.

5.2.2.1.1 Total gas flow rate, $f_t = 400$ sccm

Figure 5.46 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s for the total gas flow rate fixed at 400 sccm. The value of growth parameter α is included in Figure 5.46. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 5.46. For $T_s \geq 1050^\circ\text{C}$ the deposition showed to be very non-uniform across the substrate. For this reason the linear growth rate analysis was limited to $T_s < 1050^\circ\text{C}$. As shown in Figure 5.46, the linear growth rate increased monotonically with the substrate temperature but with respect to methane concentration in hydrogen, it increased up to $\text{CH}_4/\text{H}_2 = 1.50\%$ and dropped beyond this point. For $f_t = 400$ sccm, the deposition condition $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 1000^\circ\text{C}$ resulted in the maximum linear growth rate of $0.663 \mu\text{m/hr}$ where $\alpha \cong 3$.

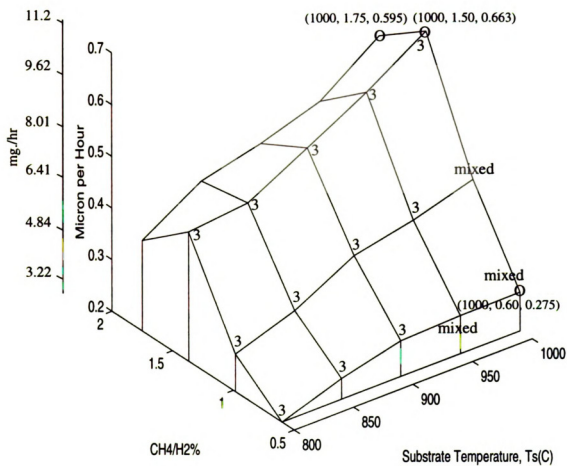


Figure 5.46. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 400 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates

5.2.2.1.2 Total gas flow rate, $f_t = 200$ sccm

Figure 5.47 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s for the total gas flow rate fixed at 200 sccm. The value of growth parameter α is included in Figure 5.47. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 5.47. As with the 400 sccm total flow rate (Figure 5.46), the linear growth rate increased monotonically with the substrate temperature but with respect to CH_4/H_2 , it increased up to $\text{CH}_4/\text{H}_2 = 1.50\%$ and dropped beyond this point. For $f_t = 200$ sccm, the maximum growth rate of $0.66 \mu\text{m/hr}$ occurred at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 1000^\circ\text{C}$ deposition condition where $\alpha \cong 3$.

5.2.2.1.3 Total gas flow rate, $f_t = 100$ sccm

Figure 5.48 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s for the total gas flow rate fixed at 100 sccm. The value of growth parameter α is included in Figure 5.48. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 5.48. As shown, the linear growth rate increased monotonically with the substrate temperature but with respect to the methane concentration in hydrogen, it increased up to $\text{CH}_4/\text{H}_2 = 2.0\%$ and dropped beyond this point. For $f_t = 100$ sccm, the maximum growth rate of $0.59 \mu\text{m/hr}$ occurred at $\text{CH}_4/\text{H}_2 = 2.0\%$, $T_s = 1000^\circ\text{C}$ deposition condition where $\alpha \cong 3$.

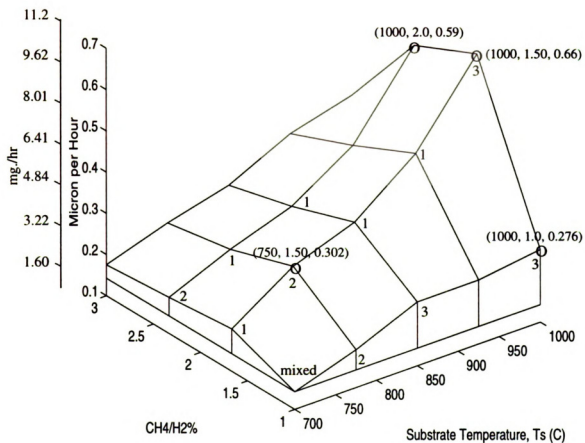


Figure 5.47. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 200 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , CH_4/H_2 , $\mu\text{m/hr}$) coordinates.

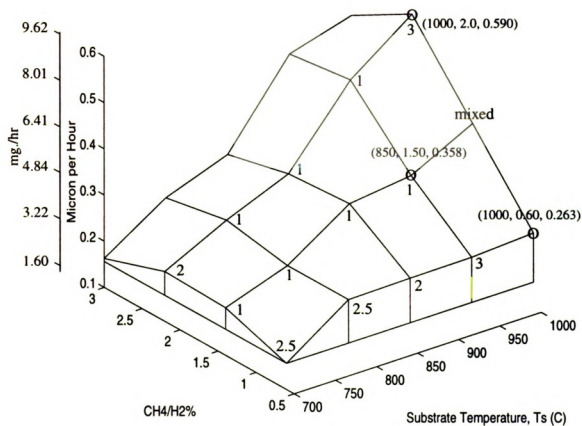


Figure 5.48. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 100 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , CH_4/H_2 , $\mu\text{m/hr}$) coordinates.

5.2.2.1.4 Total gas flow rate, $f_t = 60$ sccm

Figure 5.49 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s for the total gas flow rate fixed at 60 sccm. The value of growth parameter α is included in Figure 5.49. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 5.49. The linear growth rate increased monotonically with substrate temperature but with respect to methane concentration in hydrogen, it increased up to $\text{CH}_4/\text{H}_2 = 2.0\%$ and dropped beyond this point. For $f_t = 60$ sccm, the maximum growth rate of $0.591 \mu\text{m/hr}$ occurred at $\text{CH}_4/\text{H}_2 = 2.0\%$, $T_s = 1000^\circ\text{C}$ deposition condition where $\alpha \cong 3$.

5.2.2.1.5 Total gas flow rate, $f_t = 30$ sccm

Figure 5.50 illustrate the dependence of the linear growth rate on T_s and CH_4/H_2 . The value of growth parameter α is included in Figure 5.50. The linear growth rate increased with T_s and CH_4/H_2 in their respected range of $T_s \in [700, 900]$ and $0.60 \leq \text{CH}_4/\text{H}_2 \leq 2.0$. For $f_t = 30$ sccm, the maximum growth rate of $\sim 0.53 \mu\text{m/hr}$ occurred at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 900^\circ\text{C}$ deposition condition.

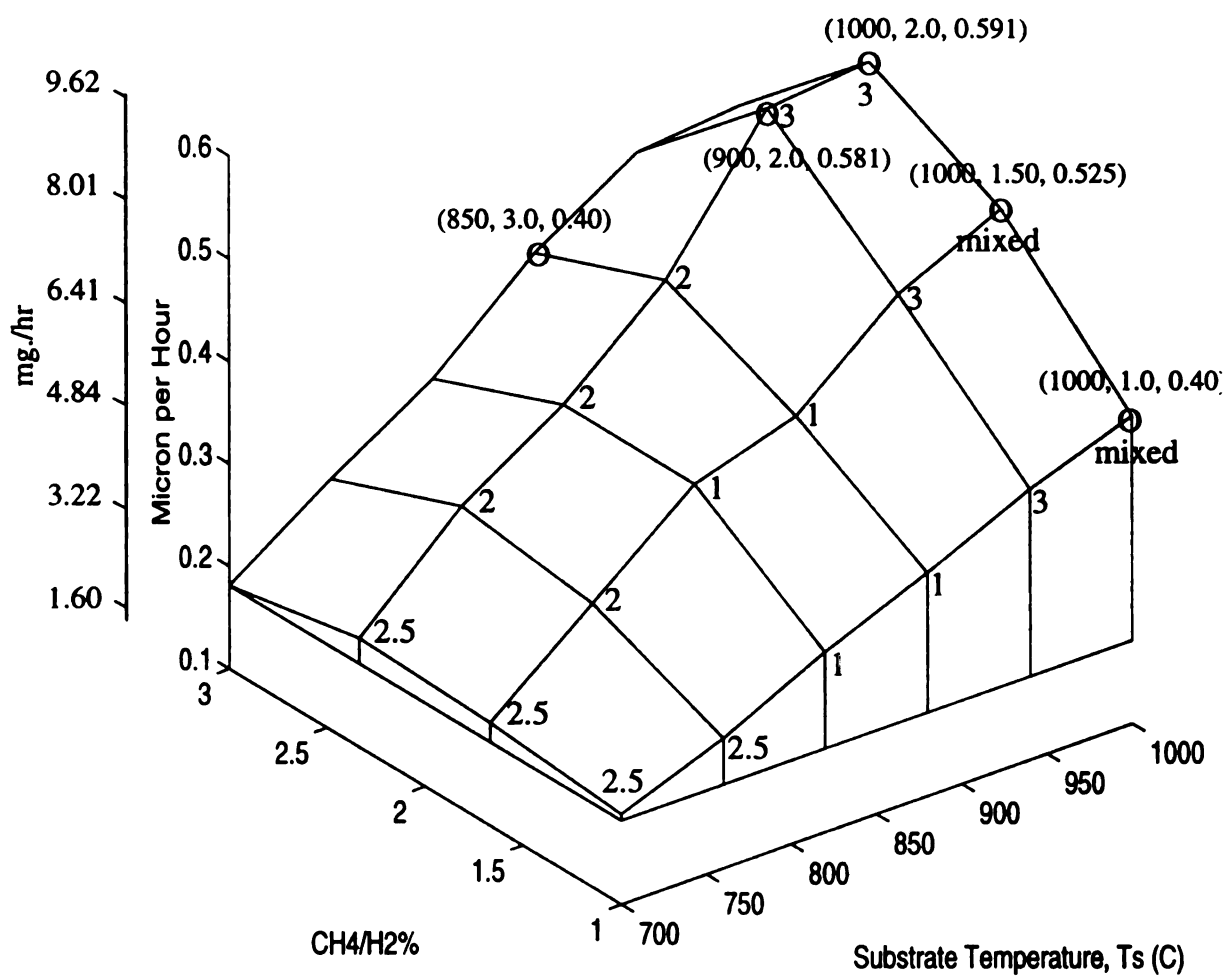


Figure 5.49. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 60 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates.

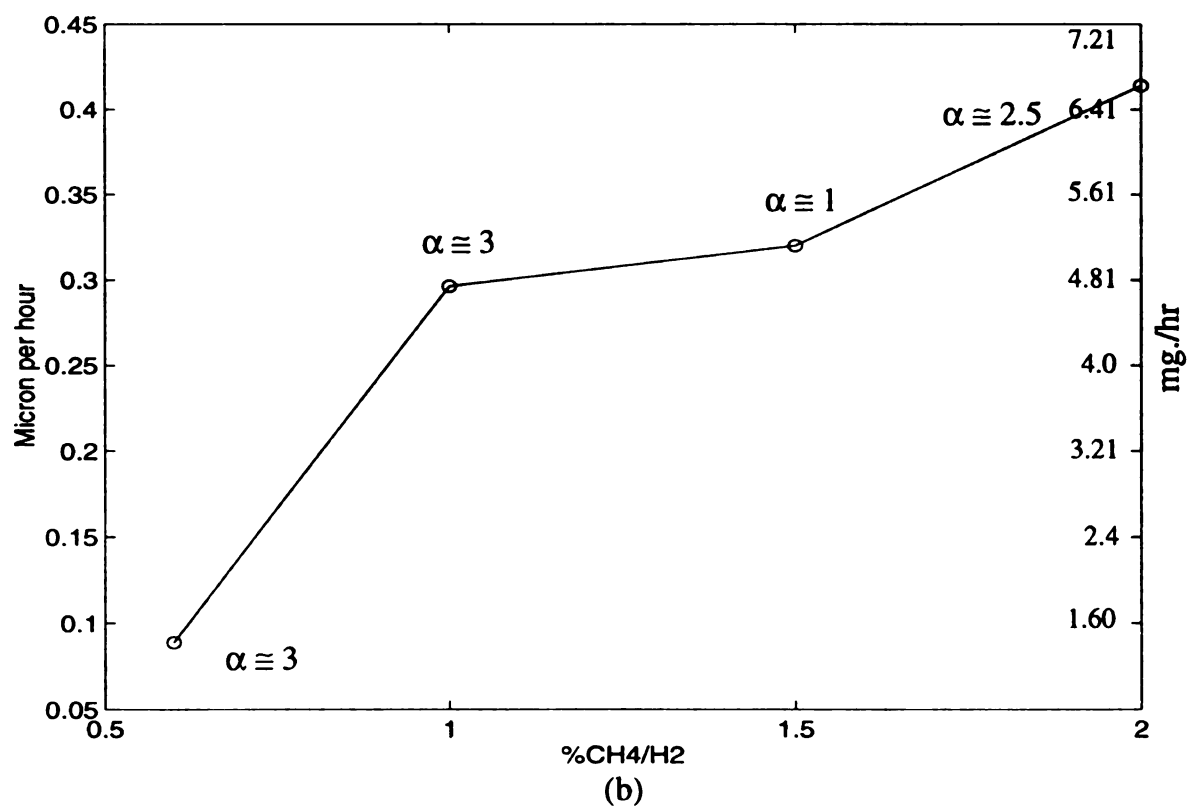
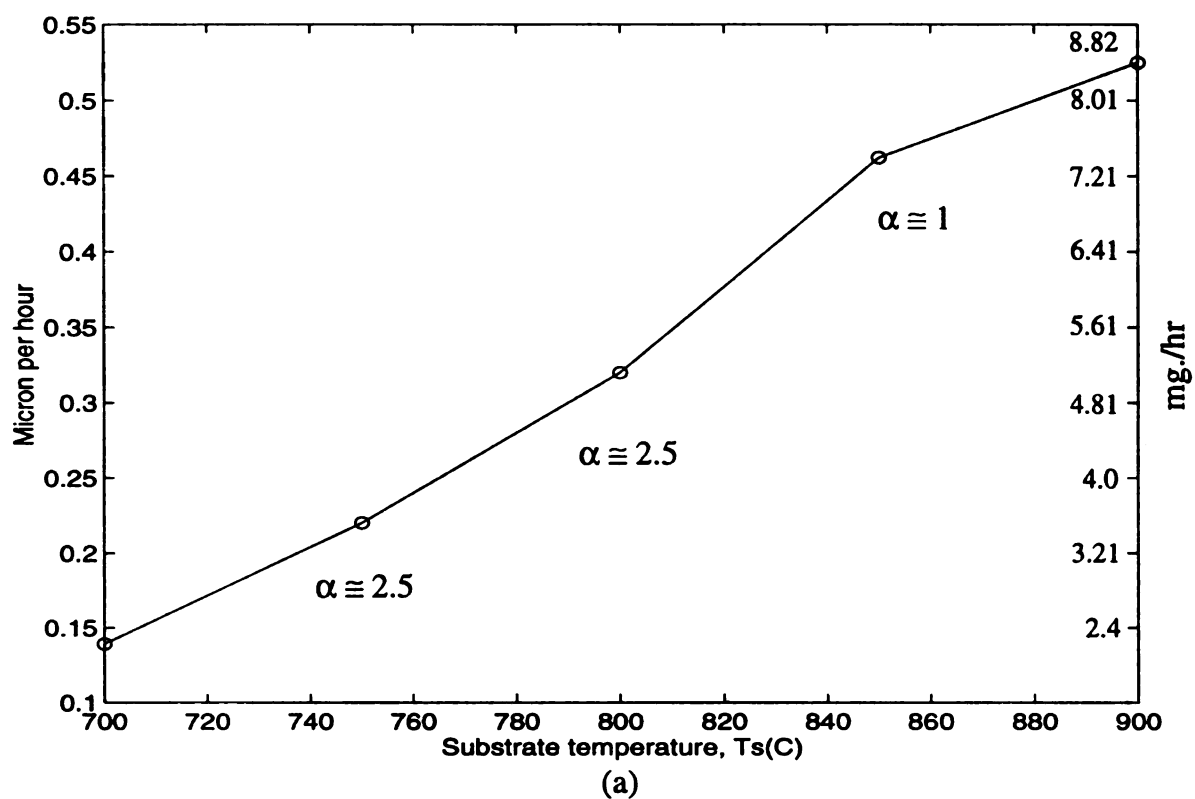


Figure 5.50. Linear growth rate vs. (a) substrate temperature with $\text{CH}_4/\text{H}_2 = 1.50\%$ and (b) CH_4/H_2 with $T_s = 850^\circ\text{C}$. The α values are included in the plots. The total gas flow rate is fixed at 30 sccm.

5.2.2.2 Carbon conversion efficiency

Carbon conversion efficiency is defined as the ratio of carbon added to the film to the total amount of carbon supplied by the input gas. Section 4.5.5 equations 4.2, 4.3, and 4.4 describe how carbon conversion efficiency is calculated

5.2.2.2.1 Total gas flow rate, $f_t = 400$ sccm

For the flow rate, f_t , fixed at 400 sccm, Figure 5.51 shows the dependence of carbon conversion efficiency on substrate temperature and methane gas concentration in hydrogen. It shows that carbon conversion efficiency increased with substrate temperature (consistent with the fact that growth rate increased monotonically with substrate temperature as shown in Figure 5.46) but decreased with methane concentration. The decrease of carbon conversion efficiency with methane concentration indicated that although up to a certain point film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

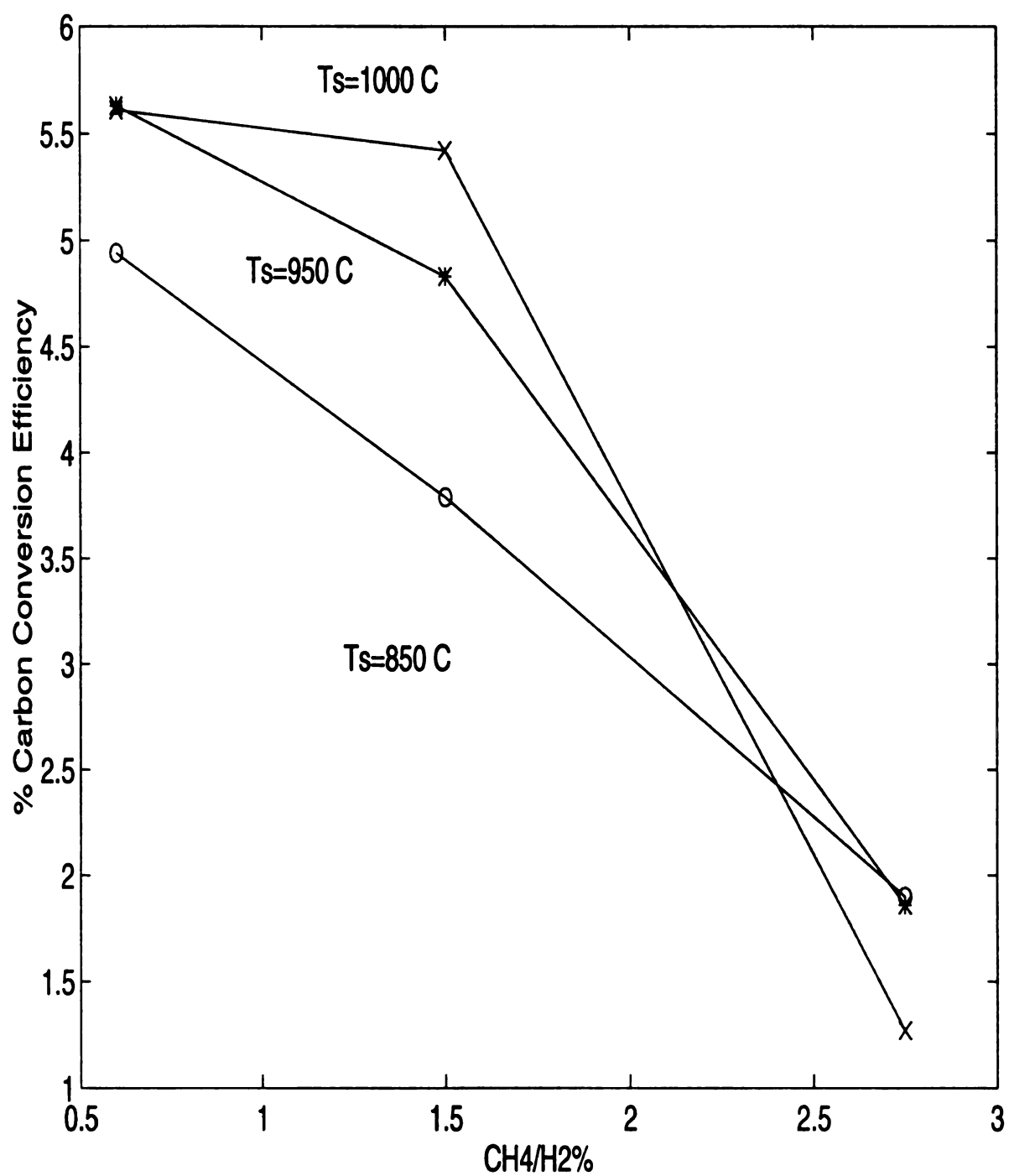


Figure 5.51. %Carbon conversion efficiency vs. substrate temperature and CH₄/H₂% for $f_t = 400$ sccm.

5.2.2.2.2 Total gas flow rate, $f_t = 200$ sccm

For the flow rate, f_t , fixed at 200 sccm, Figure 5.52 shows the dependence of carbon conversion efficiency on substrate temperature and CH_4/H_2 gas chemistry. As shown, the carbon conversion efficiency increased with the substrate temperature (consistent with the fact that growth rate increased monotonically with the substrate temperature as shown in Figure 5.47) but decreased with methane concentration. As with $f_t = 400$ sccm, the decrease of carbon conversion efficiency with methane concentration indicated that although up to a certain point film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

5.2.2.2.3 Total gas flow rate, $f_t = 100$ sccm

For the flow rate, f_t , fixed at 100 sccm, Figure 5.53 shows the dependence of carbon conversion efficiency on substrate temperature and CH_4/H_2 chemistry. As shown, the carbon conversion efficiency increased with the substrate temperature (consistent with the fact that growth rate increased monotonically with substrate temperature as shown in Figure 5.48) but decreased with methane concentration. As with $f_t = 400$ and $f_t = 200$ sccm, the decrease of carbon conversion efficiency with methane concentration indicated that although up to a certain point film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

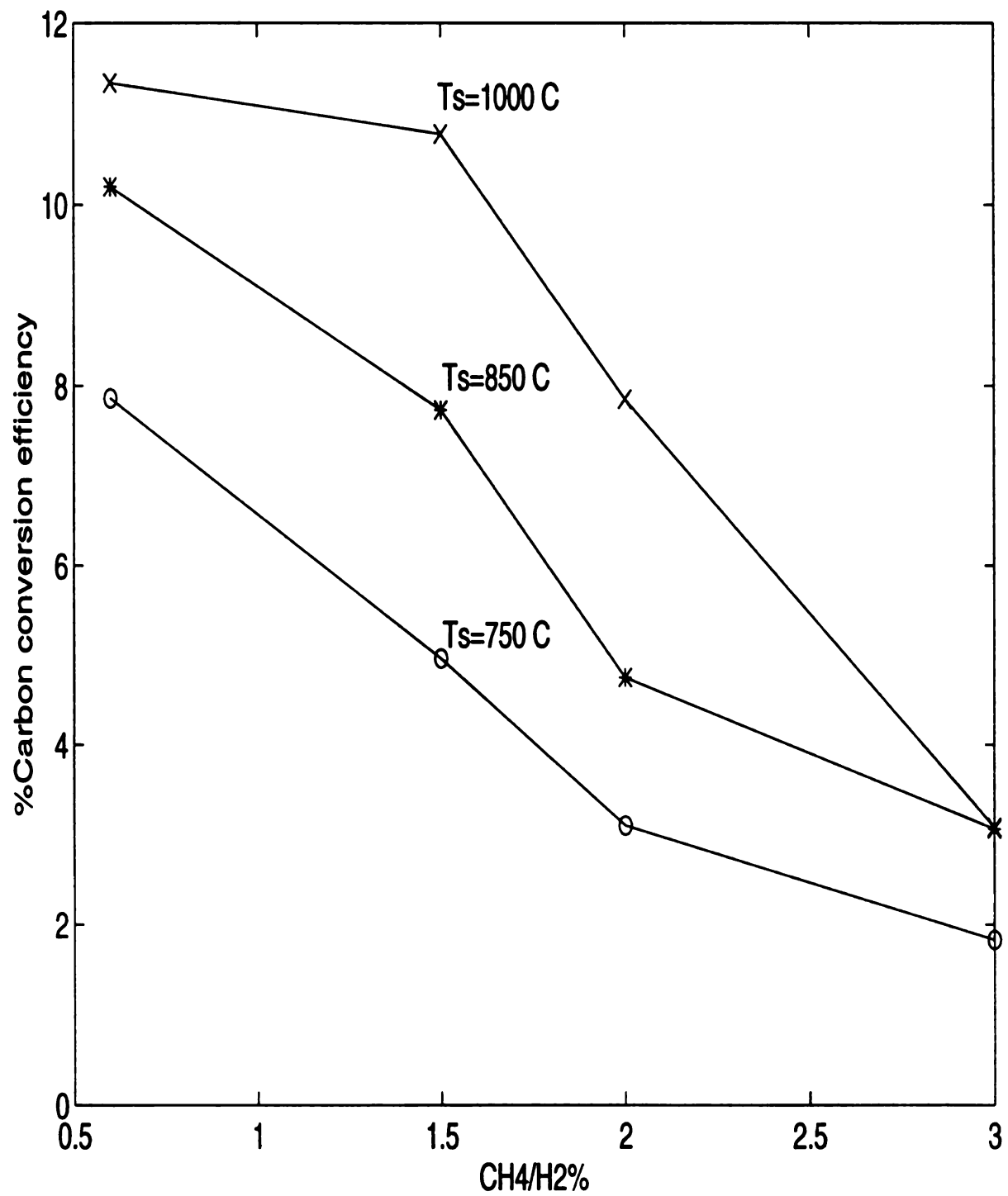


Figure 5.52. %Carbon conversion efficiency vs. substrate temperature and CH₄/H₂% for $f_t = 200$ sccm.

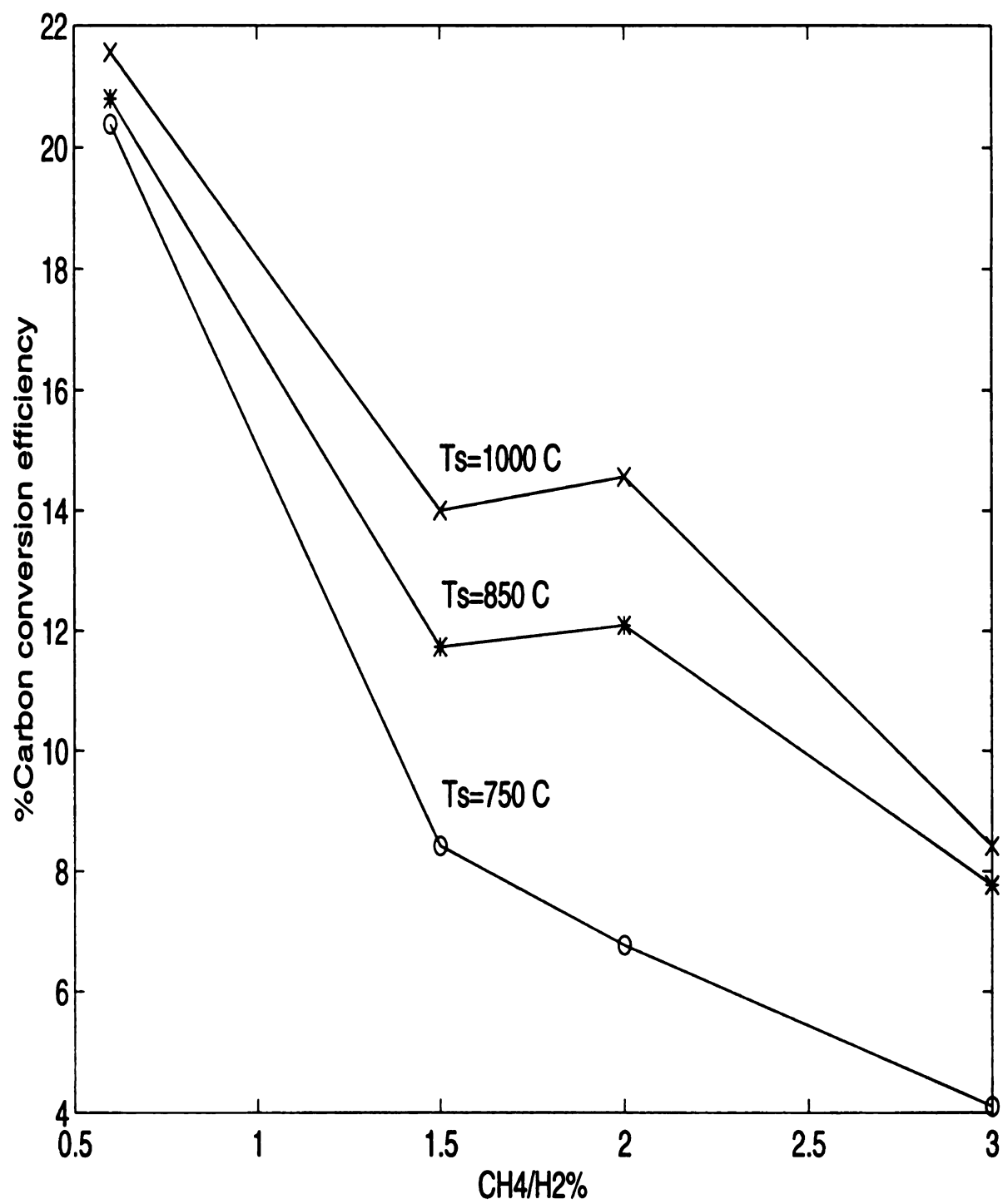


Figure 5.53. %Carbon conversion efficiency vs. substrate temperature and CH₄/H₂% for $f_t = 100$ sccm.

5.2.2.2.4 Total gas flow rate, $f_t = 60$ sccm

For the flow rate, f_t , fixed at 60 sccm, Figure 5.54 shows the dependence of carbon conversion efficiency on the substrate temperature and CH_4/H_2 gas chemistry. As shown that carbon conversion efficiency increased with the substrate temperature (consistent with the fact that growth rate increased monotonically with substrate temperature (Figure 5.49) but decreases with the methane concentration. As with other flow rate (i.e., $f_t = 400, 200, 100$ sccm), the decrease of carbon conversion efficiency with methane concentration indicated that although up to a certain point film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

5.2.2.2.5 Total gas flow rate, $f_t = 30$ sccm

Figure 5.55 show the dependence of carbon conversion efficiency on substrate temperature and CH_4/H_2 gas chemistry, respectively. The carbon conversion efficiency increased with substrate temperature (i.e., consistent with the fact that growth rate increased monotonically with substrate temperature as shown in Figure 5.50 (a)). The carbon conversion efficiency varied between $\sim 22\%$ and $\sim 50\%$ over the methane concentration range of $0.60 \leq \text{CH}_4/\text{H}_2 \leq 2.0$. The maximum value of $\sim 50\%$ was associated with $\text{CH}_4/\text{H}_2 = 1.0\%$. The increase of carbon conversion efficiency for $0.60 \leq \text{CH}_4/\text{H}_2 \leq 1.0$ was an indication that over this methane concentration range, a large portion of the supplied carbon from the feed gas was added to the film so that the

numerator in equation 4.4 grew faster than the denominator in this equation. The drop in the carbon conversion efficiency after $\text{CH}_4/\text{H}_2 = 1.0\%$ indicated that beyond this methane concentration, a smaller amount of supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

This concludes the detailed examination of the reactor performance for various flow rates with deposition time fixed at 8 hours. A number of experiments were carried out to examine the effect of the deposition time on output variables $\mathbf{Y} = [\mathbf{Y}_1, \mathbf{Y}_2]$. This subject is discussed in the next section.

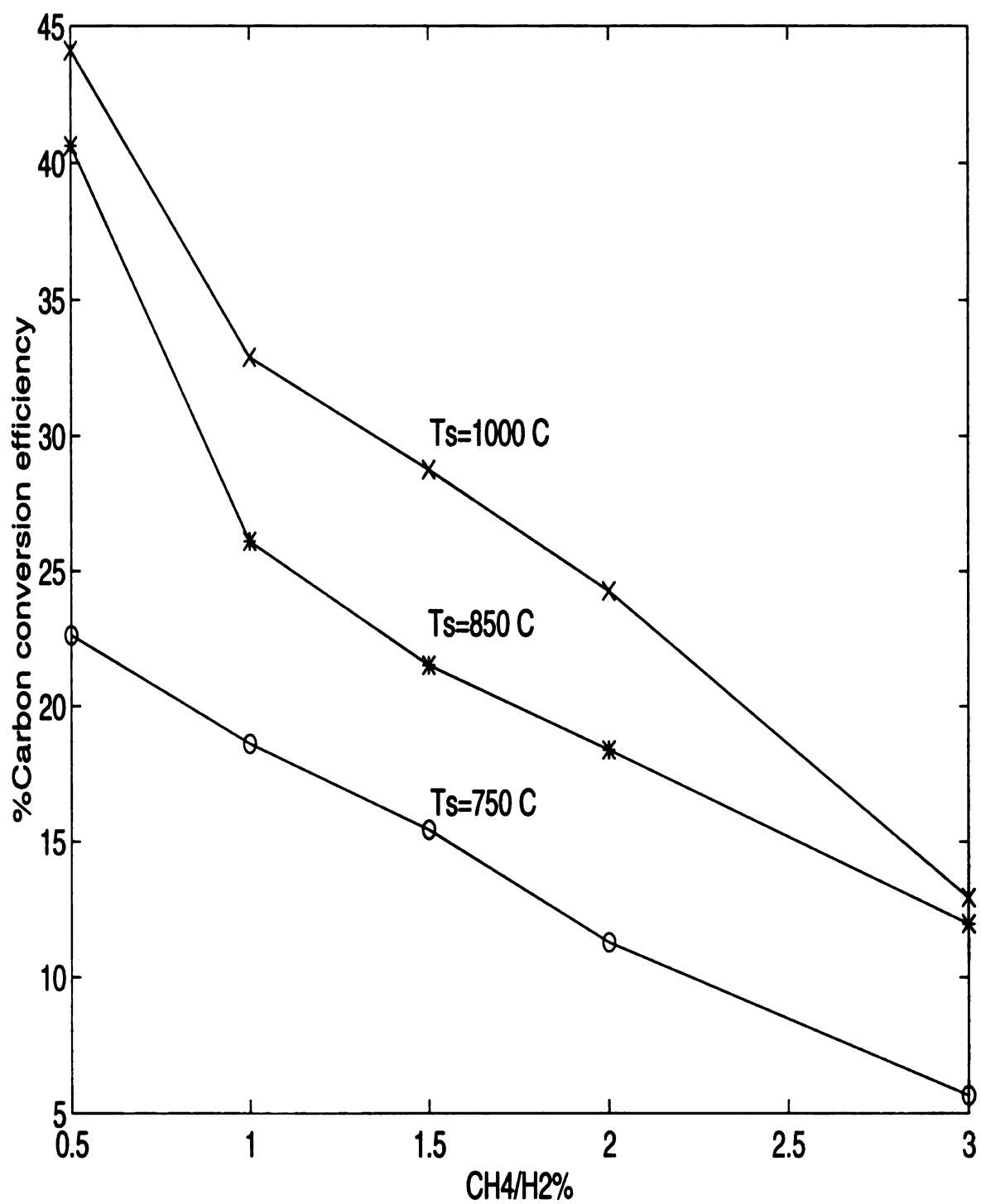


Figure 5.54. %Carbon conversion efficiency vs. substrate temperature and CH₄/H₂% for $f_t = 60$ sccm.

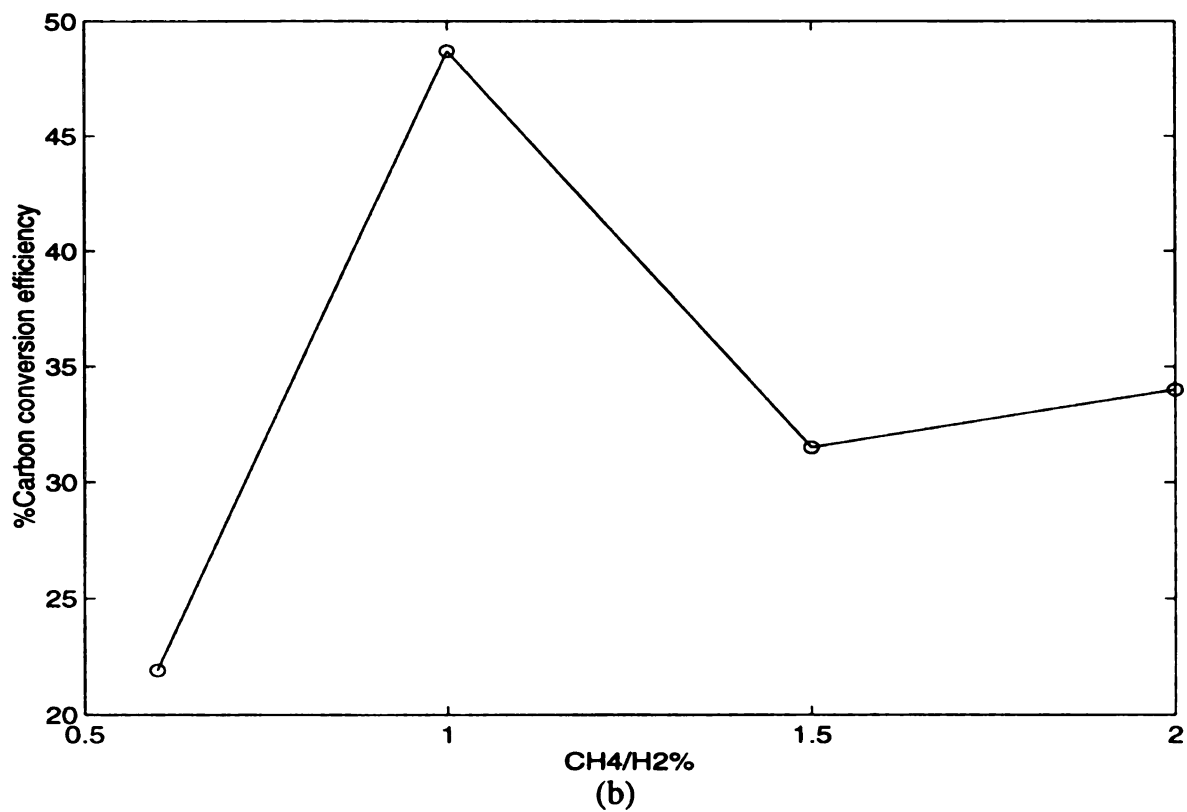
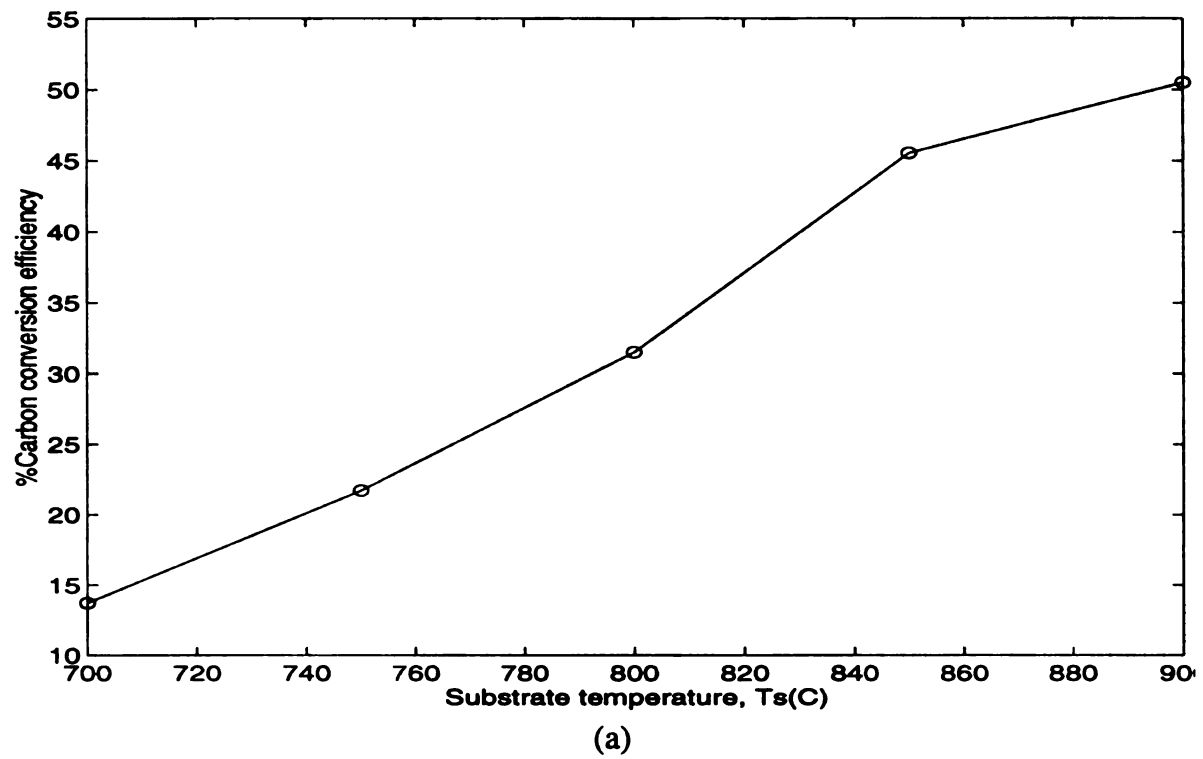


Figure 5.55. % Carbon conversion efficiency vs. (a) substrate temperature, and (b) CH_4/H_2 for total gas flow rate fixed at 30 sccm.

5.3 Effect of deposition time on output variables (Y)

It was of interest to examine the effect of deposition time on the film morphology and other film properties (Y_1) and on the reactor performance variables (Y_2). It was of a particular interest to run some experiments which resulted in {100} faceted films under 8 hours of deposition (i.e., SK62 sample under $f_t = 60$ sccm, $CH_4/H_2 = 1.50\%$, $T_s = 850^\circ C$) for longer times to find out if longer deposition times would result in the complete coverage of the film surfaces with {100} facets (i.e., with all voids filled). Several sets of experiments were carried out for this purpose. The first three sets of experiments were conducted under a similar deposition condition of $f_t = 60$ sccm, $CH_4/H_2 = 1.50\%$, $T_s = 850^\circ C$ with deposition time as the variable and the remaining sets were conducted under $f_t = 60$ sccm and $T_s = 850^\circ C$ with CH_4/H_2 and the deposition time as the variables. The latter procedure is known as the two-step growth procedure.

5.3.1 Film properties (Y_1) vs. deposition time

5.3.1.1 Film morphology

The deposition condition of $f_t = 60$ sccm, $CH_4/H_2 = 1.50\%$, $T_s = 850^\circ C$, and deposition time, $t = 8$ hours was among the conditions that resulted in well-faceted (i.e., twin free) cubic {100} crystal structure with $\alpha = 1$ (Figure 5.56 (a)). As the first examination of the effect of deposition time on film morphology (i.e., α) (set 1), the deposition time was increased to 16 hours with other deposition conditions held fixed. Figure 5.56 (b) illustrates the film morphology at this deposition condition. As seen, {100} facets grew bigger with time but there were fewer {100} facets on this sample than

on the SK62 (deposition time, $t = 8$ hours) sample. When deposition time was increased to 41 hours, film morphology was changed to $\{111\}$ with $\alpha = 3$ as shown in Figure 5.56 (c).

Different results were achieved when different experiments were carried out to further examine the effect of the deposition time on the morphological development of the diamond films. Figure 5.57 illustrates the SEM pictures of two diamond films deposited under $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with $t = 16$ hours and 24 hours, respectively (set 2). These experiments resulted in the $\{100\}$ morphology with $\alpha \cong 1$ (almost cubic crystals) for both experiments. However, for the experiment with $t = 24$ hours the side faces of the crystals were covered with fine grain nano-crystallites. Figure 5.58 illustrates the film morphology of two other diamond films which were grown under similar deposition conditions (i.e., $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$) with $t = 16$ hours and 24 hours, respectively (set 3). For both films the crystal facets looked like $\{100\}$ with rough (jagged) edges.

The above experiments showed that the film morphology could vary with the deposition time (i.e., $\alpha = f(t)$). The change in film morphology with deposition time could not be attributed to any changes in the substrate temperature, total gas flow rate, $\text{CH}_4/\text{H}_2\%$, operating pressure, or microwave power with deposition time since these variable have proven to be independent of a variation in time. A change in the discharge radical species (i.e., CH_3 , CH_2 , C_2H_2 , C_2H_3 , etc.) vs. time seemed to be the cause of the variation of morphology with deposition time. Insitu measurements of appropriate plasma species concentrations and substrate condition was required to clearly understand the effect of deposition time variable on the film morphology (i.e., α). This was beyond the scope of

this thesis and is recommended for future research. However, it was speculated that the α variation with deposition time was caused by a change in the radical species reactions vs. time with the reactor walls which caused the walls to act as a sink for the appropriate radical species for a period of time and to reduce the number of species that interacted with the substrate. It was further speculated that more likely over time the walls became saturated and did not attract radical species any more (and possibly supplied some species to the substrate) so that more species were available to react with the substrate and change the film morphology (i.e., from {100} for $t = 8$ hours to {111} for longer deposition times). According to the Wulff criterion [36], in the crystal growth, the slowest growing facet remains and the other facets go out of existence. It seemed that over the period when species were sunk to the walls, {111} facets grew faster than {100} facets so that the diamond films showed {100} morphology. When the walls did not act as a sink for radical species any longer or when they began to supply radical species to the substrate, more species became available for {100} facets growth so that {100} facets grew out of existence and the {111} morphology became dominant. The species reaction with walls might be different from one run to another so that for some experiments i.e., (Figure 5.57) the original film morphology was almost preserved for longer deposition times.

A two-step growth procedure was examined in order to eliminate the excess available radical species that were thought to be responsible for the change in film morphology (i.e., α) over a period of time. In the two-step process, the deposition condition was changed after the initial step (step 1). The two-step process were carried out in-situ and the elimination of the excess radical species was accomplished by reducing the methane concentration in hydrogen during the second step. A limited number of two-step

growth experiments were conducted in this Chapter. The following are examples of the two-step growth process carried out in this Chapter.

Set 4:

Step 1. $f_1 = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t = 14.25$ hours.

Step 2. $f_1 = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t = 1.75$ hours.

The SEM picture of the resulting diamond film is shown in Figure 5.59. The film morphology was $\{100\}$ with $\alpha \cong 2$ (i.e., crystals with $\{100\}$ top face and sloped side faces). In an attempt to fix the α value to ~ 1 (i.e., cubic crystals) the duration of step 2 was increased in another experiment as follows:

Set 5:

Step 1. $f_1 = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t = 12$ hours.

Step 2. $f_1 = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t = 4.0$ hours.

Figure 5.60 shows the SEM picture of this diamond film. The resulting film showed $\{100\}$ morphology with $\alpha \cong 1$. The crystals were tilted and some what damaged possibly because they grew into one another. It seems that a shorter duration of step 2 (greater than that of set 1 but less than 4 hours) was needed to avoid this problem.

The two-step process was not carried out beyond this point but the above examples illustrated that the two-step growth process was a viable process to deposit thick films while maintaining the desired morphology (i.e., α).

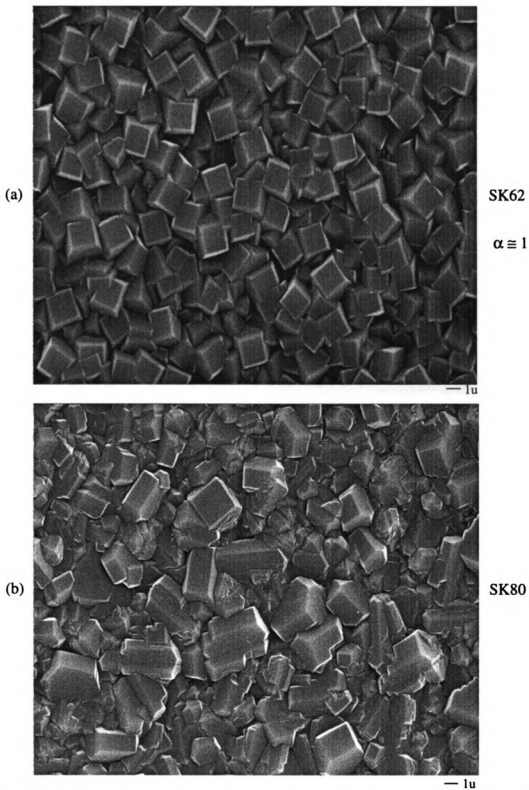


Figure 5.56. SEM pictures of samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 8$ hours, (b) $t = 16$ hours, and (c) $t = 41$ hours.

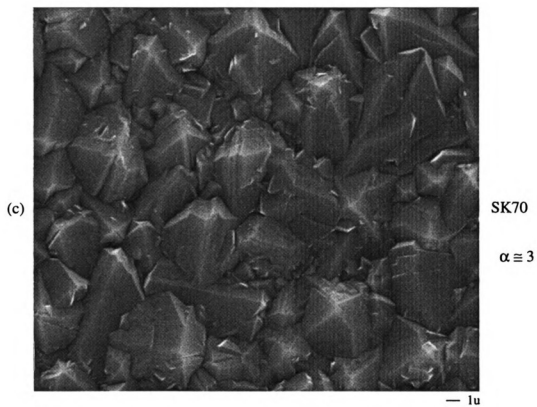
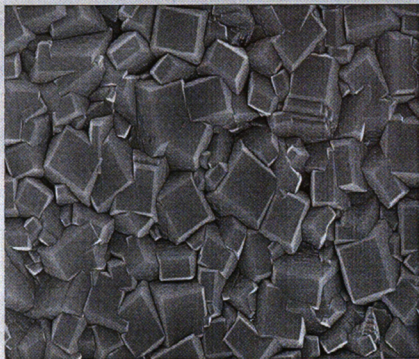


Figure 5.56. Continued.

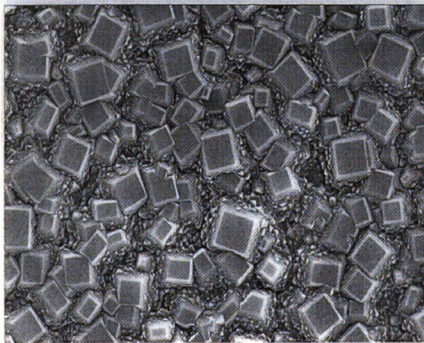
(a)



SK147

 $\alpha \cong 1$

(b)



SK153

 $\alpha \cong 1$

Figure 5.57. SEM pictures of samples deposited at $f_t=60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 16$ hours, and (b) $t = 24$ hours.

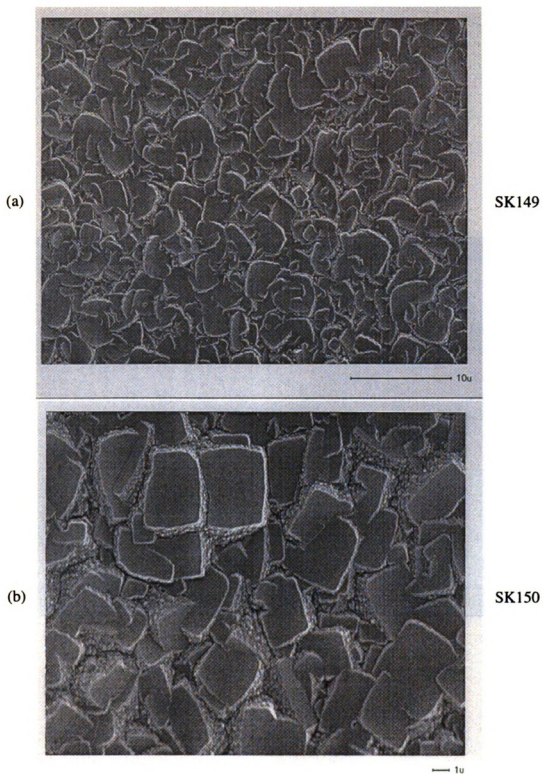
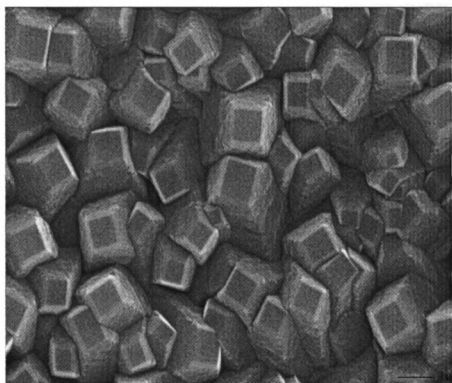


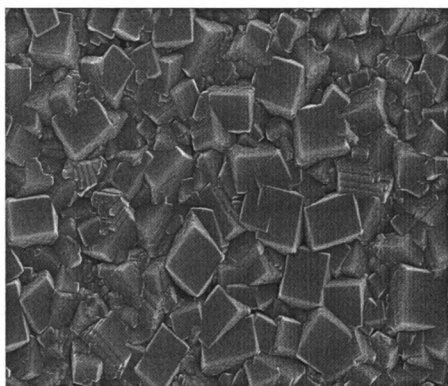
Figure 5.58. SEM pictures of samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $t = 16$ hours, and (b) $t = 24$ hours.



SK132

 $\alpha \cong 2$

Figure 5.59. SEM picture of SK132 sample deposited at: Step 1: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t_1 = 14.25$ hours. Step 2: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t_2 = 1.75$ hours.



SK133

 $\alpha \equiv 1$ — 1 μ

Figure 5.60. SEM picture of SK133 sample deposited at: Step 1: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, $t_1 = 12$ hours. Step 2: $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, $\text{CH}_4/\text{H}_2 = 0.80\%$, $t_2 = 4.0$ hours.

5.3.1.2 Structural quality

Figure 5.61 and Figure 5.62 show the variations of Raman spectra and FWHM with deposition time for the samples in set 1 (i.e., SK62, SK80, SK70). These samples were deposited under $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time $t = 8, 16$ and 41 hours. Figure 5.63 and Figure 5.64 show the variations of Raman spectra and FWHM with deposition time for the samples in set 2 (i.e., SK62, SK147, SK153). These samples were deposited under $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time $t = 8, 16$ and 24 hours. Figure 5.65 and Figure 5.66 show the variations of Raman spectra and FWHM with deposition time for the samples in set 3 (i.e., SK62, SK149, SK150). These samples were deposited under $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time $t = 8, t = 16$ and 24 hours. The SEM pictures of the samples in sets 1, 2, and 3 were shown in Figure 5.56, Figure 5.57, and Figure 5.58, respectively.

The Raman spectra showed strong diamond peaks for all these samples. For experiment sets 1 and 3, the FWHM decreased with deposition time as the deposition time was increased from 8 to 16 hours and increased as the deposition time was further increased. For experiment set 2 the FWHM decreased monotonically with the deposition time. The FWHM varied between a minimum of 5.84 cm^{-1} and a maximum of 10.58 cm^{-1} indicating that the deposition time can have an important effect on the structural quality of the diamond films.

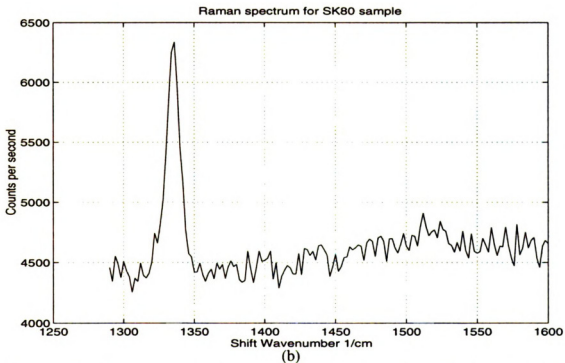
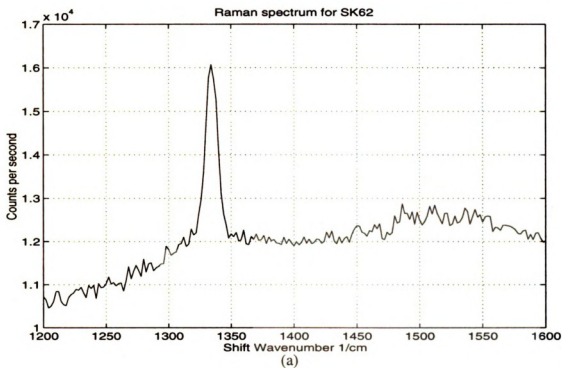
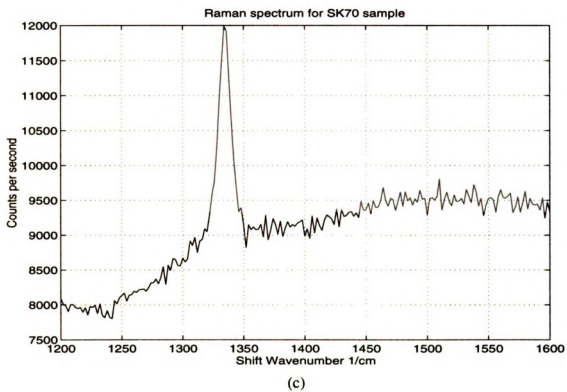
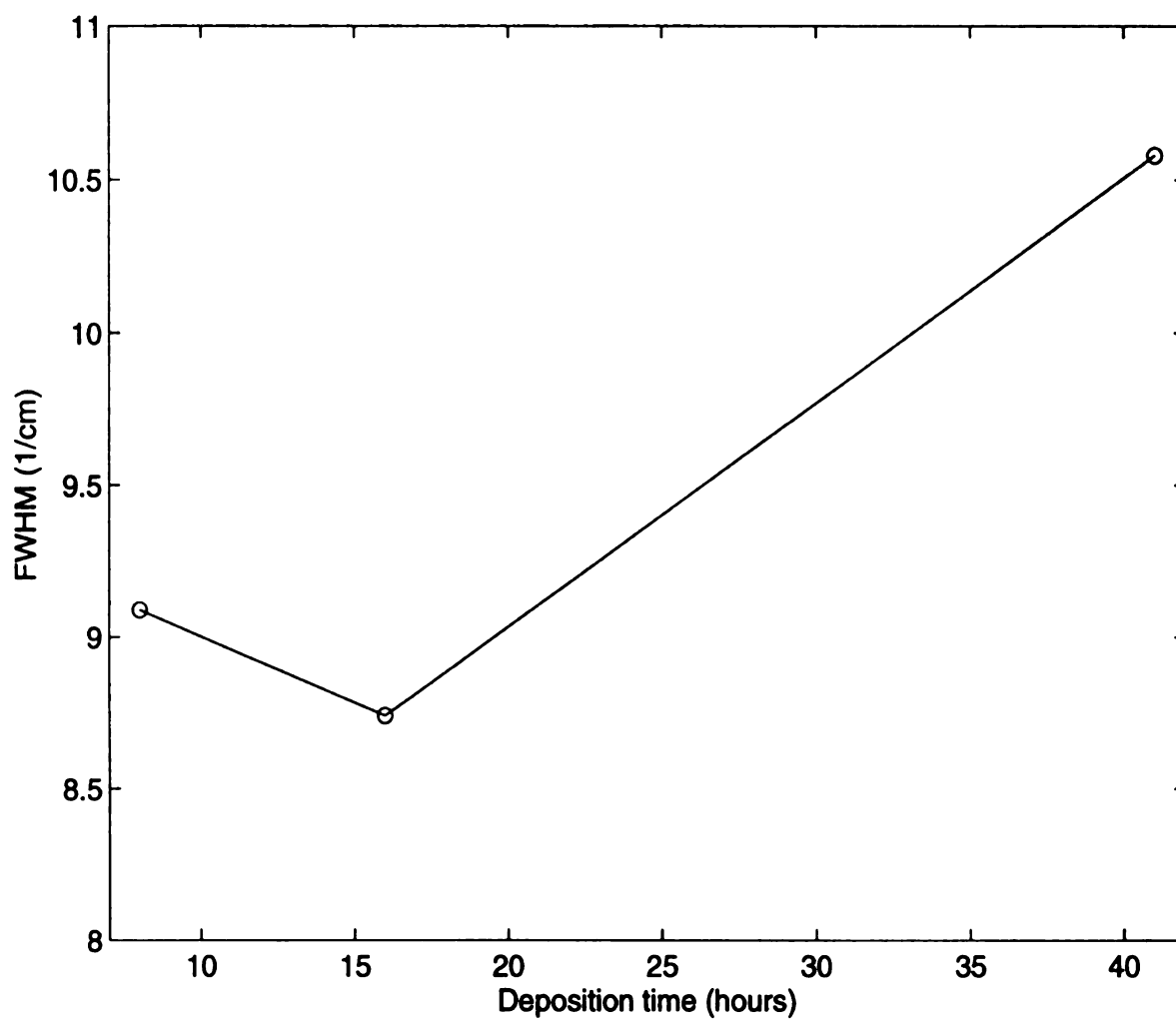


Figure 5.61. Raman spectra of samples in set 1 (i.e., SK62, SK80, and SK70) deposited at $f_1 = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 41$ hours.

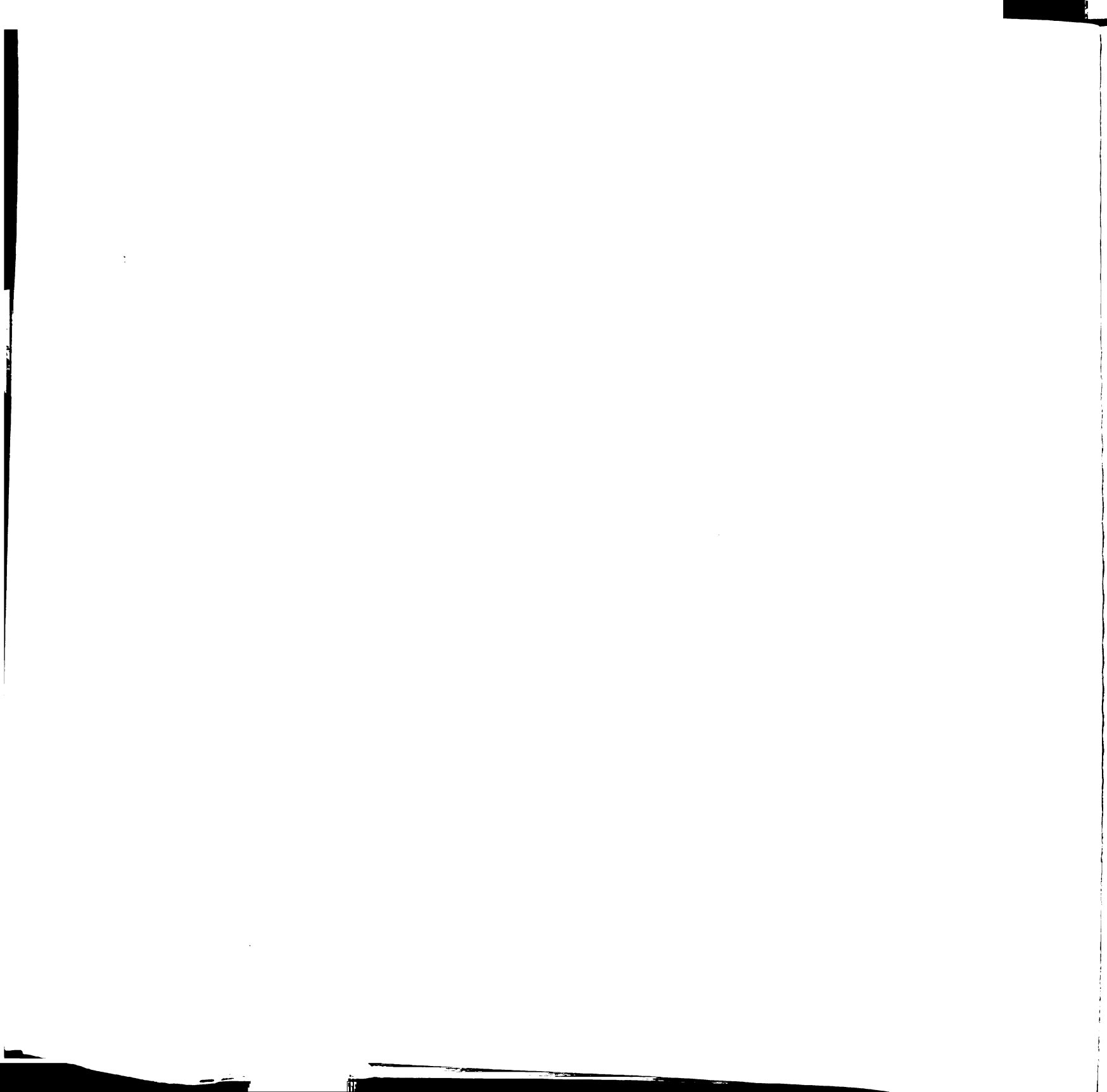


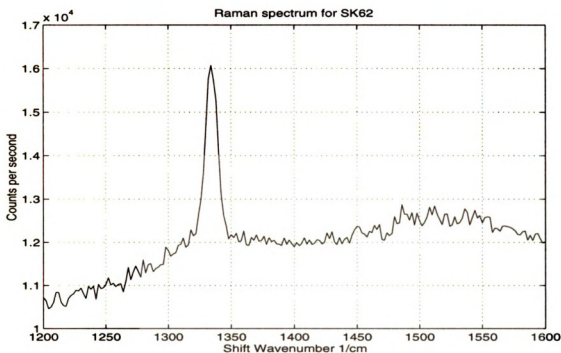
Figures 5.61. Continued.



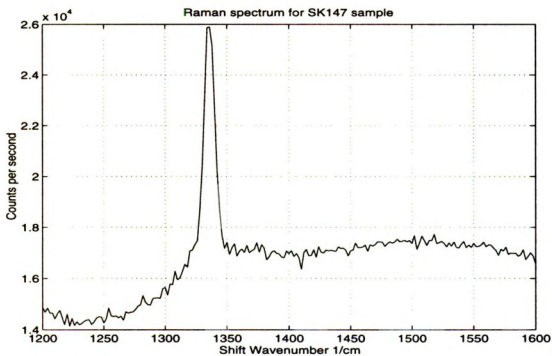
Sample	Deposition time (hour)	FWHM (cm ⁻¹)
SK62	8	9.09
SK80	16	8.74
SK70	41	10.58

Figure 5.62. Plot of FWHM vs. deposition time for samples in set 1 (i.e., SK62, SK80 and SK70); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s = 850^\circ\text{C}$.



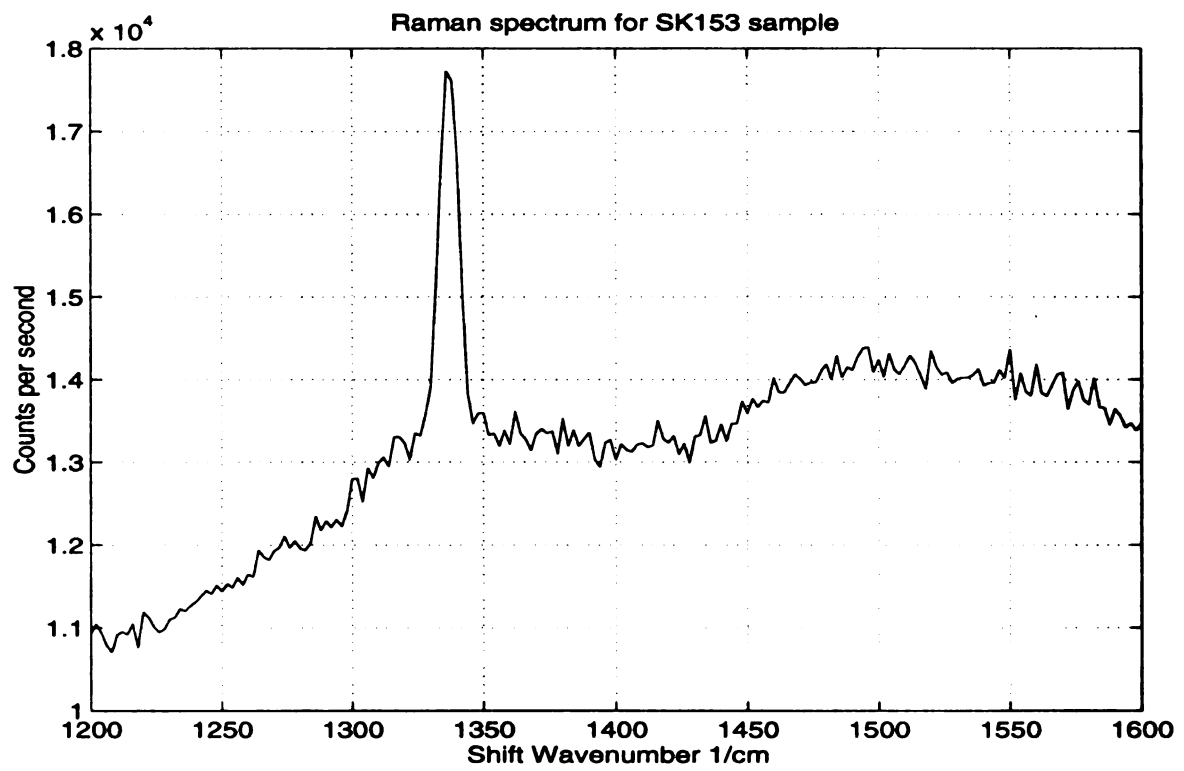


(a)

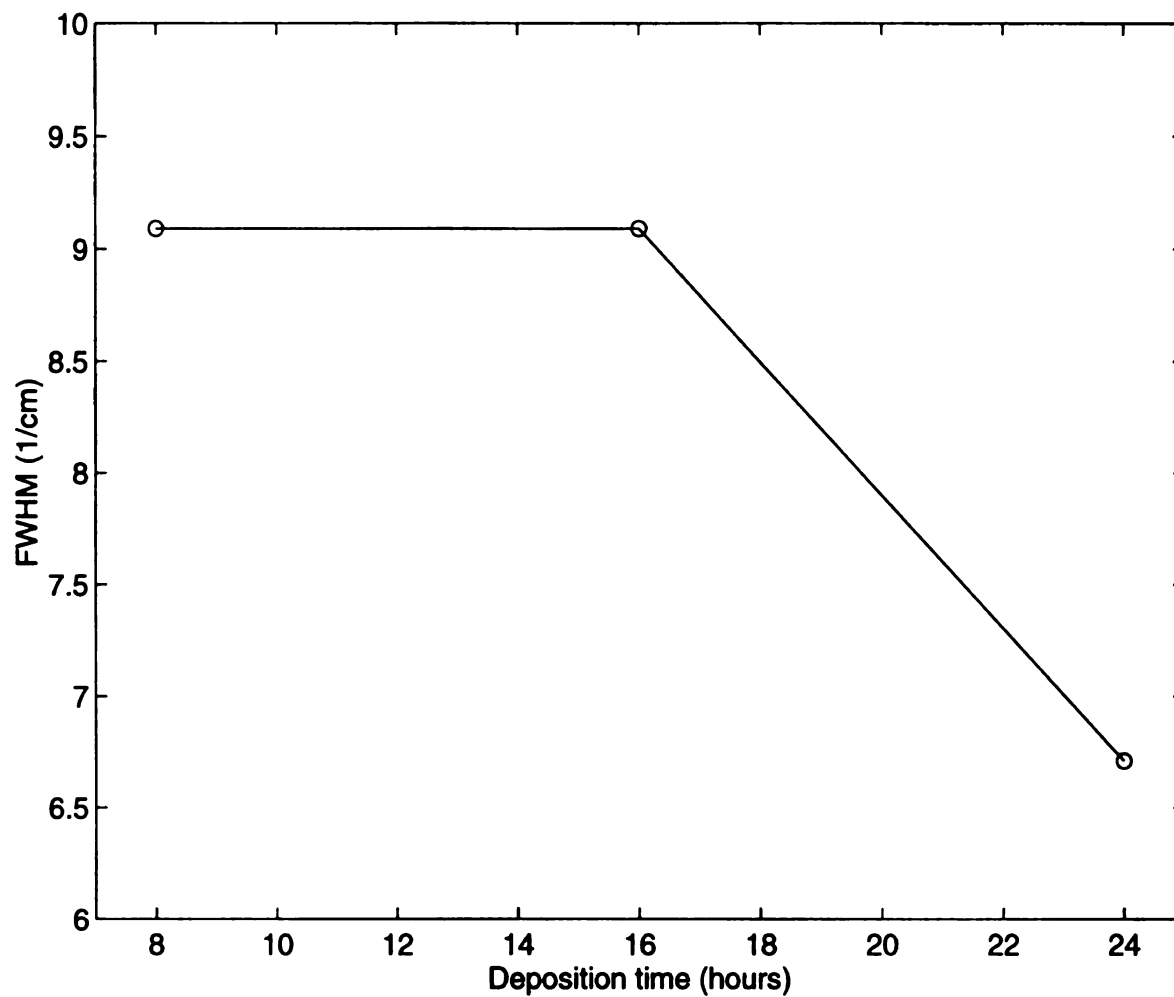


(b)

Figure 5.63. Raman spectra of samples in set 2 (i.e., SK62, SK147, and SK153) deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 24$ hours.

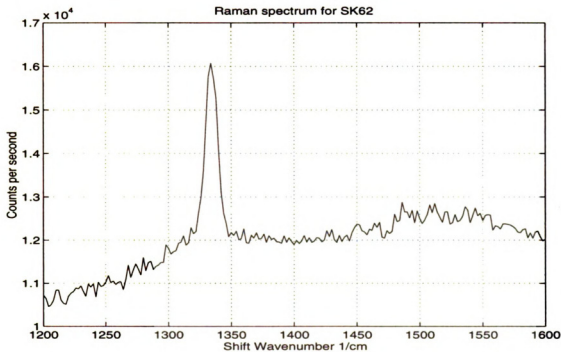


(c)

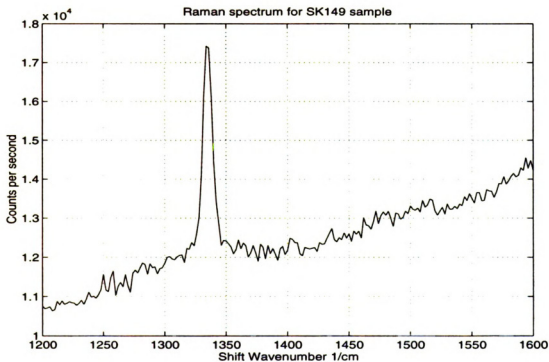


Sample	Deposition time (hour)	FWHM (cm ⁻¹)
SK62	8	9.09
SK147	16	9.09
SK153	24	6.71

Figure 5.64. Plot of FWHM vs. deposition time for samples in set 2 (i.e., SK62, SK147, and SK153); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$.

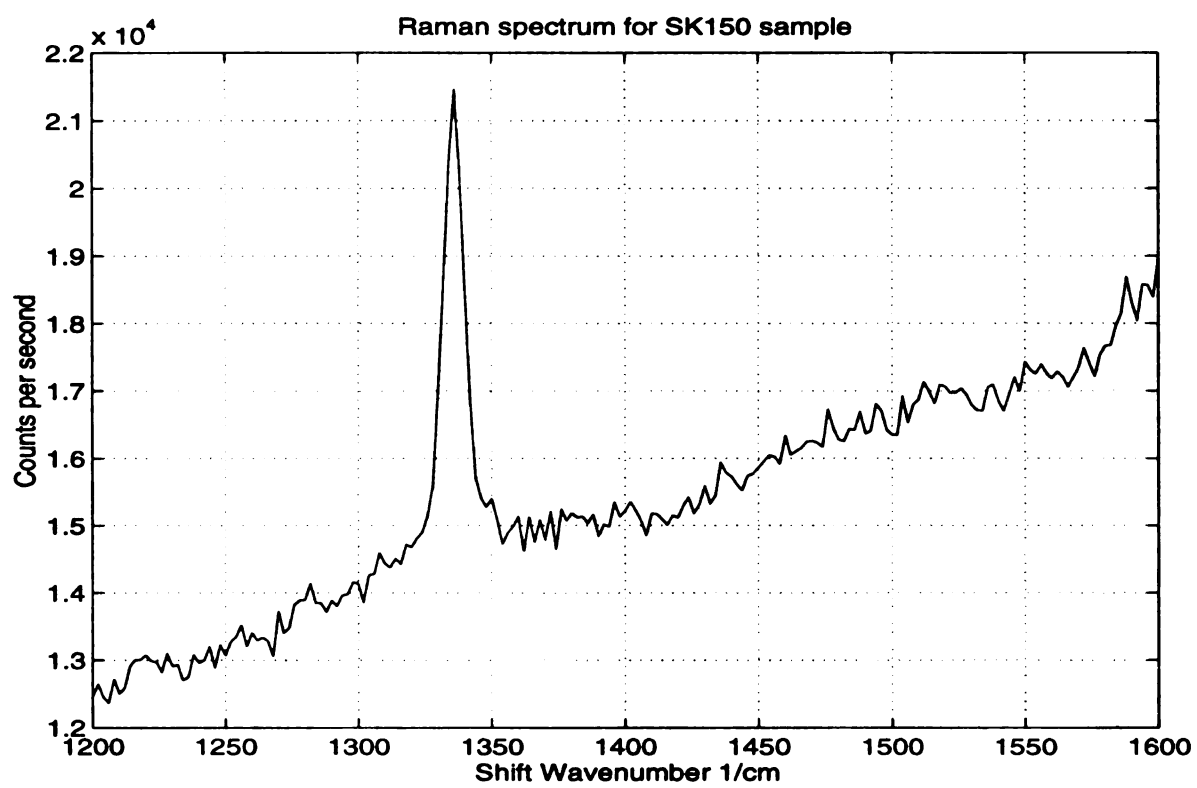


(a)



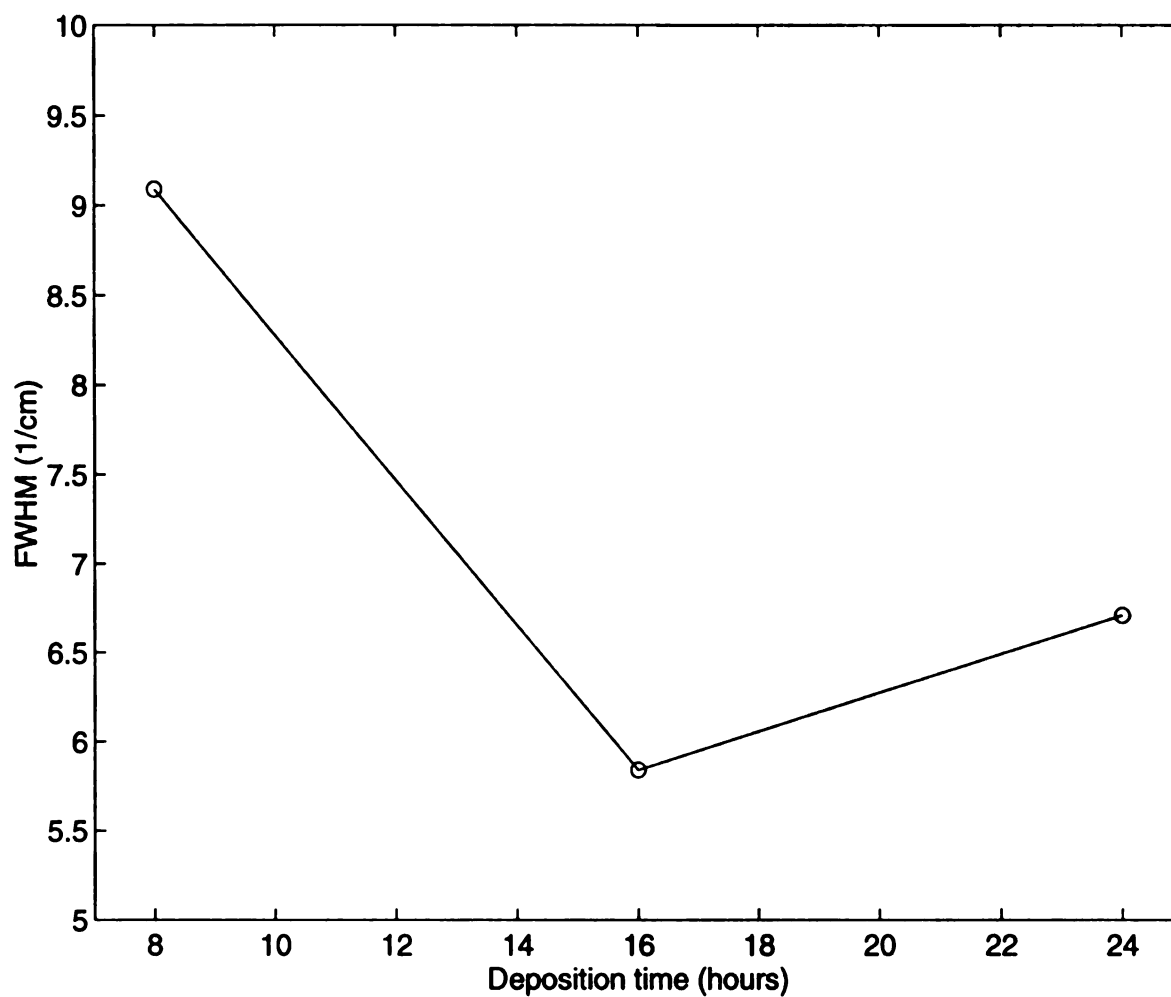
(b)

Figure 5.65. Raman spectra of samples in set 3 (i.e., SK62, SK149, and SK150) deposited at $f_1 = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$ with deposition time, (a) $t = 8$, (b) $t = 16$, and (c) $t = 24$ hours.



(c)

Figures 5.65. Continued.



Sample	Deposition time (hour)	FWHM (cm ⁻¹)
SK62	8	9.09
SK149	16	5.84
SK150	24	6.71

Figure 5.66. Plot of FWHM vs. deposition time for samples in set 3 (i.e., SK62, SK149, and SK150); $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$.

5.3.2 Reactor performance (Y_2) vs. deposition time

5.3.2.1 Linear growth rate

The linear growth rate calculated from eq. 4.1 of Section 4.5.4 changed with deposition time as shown in Figure 5.67. For set 1, the linear growth rate sharply decreased as the deposition time increased from 8 to 16 hours and slightly increased as the deposition time was further increased from 16 to 41 hours. For sets 2, and 3 the linear growth rate did not vary significantly with the deposition time. The value of growth parameter α is included in Figure 5.67.

5.3.2.2 Carbon conversion efficiency

Figure 5.68 illustrates percent carbon conversion efficiency vs. deposition time for experiment sets 1, 2, and 3. Since the total flow rate and CH_4/H_2 were kept constant, the percent carbon conversion efficiency vs. deposition time plots resembled the corresponding growth rate vs. deposition time plots.

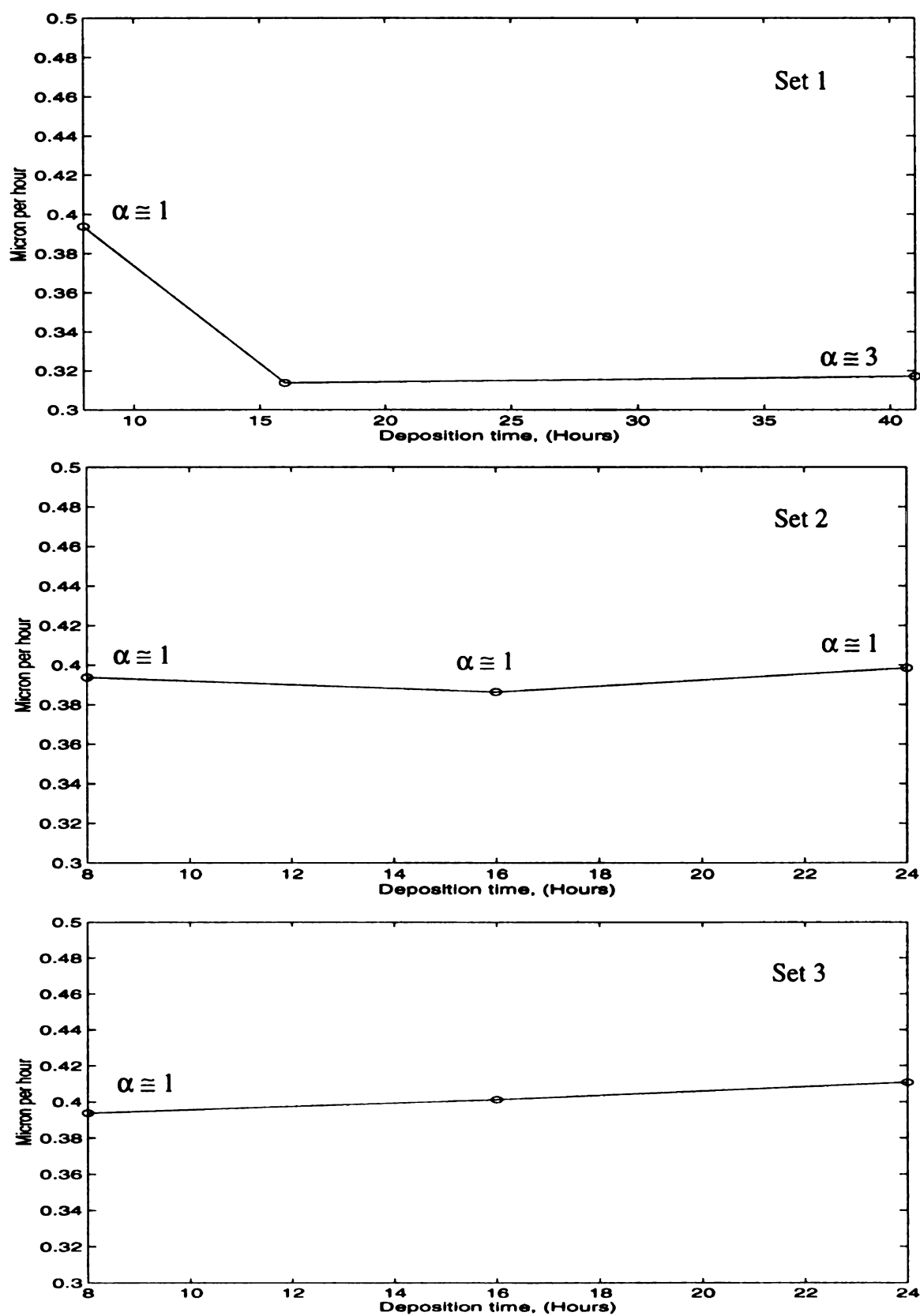


Figure 5.67. Linear growth rate vs. deposition time for different sets of films deposited under $f_t=60$ sccm, $\text{CH}_4/\text{H}_2=1.50\%$, and $T_s=850^\circ\text{C}$.

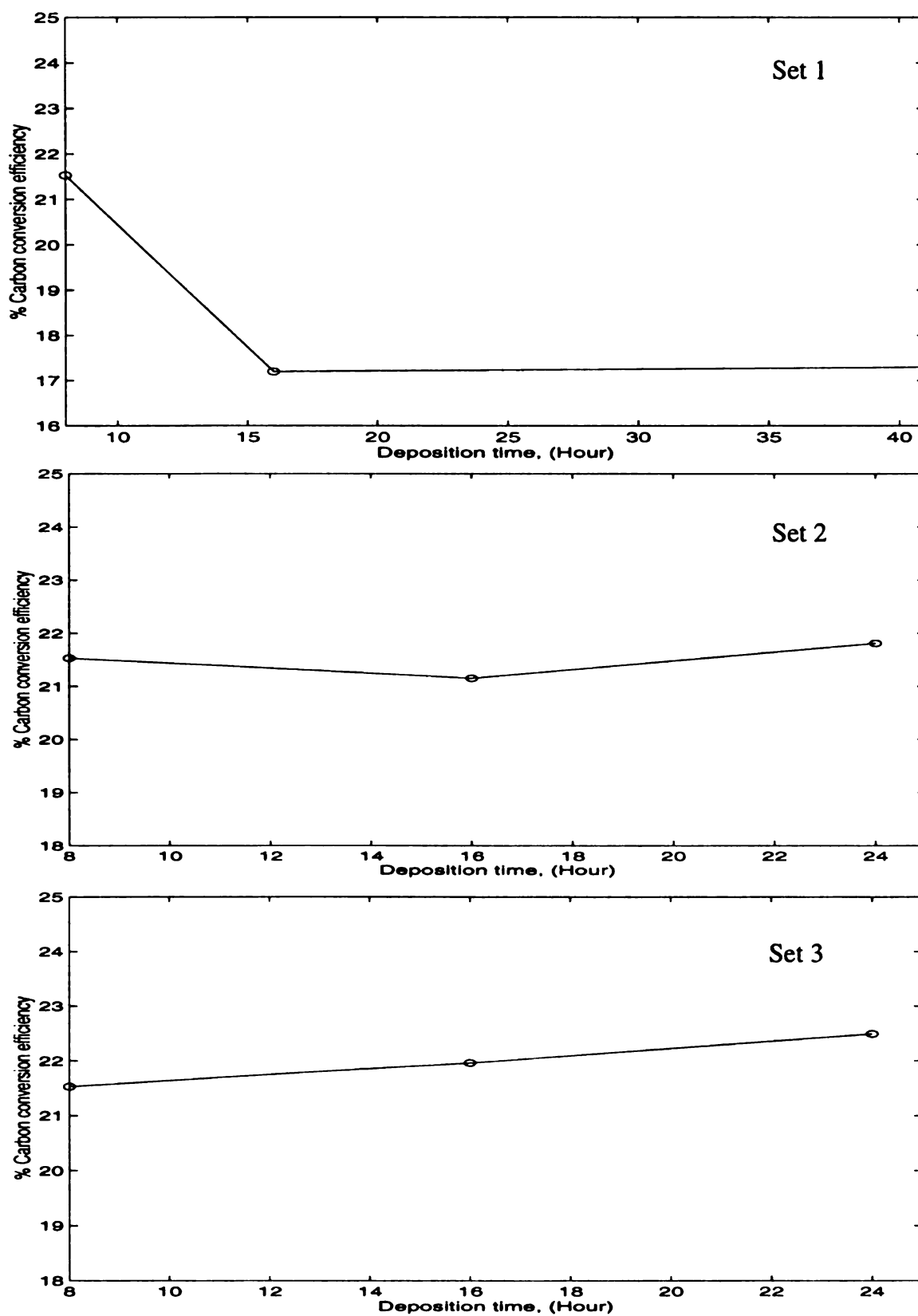


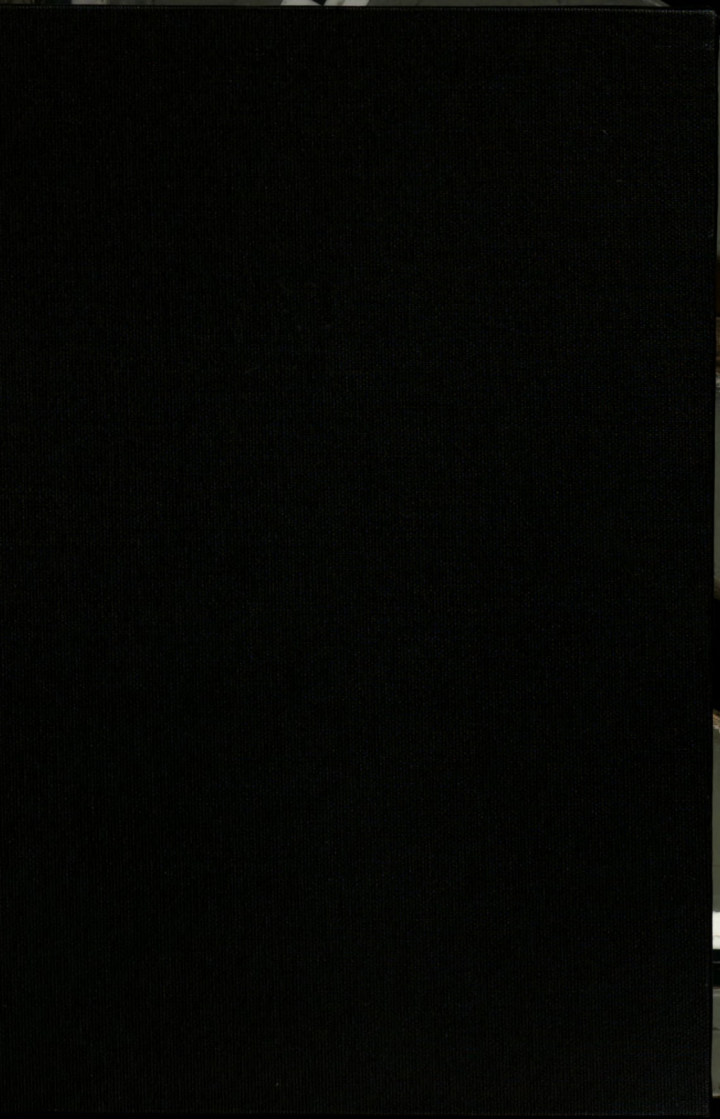
Figure 5.68. Percent carbon conversion efficiency vs. deposition time for sample sets 1, 2, and 3 deposited at $f_t=60$ sccm, $\text{CH}_4/\text{H}_2=1.50\%$, and $T_s=850^\circ\text{C}$.

MICHIGAN STATE UNIV. LIBRARIES



31293015706876





THESIS
6



LIBRARY
Michigan State
University

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.

DATE DUE		
NOW 3 1 1990 11 1 0 0 1 2 2 0 0 SEP 25 2007	_____	_____
MAY 28 2009	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

CONTR

U

**CONTROLLED SYNTHESIS OF DIAMOND FILMS
USING A MICROWAVE DISCHARGE
(NON-EQUILIBRIUM PLASMA)**

By

Saeid Khatami

Volume 2

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of**

DOCTOR OF PHILOSOPHY

Department of Electrical Engineering

1997

5.4 Summary

deposition time

The pro

Plasma Reactor

CH_4/H_2 gas

microwave po

and 30 sccm v

at each of the

rate, as well. I

variables $\mathbf{Y}$ is

sections.

5.4.1 Film prop

5.4.1.1 Film m

For a fixe

5.69 illustrates

parameter α) on

5.70 illustrate th

0.60%, the morp

$\text{CH}_4/\text{H}_2 = 1.50\%$

the morphologica

5.69 and Figure

5.4 Summary of the effect of total gas flow rate on output variables for a fixed deposition time of eight hours

The preceding sections dealt with a detailed analysis of the Microwave Cavity Plasma Reactor output film properties (Y_1) and reactor performance variables (Y_2) vs. the CH_4/H_2 gas chemistry and the substrate temperature (hence operating pressure and microwave power) for several fixed flow rates. The total flow rates of 400, 200, 100, 60, and 30 sccm were examined in detail. An examination of the output variables $Y = [Y_1, Y_2]$ at each of these flow rates revealed the dependence of these variables on the total gas flow rate, as well. In this section a summary of the effect of the total gas flow rate on output variables Y is provided. The data provided in this section were taken from the previous sections.

5.4.1 Film properties (Y_1) vs. total gas flow rate

5.4.1.1 Film morphology

For a fixed substrate temperature of $T_s = 850^\circ\text{C}$, the morphology field map of Figure 5.69 illustrates the dependence of the film morphology (expressed by the growth parameter α) on the total gas flow rate for various $CH_4/H_2\%$. The SEM pictures in Figure 5.70 illustrate the variation of film morphology with the total gas flow rate. For $CH_4/H_2 = 0.60\%$, the morphology of the films was $\{111\}$ for $f_t = 30 - 600$ sccm with $\alpha \cong 3$ but for $CH_4/H_2 = 1.50\%$ and $CH_4/H_2 = 2.0\%$ the total gas flow rate had a significant influence on the morphological development of the diamond films. For instance, as shown in Figure 5.69 and Figure 5.70, for $CH_4/H_2 = 1.50\%$ the film morphology changed from $\{100\}$

($\alpha \equiv 1$) to $\{111\}$

scm. It changed

scm to 200 scm

scm changed to

cauliflower. Figu

above.

($\alpha \cong 1$) to {111} ($\alpha \cong 3$) as the total gas flow rate was increased from 30 sccm to 100 sccm. It changed back to {100} ($\alpha \cong 1$) as the total gas flow rate was increased from 100 sccm to 200 sccm. Further increases of the total flow rate from 200 sccm to 400 and 600 sccm changed the film morphology from {100} to {111} ($\alpha \cong 3$) and from {111} to cauliflower. Figure 5.71 depicts the variation of α with the total gas flow rate as described above.



Figure 5.69.

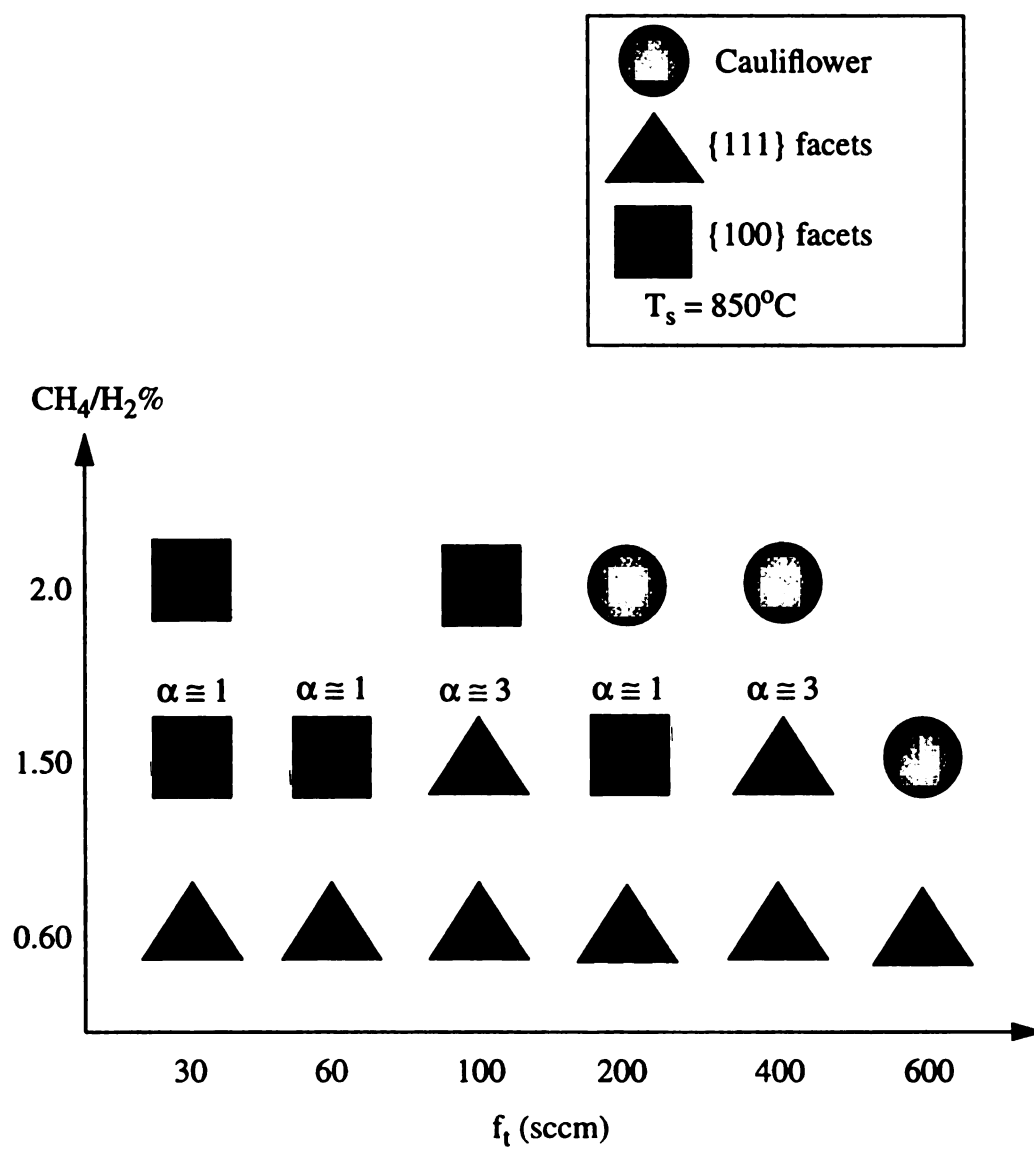


Figure 5.69. Morphology vs. flow rate for substrate temperature fixed at 850°C .

(a)

(b)

Figure 5.7
 $f_1 = 30$ scc
(f) $f_1 = 60$

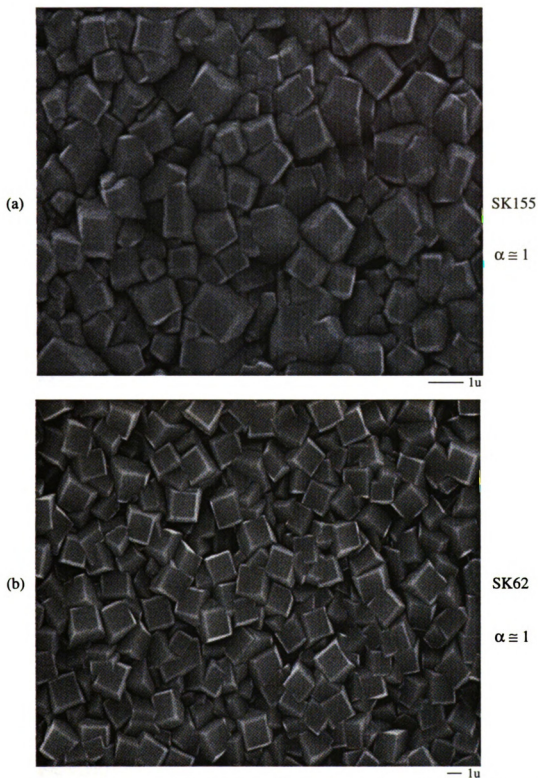


Figure 5.70. SEM pictures of samples deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $f_t = 30$ sccm, (b) $f_t = 60$ sccm, (c) $f_t = 100$ sccm, (d) $f_t = 200$ sccm, (e) $f_t = 400$ sccm, and (f) $f_t = 600$ sccm.

(c)

(d)

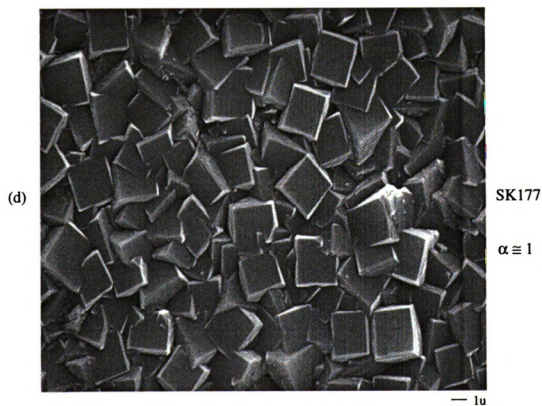


Figure 5.70. Continued.

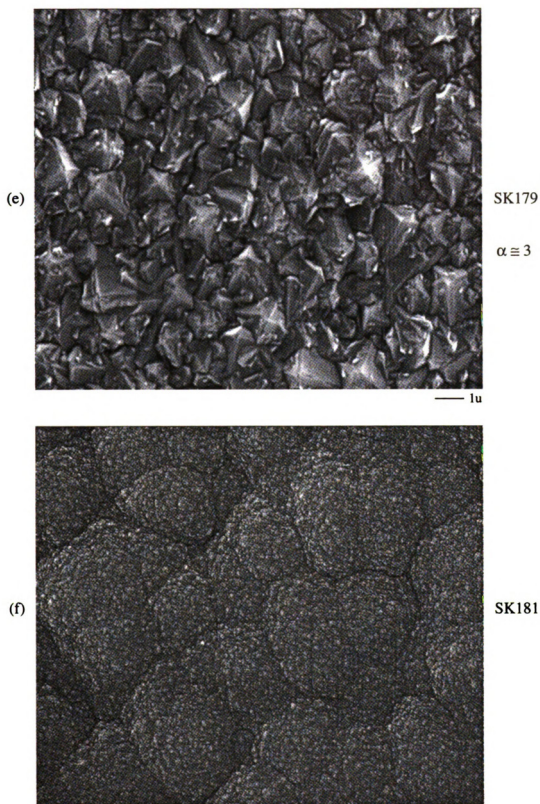


Figure 5.70. Continued.

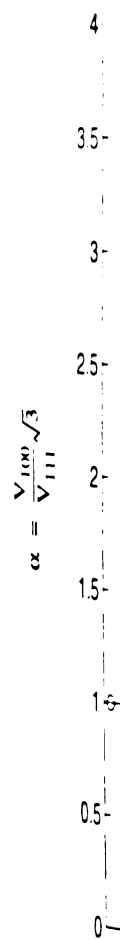


Figure 5.7

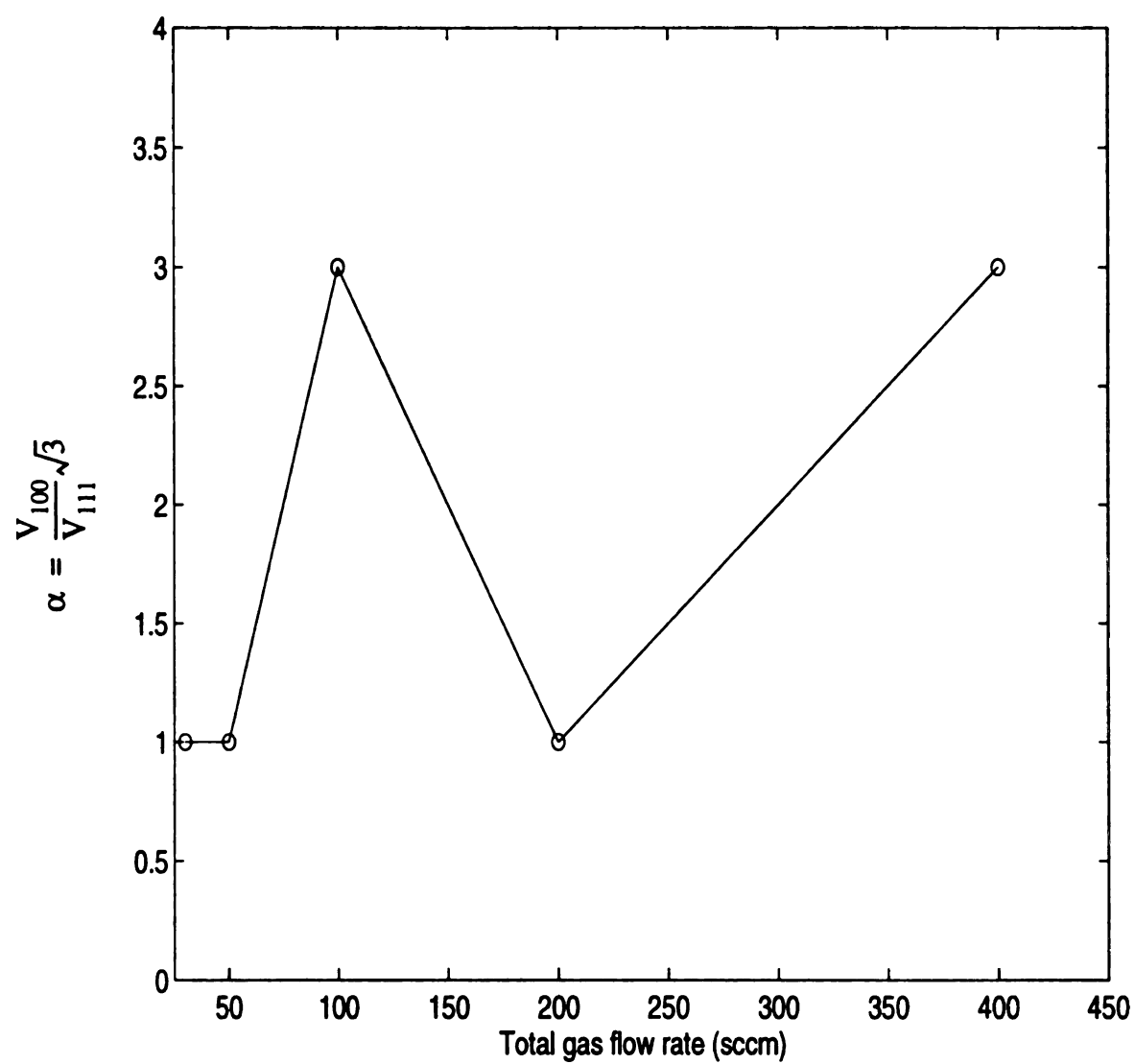


Figure 5.71. Variation of the growth parameter with the total gas flow rate.

5.4.1.2 Str

The c

rate is evid

deposited a

respectively

$H_2 = 1.50\%$

cm^{-1} were ass

5.4.2 Reactor

5.4.2.1 Linear

Figure 5.7

deposited at CH

included in Figur

5.4.2.2 Carbon co

Carbon conve

5.75 shows the var

diamond films de

conversion efficien

sharply from ~ 32%

sccm.

5.4.1.2 Structural quality

The dependence of the structural quality of the diamond films on the total gas flow rate is evident from Figure 5.72 which shows the Raman spectra of the diamond films deposited at various flow rates with CH_4/H_2 and T_s fixed at 1.50% and 850°C , respectively. The plot of FWHM vs. total gas flow rate is shown in Figure 5.73. For $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$, the minimum and maximum FWHM of 7.05 cm^{-1} and 16.27 cm^{-1} were associated with $f_t = 200\text{ sccm}$ and $f_t = 600\text{ sccm}$, respectively.

5.4.2 Reactor performance (Y_2) vs. total gas flow rate

5.4.2.1 Linear growth rate

Figure 5.74 shows the plot of linear growth rate vs. total gas flow rate for the films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$. The value of growth parameter α is included in Figure 5.74.

5.4.2.2 Carbon conversion efficiency

Carbon conversion efficiency strongly depended on the total gas flow rate. Figure 5.75 shows the variation of carbon conversion efficiency with the total gas flow rate for diamond films deposited at $T_s = 850^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1.50\%$. It shows that carbon conversion efficiency was inversely proportional to the total gas flow rate and decreased sharply from $\sim 32\%$ to $\sim 4.0\%$ as the total gas flow rate was increased from 30 sccm to 600 sccm .

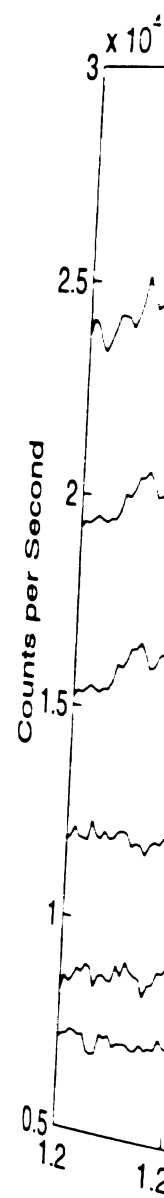


Figure 5.72. Struct
850°C and CH_4/H_2

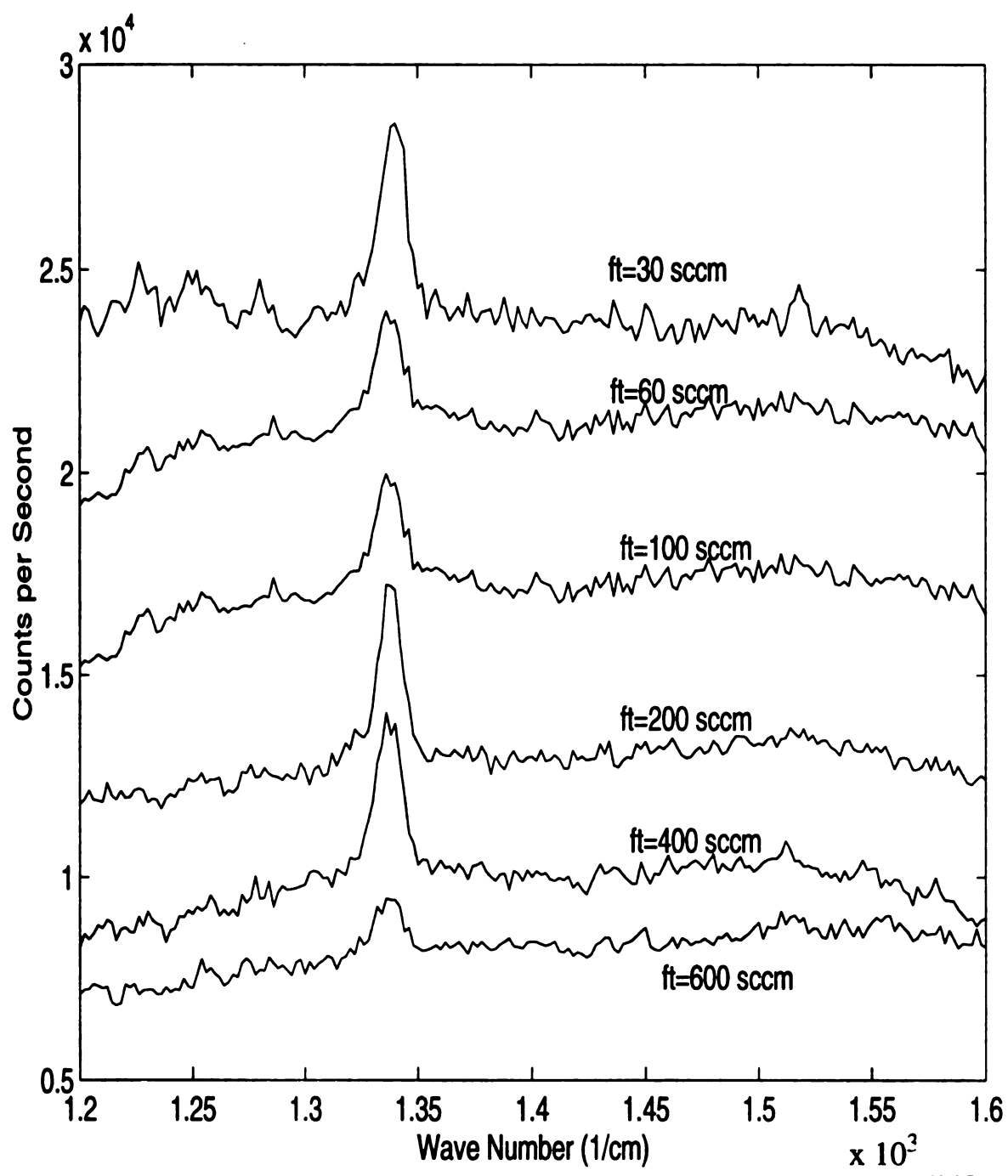


Figure 5.72. Structural quality vs. total gas flow rate with substrate temperature fixed at 850°C and $\text{CH}_4/\text{H}_2 = 1.50\%$.

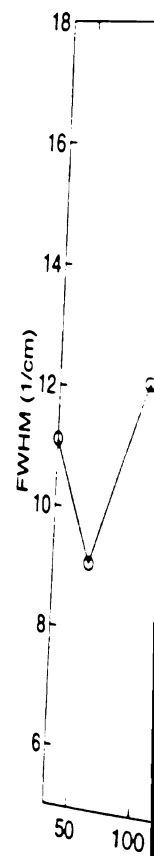
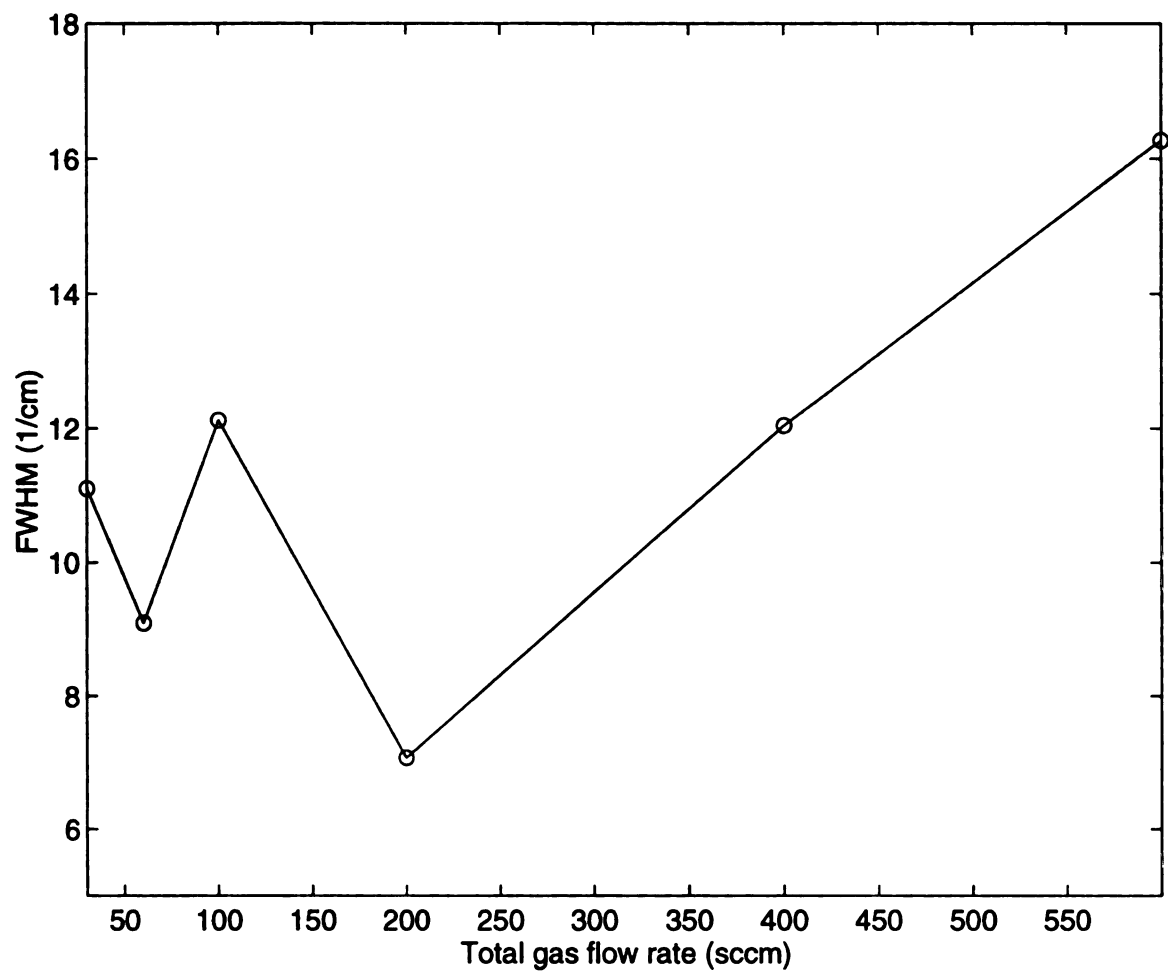


Figure 5.73. Plot of
 $\text{CH}_4/\text{H}_2 = 1.50\%$ an.



Sample	Flow rate (sccm)	FWHM (cm-1)
SK155	30	11.1
SK62	60	9.09
SK195	100	12.12
SK177	200	7.05
SK179	400	12.04
SK181	600	16.27

Figure 5.73. Plot of FWHM vs. total gas flow rate for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$.

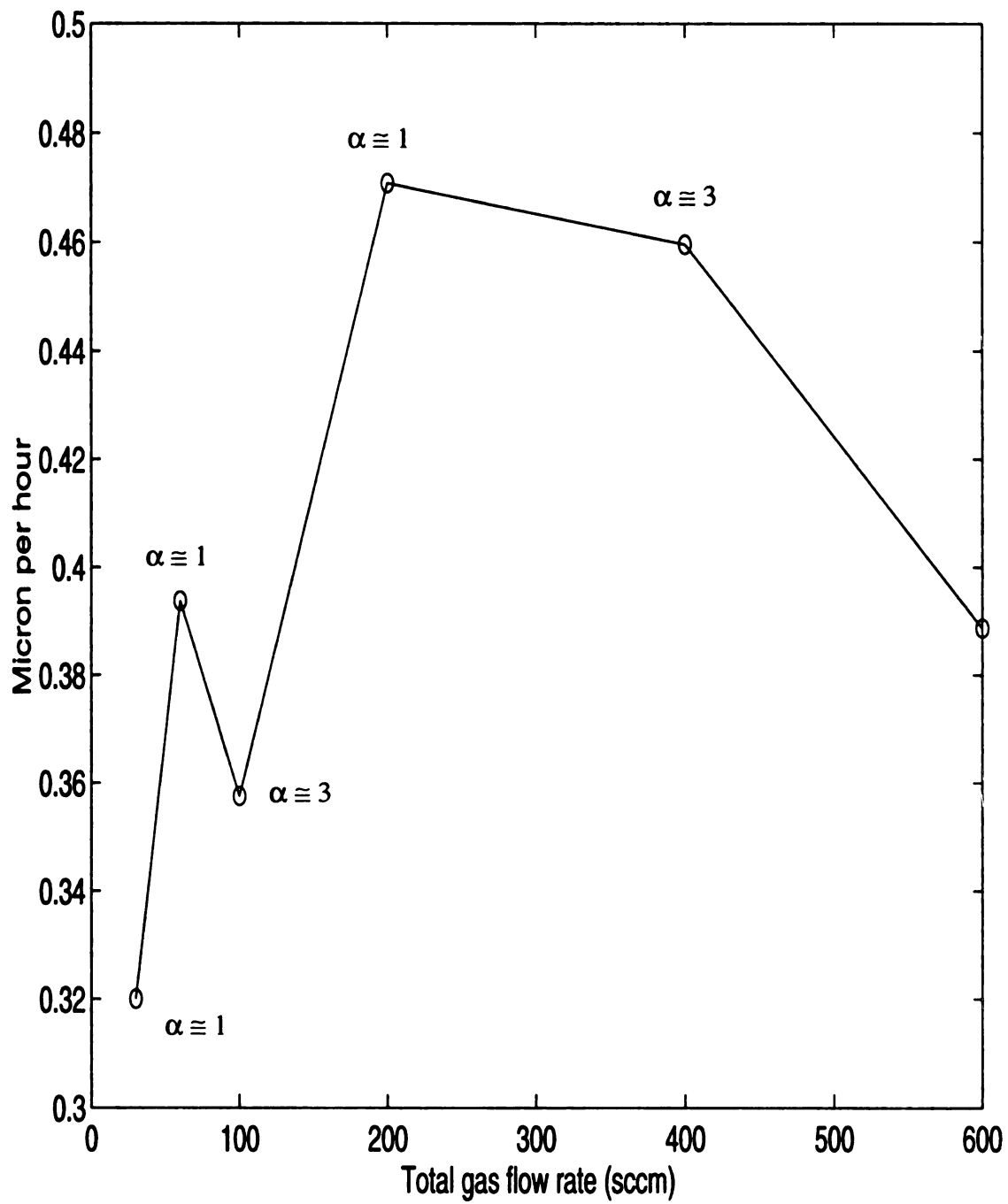


Figure 5.74. Linear growth rate vs. total gas flow rate for diamond films deposited at $T_s = 850^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1.50\%$.

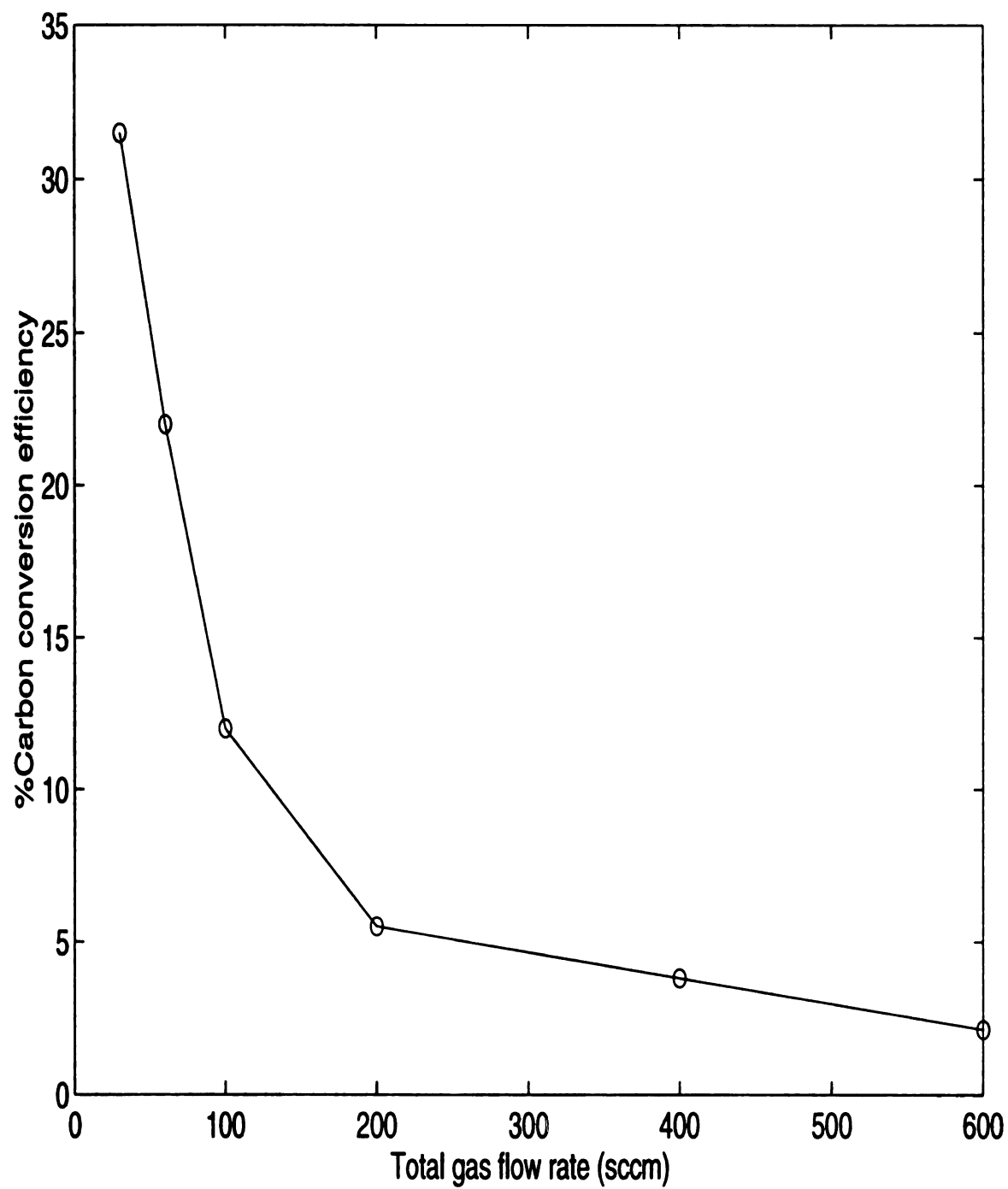


Figure 5.75. %Carbon conversion efficiency vs. total gas flow rate for diamond films deposited at $T_s = 850^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1.50\%$.

5.5 R

$Y_2]$ m

temper

out. In

between

investig

5.5.1 Rel

5.5.1.1 R

Ram

FWHM. T

than films

peaks. The

faceted film

larger FWH

films were d

FWHM

close to one

quality. Howe

{100} films, a

5.5 Relationship between output variables

In the preceding sections, a detailed investigation of how output variables $Y = [Y_1, Y_2]$ mapped into various input variables (i.e., pressure, microwave power, substrate temperature, CH_4/H_2 gas chemistry, total gas flow rate, and deposition time) was carried out. In this section the relationships between film properties (i.e., $Y_{1i} \longleftrightarrow Y_{1j}$) and between film properties and reactor performance variables (i.e., $Y_1 \longleftrightarrow Y_2$) are investigated.

5.5.1 Relationships between film properties ($Y_{1i} \longleftrightarrow Y_{1j}$)

5.5.1.1 Relationship between film morphology and structural quality

Raman spectra of the films which showed cauliflower morphology yielded higher FWHM. This is an indication that films with cauliflower structures were of poorer quality than films with well-faceted crystals. They also showed bigger and broader graphitic peaks. These films were generally deposited at higher CH_4 concentrations than well-faceted films. In cauliflower zones, the higher the CH_4 concentration became, the poorer (larger FWHM) the films became, an indication that the size of stress and/or defects in the films were directly proportional to CH_4 concentration.

FWHM of the diamond films with well-faceted (i.e., $\{100\}$ and $\{111\}$) crystals were close to one another, an indication that both crystal structures were of relatively similar quality. However, for fixed flow rates, the minimum FWHM values primarily belonged to $\{100\}$ films, an indication that $\{100\}$ films were of even a better quality.

5.5

(Y₁)

5.5.1

caulif

smalle

5.5.2.2

(Y₂)

Car

and invers

typically

$f_1 \leq 200 \text{ scc}$

showed that

than those of

5.5.2 Relationship between film properties and reactor performance variables

($Y_1 \longleftrightarrow Y_2$)

5.5.2.1 Relationship between film morphology (Y_1) and linear growth rate (Y_2)

In general, film linear growth rate experienced a decrease when films entered the cauliflower zone. Furthermore, the deeper in the cauliflower zone the films were, the smaller their linear growth rate became.

5.5.2.2 Relationship between film morphology (Y_1) and carbon conversion efficiency

(Y_2)

Carbon conversion efficiency was shown to be directly proportional to weight gain and inversely proportional to CH_4 concentration and total gas flow rate. Well-faceted films typically grew in environments where total flow rate was relatively small (i.e., $f_t \leq 200 \text{ sccm}$) and CH_4 concentration was relatively low ($\text{CH}_4/\text{H}_2 \leq 2.0\%$). This showed that carbon conversion efficiencies of well-faceted films were generally higher than those of cauliflower films.

5

5.

ra

5.6

5.6.

invest

substr

concent

morpho

Therefor

affects th

reason fo

morpholo

is closely

Kondoh (S

be expected

high. The {

relatively low

be due to a sm

a smaller H_2 -

structure is pre

5.6 Discussion

5.6.1 Output variables (Y) vs. gas chemistry and substrate temperature (fixed flow rate)

5.6.1.1 Diamond film properties (Y_1) vs. gas chemistry and substrate temperature

5.6.1.1.1 Morphology vs. substrate temperature and CH_4/H_2

For majority of the total gas flow rates (i.e., $f_t = 200, 100, 60$, and 30 sccm) investigated in Chapter 5, the $\{100\}$ morphology (i.e., $\alpha \cong 1 - 2.5$) appeared at lower substrate temperature regimes (i.e., $T_s \leq 850^\circ\text{C}$) and relatively higher methane concentration range (i.e., $\text{CH}_4/\text{H}_2 > 0.50\%$) than $\{111\}$ morphology (i.e., $\alpha \cong 3$). Film morphology is a function of surface energy and chemical reactions on the film surface. Therefore a change in any factor (i.e., gas chemistry, pressure, temperature, etc.) that affects the chemical reactions on the surface will also affect the film morphology. One reason for obtaining the $\{100\}$ morphology at lower temperatures than the $\{111\}$ morphology could be due to the fact that the dimer structure on the $\{100\}$, (2×1) surface is closely related to hydrogen atoms in the growing environment as discussed by Eiichi Kondoh (Section 3.4.4) [52]. According to Eiichi Kondoh the $\{100\}$, (2×1) structure can be expected to be broken by hydrogen irradiation when the gas-phase H concentration is high. The $\{100\}$ -preferred morphology of microwave plasma CVD diamond films at relatively lower substrate temperatures and higher methane concentrations is believed to be due to a smaller concentration of atomic hydrogen in methane rich environment (due to a smaller $\text{H}_2 \rightarrow 2\text{H}$ dissociation rate at lower temperatures) in which the $\{100\}$, (2×1) structure is preserved [52]. At high atomic hydrogen concentration, almost all the surface

bonds may be sat
so that both {100
competition betw
dominant structur
twins as explained

5.6.1.1.2 Structu

Natural dia
maximum (FWH
spectra carried ou
of the laser beam
diamond films use
encompassed a co
carried out in this
this thesis did no
including the gra
films in this thesi
discussed in Secti

5.6.1.1.2.1 Structu

Atomic hyd
of graphite (sp^2)

bonds may be saturated with hydrogen atoms which then prevent surface reconstruction, so that both {100} and {111} faces would have the primitive (1 x 1) structure and the competition between the growth rates of {100} and {111} faces results in a {111} dominant structure [52] since {111} faces have faster growth rate due to the formation of twins as explained in [29].

5.6.1.1.2 Structural quality of the diamond films

Natural diamond shows a sharp Raman shift at 1332 cm^{-1} with the full width at half maximum (FWHM) in the range of 2 cm^{-1} . The FWHM measurements of the Raman spectra carried out in this thesis were larger than that of the natural diamond. The spot size of the laser beam on the sample was approximately $25\text{ }\mu\text{m}$. The typical grain size of the diamond films used for Raman analysis was about $2\text{ }\mu\text{m}$. Hence, the laser beam spot size encompassed a collection of grains including grain boundaries for each Raman analysis carried out in this thesis. Thus the structural analysis of the diamond films carried out in this thesis did not correspond to a single diamond grain but to a collection of grains including the grain boundaries. The FWHM widening of the polycrystalline diamond films in this thesis is caused by the internal and external stresses in the diamond films as discussed in Section 4.5.3.1.

5.6.1.1.2.1 Structural quality vs. CH_4/H_2

Atomic hydrogen enhances formation of diamond (sp^3 bonds) and inhibits formation of graphite (sp^2 bonds). A higher $\text{CH}_4/\text{H}_2\%$ means an increased carbon radical species

that a

reach

such t

bigger

which

pronou

suggest

that th

5.6.1.1

It

pressur

diamon

increas

higher

films o

quality

It

and sta

that th

phenon

showed

sample

that are responsible for sp^2 bond formation. When methane concentration in hydrogen reaches a point that there is a high concentration of sp^2 forming carbon radical species such that there is not enough atomic hydrogen to suppress them, the graphitic phase grows bigger and diamond phase becomes weaker. This feature was common in cauliflower films which were deposited at higher $CH_4/H_2\%$ than well-faceted films and showed more pronounced graphitic peaks. The FWHM widening at higher methane concentrations suggests that at these concentrations there is a larger stress associated with the films and that the defect density is higher in these films.

5.6.1.1.2.2 Structural quality vs. T_s

It is expected to have more H_2 to $2H$ dissociation at higher temperatures (or pressures) and it is well known that atomic hydrogen enhances growth of sp^3 (i.e., diamond) phase and suppresses the growth of sp^2 (i.e., graphitic) phase. Also crystal size increases with temperature so that there are fewer grain boundaries in films deposited at higher substrate temperatures and since crystal defects are abundant in grain boundaries, films deposited at higher temperatures show smaller FWHM (i.e., better structural quality).

It was established in Chapter 3 that the crystal defects such as twinning, dislocations and stacking faults do not normally take place on $\{100\}$ facets. This together with the fact that the structural quality was improved with the substrate temperature explain the phenomenon of Figure 5.31, Figure 5.33, Figure 5.37, Figure 5.42, and Figure 5.44 which showed that FWHM was minimum for samples with clear $\{100\}$ morphology and/or for samples deposited at higher temperatures.

5.6.1.2

flow m

5.6.1.2

A

remove

diamon

rate w

increas

smaller

the line

in hydr

T

that wit

instead

diamon

became

gas flow

5.6.1.2.

Li

tempera

containi

5.6.1.2 Reactor performance (Y_2) vs. gas chemistry and substrate temperature (fixed flow rate)

5.6.1.2.1 Linear growth rate vs. CH_4/H_2

At sufficiently high methane concentrations, the concentration of atomic hydrogen to remove sp^2 bonding and promote sp^3 bonding becomes insufficient. This could cause the diamond growth process to slow down or stop and could explain the drop in the growth rate with respect to $\text{CH}_4/\text{H}_2\%$ after a certain point. Note that although graphitic phase increased at higher methane concentrations, the density of graphite ($\sim 2.7 \text{ gram/cm}^3$) is smaller than that of diamond (3.515 gram/cm^3) and since weight gain was used to obtain the linear growth rate, the linear growth rate showed a decline after methane concentration in hydrogen reached a certain point (i.e., $\text{CH}_4/\text{H}_2 = 1.75\%$ for 400 sccm, etc.).

The difference between the growth rate plots of 60 sccm and the preceding ones is that with the growth rate plot of 60 sccm, the growth rate increased up to $\text{CH}_4/\text{H}_2 = 2.0\%$ instead of 1.50%. It may be useful to point out that with 60 sccm total gas flow rate, CVD diamond crystals were well-faceted ($\{100\}$ and $\{111\}$) at and below $\text{CH}_4/\text{H}_2 = 2.0\%$ and became cauliflower at higher methane concentrations while with 400 and 200 sccm total gas flow rates the cauliflower zone began as CH_4/H_2 exceeded 1.50%.

5.6.1.2.2 Linear growth rate vs. substrate temperature, T_s

Linear growth rate as measured via weight gain increased with substrate temperature. At higher temperatures there are more dissociation of H_2 and carbon containing radical species which result in increased growth rates. Furthermore, diamond is

dense

film t

great

show

temp

subst

temp

5.6.2

5.6.2

5.6.2

fit)

to a

pres

ind

CH

wit

and

var

rec

dep

denser than other carbon phases, therefore for two films with equal deposition time, the film that contains more diamond component (or less non-diamond component) will have a greater weight gain than the one with less diamond component. Structural quality was shown to improve with substrate temperature. This means that at higher substrate temperatures, there were stronger diamond phases vs. non-diamond phases than at lower substrate temperatures. This explain why linear growth rate increased with the substrate temperature.

5.6.2 Output variables (Y) vs. deposition time (fixed flow rate)

5.6.2.1 Diamond film properties (Y_1) vs. deposition time

5.6.2.1.1 Film morphology vs. deposition time

It was shown that film morphology could vary with the deposition time (i.e., $\alpha = f(t)$). The change in crystal morphology as deposition time changed could not be attributed to any changes in the substrate temperature, total gas flow rate, $\text{CH}_4/\text{H}_2\%$, operating pressure, or microwave power with deposition time since these variable have proven to be independent of a variation in time. A change in the discharge radical species (i.e., CH_3 , CH_2 , C_2H_2 , C_2H_3 , etc.) vs. time seemed to be the cause of the variation of morphology with deposition time. Insitu measurements of appropriate plasma species concentrations and substrate condition was required to clearly understand the effect of deposition time variable on the film morphology (i.e., α). This was beyond the scope of this thesis and is recommended for future research. However, it was speculated that the α variation with deposition time was caused by a change in the radical species reactions vs. time with the

reactor walls with

a period of time

was further spec

attract radical sp

that more spec

morphology (

According to

remains and

5.76. Lets V

respectively.

(cubo-octah

$\langle 111 \rangle$ direc

survive (octa

It seem

grew faster th

the walls did n

radical species t

that $\{100\}$ facets

seems to be the

sample) to $\{111\}$;

The species r

some experiments

for longer deposi

reactor walls which caused the walls to act as a sink for the appropriate radical species for a period of time and to reduce the number of species that interacted with the substrate. It was further speculated that more likely over time the walls became saturated and did not attract radical species any more (and possibly supplied some species to the substrate) so that more species became available to react with the substrate and change the film morphology (i.e., from $\{100\}$ for $t = 8$ hours to $\{111\}$ for longer deposition times). According to the Wulff criterion [36], in the crystal growth, the slowest growing facet remains and the other facets go out of existence. This phenomenon is shown in Figure 5.76. Let V_{100} and V_{111} denote growth velocities in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions, respectively. Assuming that at some point crystals with both $\{100\}$ and $\{111\}$ facets exist (cubo-octahedron crystal habit), then if the growth in $\langle 100 \rangle$ direction is faster than in $\langle 111 \rangle$ direction, the $\{100\}$ facets will go out of existence and only $\{111\}$ facets will survive (octahedron crystal habit) and the resulting film will have $\{111\}$ morphology.

It seemed that over the period when species were sunk to the walls $\{111\}$ facets grew faster than $\{100\}$ facets so that the diamond films showed $\{100\}$ morphology. When the walls did not act as a sink for radical species any longer or when they began to supply radical species to the substrate, more species became available for $\{100\}$ facets growth so that $\{100\}$ facets grew out of existence and the $\{111\}$ morphology became dominant. This seems to be the reason for the morphological transformation of $\{100\}$ facets (SK62 sample) to $\{111\}$ facets (SK70 sample) as time progressed from 8 to 41 hours.

The species reaction with walls might be different from one run to another so that for some experiments i.e., (Figure 5.57) the original film morphology was almost preserved for longer deposition times.



...

Oo
(11

Figure 5.76. A 2
faster growing fa

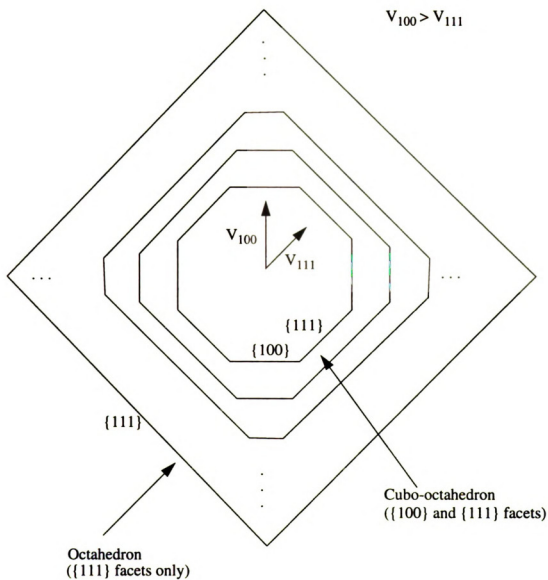


Figure 5.76. A 2-dimensional schematic demonstration of the Wulff criterion [36]. The faster growing face (i.e., {100} in this example) is growing out of existence.

5.6.2.1.2 St

Film s

grow bigger

morphology

crystal defe

increases wi

increases wi

the causes of

morphology

crystal defect

Si substrate w

5.6.2.2 React

5.6.2.2.1 Line

As with

(i.e., CH_3 , CH

linear growth r

5.6.3 Output v

5.6.3.1 Film pr

5.6.3.1.1 Film r

Film morp

surface. Therefo

5.6.2.1.2 Structural quality vs. deposition time

Film structural quality is expected to increase with deposition time since the grains grow bigger and there are less grain boundaries. However, if crystal orientation and/or morphology changes with time (as in this example) such that more twinning and/or other crystal defects occur or their populations significantly increase with time, FWHM increases with deposition time. In addition, the compressive stress that builds up in a film increases with film thickness and this factor widens the FWHM. These effects seem to be the causes of having slightly higher FWHM when $t = 41$ hours. For this sample, the crystal morphology has changed from $\{100\}$ to $\{111\}$ which as proven in Chapter 3 has more crystal defects associated with it, and it is a lot easier to peel off the diamond film from the Si substrate which is an indication of a considerable stress in the film.

5.6.2.2 Reactor performance (Y_2) vs. deposition time (fixed flow rate)

5.6.2.2.1 Linear growth rate vs. deposition time

As with morphology vs. deposition time, the change in the discharge radical species (i.e., CH_3 , CH_2 , C_2H_2 , C_2H_3 , etc.) vs. time seemed to be the cause of the variation of linear growth rate with deposition time.

5.6.3 Output variables (Y) vs. total gas flow rate

5.6.3.1 Film properties (Y_1) vs. total gas flow rate

5.6.3.1.1 Film morphology vs. total gas flow rate

Film morphology is a function of surface energy and chemical reactions on the film surface. Therefore a change in any factor (i.e., gas chemistry, pressure, temperature, etc.)

tha

tim

wh

the

Gas

bef

hyd

bef

resi

high

with

have

ator

me

proc

mor

The

point

disc

rate

that affects the chemical reactions on the surface will also affect the film morphology.

The change of film morphology with flow rate may be attributed to the gas residence time which is determined from the following equation [14].

$$\tau_r = \frac{pV_q}{f_t} \quad (\text{sec}) \quad (\text{eq. 5.1})$$

where p (expressed in Torr) is the pressure, V_q (in liters) is the quartz dome volume above the substrate, and f_t (in torr-liter/sec, 1 torr-liter/sec = 79.05 sccm) is the total flow rate. Gas residence time is a measure of how long supplied gas species stay over the substrate before they are pumped out. A high gas residence time means that gas species (i.e., hydrocarbon radicals) have a longer time to react with the substrate and with each other before they are pumped out (i.e., slower pumping speed). Eq. 5.1 shows that the gas residence time is inversely proportional to the total gas flow rate which means that at higher total flow rates the gas species spend a shorter time to react with the substrate and with each other. At sufficiently high residence time, the incoming carbon radical species have enough time to go to correct points in the diamond lattice, so a complete plane of atoms is formed before other carbon species are attached (i.e., twin free growth mechanism). This makes high gas residence time be associated with slower growth process which is a characteristic of $\{100\}$ planes. Note that $\{111\}$ planes are proven to be more prone to formation of twinning, dislocations and stacking faults (see Chapter 3). These structural defects enhance formation of $\{111\}$ planes. $\{100\}$ planes are subject to point defects only. So $\{100\}$ planes grow slower than $\{111\}$ planes. From the above discussion, films with $\{100\}$ morphology are expected to grow under typically low flow rate conditions. This is precisely what has been observed in the current work. Occurrence

of {100} (

conditions

5.6.3.1.2 S

The c

previous di

high gas flo

5.6.3.2 Reac

5.6.3.2.1 Lin

The dep

dependence c

growth rate ar

5.6.3.2.2 Carl

Carbon c

proportional to

of in coming hy

This makes car

time. Therefore

deposition proce

Finally, from

high carbon con

of {100} film deposition is scarce under 400 sccm flow rate, while under lower flow rate conditions a large proportion of the films show {100} morphology.

5.6.3.1.2 Structural quality vs. total gas flow rate

The dependence of film structural quality on total gas flow rate is apparent from the previous discussion (i.e., morphology vs. gas flow rate). Small gas residence times (i.e., high gas flow rates) could result in introduction of defects in the crystal lattice.

5.6.3.2 Reactor performance (Y_2) vs. total gas flow rate

5.6.3.2.1 Linear growth rate vs. total gas flow rate

The dependence of film structural quality on the total gas flow rate explains the dependence of linear growth rate on total gas flow rate since structural quality and film growth rate are interrelated.

5.6.3.2.2 Carbon conversion efficiency vs. total gas flow rate

Carbon conversion efficiency was shown (eq. 4.2, eq. 4.3, and eq. 4.4) to be inversely proportional to the total gas flow rate because at higher total flow rates, bigger proportions of incoming hydrocarbon gas species are pumped out before they react with the substrate. This makes carbon conversion efficiency become directly proportional to gas residence time. Therefore, a higher carbon conversion efficiency is proportional to a slower deposition process, and vice versa.

Finally, from this discussion, {100} crystals are expected to grow under typically high carbon conversion efficiency conditions and this is what has been observed

t

a

w

sh

ef

fr

fil

5.7

outp

grai

grow

temp

as th

depos

arrang

pressu

the tri

reactor

U

depende

upon tot

throughout the current research. For $f_t = 400$ sccm, the carbon conversion efficiency was around 3.0% and the occurrence of {100} facets was scarce while at lower flow rates where carbon conversion efficiency was higher, more films showed {100} morphology. It should be mentioned that not all CVD diamond films grown under high carbon conversion efficiency condition showed {100} morphology. There are other factors such as surface free energy, surface restructuring, etc. that also affect morphological formation of the films.

5.7 Summary

For the 5" quartz dome/3" substrate reactor configuration the relationships between output variables $Y = [Y_1, Y_2]$ with Y_1 as the film property variables (i.e., film morphology, grain size, and structural quality) and Y_2 as the reactor performance variables (i.e., linear growth rate and carbon conversion efficiency) and the operating pressure-substrate temperature-absorbed microwave power, $CH_4/H_2\%$ concentration, and total gas flow rate as the reactor's independent input variables (U_1) and deposition time as the reactor's deposition variable (U_2) were investigated. No substrate external heating or cooling arrangement was utilized which made the microwave power, substrate temperature, and pressure to be interrelated and thus be considered as essentially one input variable called the triad of substrate temperature-pressure-and microwave power input variable. The reactor's deposition procedure variables (U_3) were held fixed as described in Chapter 4.

Under a fixed reactor geometry, film properties (Y_1) and reactor performance (Y_2) depended not only upon gas chemistry (i.e., $CH_4/H_2\%$) and pressure but also depended upon total flow rate and deposition time.

For f

avored a

CH_3/H

tempera

Caulif

aggre

$\alpha \equiv$

2.0°

wen

0.6.

conce

regime

were dep

For t_f

appeared at

was favored

predominantly ca

$T_f \in [700, 1000]$

For $t_f = 60$

For $f_t = 400$ sccm total gas flow rate films with $\{111\}$ morphology (i.e., $\alpha \cong 3$) were favored at low substrate temperatures ($T_s < 950^\circ\text{C}$) and a broad $\text{CH}_4/\text{H}_2\%$ range (i.e., $\text{CH}_4/\text{H}_2 \in [0.6, 1.50]\%$) while $\{100\}$ crystals appeared at relatively higher substrate temperatures ($T_s \geq 950^\circ\text{C}$) and a narrower $\text{CH}_4/\text{H}_2\%$ range ($\text{CH}_4/\text{H}_2 \leq 1.0\%$). Cauliflower and microcrystallites structures appeared at high $\text{CH}_4/\text{H}_2\%$ with small aggregates appearing in a high substrate temperature zone.

For $f_t = 200$ sccm total gas flow rate films displayed primarily $\{100\}$ ($\alpha \cong 1$ and $\alpha \cong 2$) and $\{111\}$ ($\alpha \cong 3$) facets when CH_4/H_2 did not exceed 2.0%. Beyond $\text{CH}_4/\text{H}_2 = 2.0\%$, films showed predominately cauliflower structure. Films with $\{100\}$ morphology were deposited at low substrate temperatures ($T_s \leq 850^\circ\text{C}$) and mainly in $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ regime. Films with $\{111\}$ morphology grew at the same methane concentration range (i.e., $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$) but at a higher substrate temperature regime ($T_s > 850^\circ\text{C}$). At a low methane concentration of 0.60%, predominantly $\{111\}$ films were deposited.

For $f_t = 100$ sccm total gas flow rate films with $\{100\}$ morphology ($\alpha \cong 1 - 2.5$) appeared at $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ when $T_s \leq 850^\circ\text{C}$. The $\{111\}$ morphology ($\alpha \cong 3$) was favored at $0.6 < \text{CH}_4/\text{H}_2 \leq 2.0\%$ when $T_s \geq 850^\circ\text{C}$. For $\text{CH}_4/\text{H}_2 > 2.0\%$, predominantly cauliflower structure was favored for all substrate temperatures in the $T_s \in [700, 1000]^\circ\text{C}$ range.

For $f_t = 60$ sccm total gas flow rate films displayed $\{100\}$ and $\{111\}$ facets when

CH_4/H_2 did

cauliflower

low substr

morphol

when l

(i.e.,

$T_s \in$

morp

crys

the s

power

variatio

etc.) vs.

Film.

which was a

films. Caulifl

graphitic phase

Raman spectra

improved with th

increased sharp

CH_4/H_2 did not exceed 2.0%. For $\text{CH}_4/\text{H}_2 > 2.0\%$, films showed predominately cauliflower structure. Films with $\{100\}$ morphology (i.e., $\alpha \cong 1 - 2.5$) were deposited at low substrate temperatures ($T_s \leq 850^\circ\text{C}$) and $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. Films with $\{111\}$ morphology (i.e., $\alpha \cong 3$) grew at a higher substrate temperature regime of ($T_s > 850^\circ\text{C}$) when $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. At a low methane concentration of 0.50% only $\{111\}$ films (i.e., $\alpha \cong 3$) were deposited at all substrate temperatures in the range of $T_s \in [700, 1000]^\circ\text{C}$. At $T_s = 1000^\circ\text{C}$, for $\text{CH}_4/\text{H}_2 < 2.0\%$ some $\{110\}$ (i.e., roof like morphology) and $\{100\}$ crystal facets grew in addition to $\{111\}$ crystals.

Film morphology could vary with the deposition time (i.e., $\alpha = f(t)$). The change in crystal morphology as deposition time changes could not be attributed to any changes in the substrate temperature, total gas flow rate, $\text{CH}_4/\text{H}_2\%$, operating pressure, or microwave power with deposition time since these variable have proven to be independent of a variation in time. A change in the discharge radical species (i.e., CH_3 , CH_2 , C_2H_2 , C_2H_3 , etc.) vs. time seemed to be the cause of the variation of morphology with deposition time.

Films with $\{100\}$ and $\{111\}$ facets showed strong Raman peak around 1332 cm^{-1} which was an indication of having predominantly the diamond phase (sp^3 bonds) in the films. Cauliflower films showed wider FWHM (i.e., poorer structural quality) and the graphitic phase (indicated by a broad peak around 1550 cm^{-1}) was more pronounced in the Raman spectra of the films with cauliflower structure. The FWHM was generally improved with the substrate temperature but with respect to the methane concentration it increased sharply at high methane concentrations where cauliflower structure was

domi

Wit

co

2

n

d

T

g

c

c

0

Ca

amount

variation

flow rate va

Dome

film morpholo

dominant.

Linear growth rate was shown to improve monotonically with substrate temperature. With respect to CH_4/H_2 the linear growth rate increased up to a certain methane concentration (i.e., $\text{CH}_4/\text{H}_2 = 1.50\%$ for $f_t = 400$ sccm and $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 2.0\%$ for $f_t = 100$ sccm and $f_t = 60$ sccm total gas flow rates) and decreased for higher methane concentrations. Table 5.2 lists the maximum growth rate and the corresponding deposition conditions for each total gas flow rate experimentally investigated in Chapter 5.

Table 5.2. Maximum growth rate and the corresponding deposition conditions for the total gas flow rate experimentally investigated in Chapter 5.

Maximum growth rate $\mu\text{m/hr}$	Total gas flow rate (sccm)	$\text{CH}_4/\text{H}_2\%$	Substrate temperature ($^{\circ}\text{C}$)	Morphology	growth parameter α
0.663	400	1.50	1000	{111}	3
0.660	200	1.50	1000	{111}	3
0.590	100	2.0	1000	{111}	3
0.591	60	2.0	1000	{111}	3

Carbon conversion efficiency is the ratio of carbon added to the film to the total amount of carbon supplied by the input gas. It was found to be directly proportional to the variation in the substrate temperature and inversely proportional to $\text{CH}_4/\text{H}_2\%$ and total gas flow rate variations.

Dome cleanness played an important role in determining film properties, particularly film morphology. Provided that the quartz dome was clean, CVD diamond films with

almost ide

almost 3

It

output

it was

comp

geom

$\alpha = f$
(

almost identical morphologies were deposited even when the experiments were carried out almost 3 years apart.

It was shown in Chapter 5 that the for a fixed reactor geometry (U_2), Y_1 and Y_2 output variables were complex non-linear functions of many input variables. For instance,

it was shown that $\alpha = f\left(\frac{CH_4}{H_2}, T_s, f_t, t\right)$ and $d = f\left(\frac{CH_4}{H_2}, T_s, f_t, t\right)$.

The relationships between output $Y = [Y_1, Y_2]$ and input variables are indeed more complex than what is shown in Chapter 5. It is shown in Chapter 6 that the reactor geometry (U_2) has an important influence on the output variables. This means that indeed

$\alpha = f\left(\frac{CH_4}{H_2}, T_s, f_t, t, U_2\right)$, $d = f\left(\frac{CH_4}{H_2}, T_s, f_t, t, U_2\right)$, etc.

Rea

6.1 In

T

experin

Section

is very c

and output

internal va

input variab

block diagra

reactor geom

reactor config

investigated an

performance of

Figure 6.1 (b) illu

4" quartz dome

respectively. The r

CHAPTER 6

Reactor Field Map: 4" Quartz Dome/2" Substrate Reactor Geometry

Configuration

6.1 Introduction

The experimental data presented in this chapter are the results of over 60 experiments which represent about 500 hours of reactor experimental operation. In Section 1.3 (Figure 1.7) it was pointed out that the microwave plasma deposition process is very complex. It consists of a large number of input ($U = [U_1, U_2, U_3]$), internal (X), and output (Y) variables. The output variables (Y) are dependent upon the input and internal variables (i.e., $Y = g(U, X)$) and the internal variables are dependent upon the input variables ($X = f(U)$). In this chapter a subset of the parameter space shown in the block diagram of Figure 1.7 is investigated. In particular, the influence of a change in the reactor geometry (U_2) on the output variables is experimentally investigated. A fixed reactor configuration consisting of a 4" quartz dome/2" substrate is experimentally investigated and the experimental performance of this reactor is compared with the performance of the 5" quartz dome/3" substrate studied in Chapter 5. Figure 6.1 (a) and Figure 6.1 (b) illustrate the 5" quartz dome/3" substrate (investigated in Chapter 5) and the 4" quartz dome/2" substrate reactor (investigated in this chapter) configurations, respectively. The two reactors' geometry variables (U_2) are similar except in the (i) quartz

dome (2) t

substrate h

area.

Fi

in this

variabl

for the

many e

= [U₁.

Th

road m

described

(1) *Opera*

The o

large (5" qu

external sub

relationship

compares the

substrate) react

operating pressur

dome (2) base diameter, (ii) substrate size (5), (iii) substrate holder assembly (i.e., substrate holder (4) size, metal tube (7) size, quartz tube (6) size), and (iv) discharge (3) area.

Figure 6.2 illustrates the subset of the parameter space experimentally investigated in this chapter and Table 6.1 summarizes the input (**U**), internal (**X**), and output (**Y**) variables under investigation. A similar work as in Chapter 5 is carried out in this chapter for the 4" quartz dome/2" substrate reactor configuration shown in Figure 6.1 (b). Through many experiments, the relationships between reactor output variables (**Y**) and the input (**U** = [U_1 , U_2 , U_3]) and internal (**X**) variables are investigated.

The variation in the reactor geometry caused variations in the reactor's operating road map, microwave volume and area power densities and gas residence time as described below.

(1) Operating road map

The operation of the small (i.e., 4" quartz dome/2" substrate) reactor is similar to the large (5" quartz dome/3" substrate) reactor; it is operated in a thermally floating (i.e., no external substrate heating or cooling arrangement) mode of operation. The P_t - p - T_s relationship is however different from the 5" dome/3" substrate reactor. Figure 6.3 compares the two reactor operating road maps. The large (i.e., 5" quartz dome/3" substrate) reactor required slightly larger absorbed input microwave power and lower operating pressure than the small reactor to produce the same substrate temperature.

(2) Volume

The

the 4"

respect

volume

almost

dome/

3" subs

density

microw

significa

It is

where SD sta

the deposition

(3) Gas residen

For the sam

approximately 3

configuration than

(2) Volume and area microwave power densities

The discharge volumes associated with the 5" quartz dome/3" substrate reactor and the 4" quartz dome/2" substrate reactor are approximately 169 cm³ and 60 cm³, respectively. It is important to note that despite a considerable difference in the discharge volumes, the input microwave powers absorbed in the two reactor configurations were almost the same as shown in Figure 6.4. The volume power density of the small (4" quartz dome/2" substrate) reactor is significantly larger than that of the large (5" quartz dome/3" substrate) reactor. This is shown in Figure 6.5 which illustrates the volume power density vs. substrate temperature for the two reactors. The area power density (i.e., microwave power absorbed/deposition area) is also different for the two reactors and is significantly larger for the small reactor as shown in Figure 6.6.

It is seen from Figure 6.3, Figure 6.5, and Figure 6.6 that:

$$P_{SD} > P_{LD}$$

$$P_{t(SD)} < P_{t(LD)}$$

$$(P_{t(SD)}/V_{SD}) > (P_{t(LD)}/V_{LD})$$

$$(P_{t(SD)}/A_{SD}) > (P_{t(LD)}/A_{LD})$$

where SD stands for small dome, LD stand for large dome, V is the discharge volume, A is the deposition area, p is the operating pressure, and P_t is the absorbed microwave power.

(3) Gas residence time, t_r

For the same flow rate and pressure, the gas residence time as given by eq. 5.1 is approximately 3 times (i.e., $V_{LD}/V_{SD} = 169/60 = 2.82$) smaller for the small reactor configuration than the large reactor configuration.



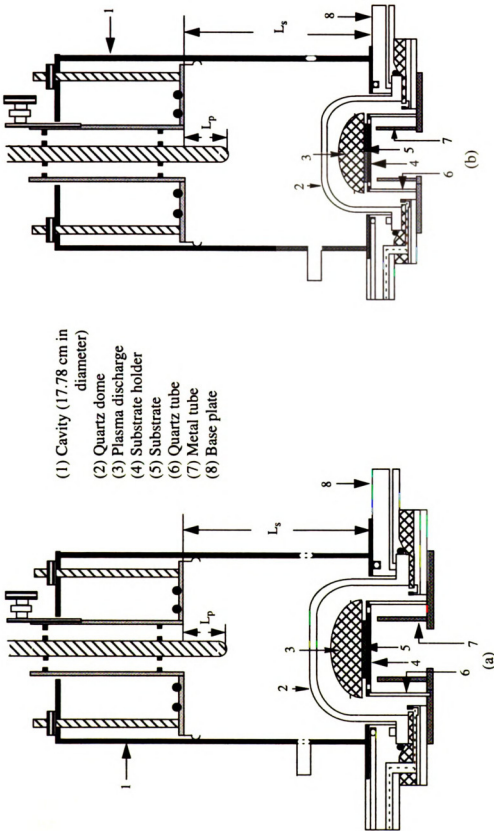


Figure 6.1. (a) The 5" quartz dome/3" substrate reactor configuration (Chapters 5). (b) The 4" quartz dome/2" substrate reactor configuration (Chapter 6).

$U = 15$

X:

Y:

In

U_1

Figure 6.2.
described in
indicating that
investigation.

U = Input variables where $U = [U_1, U_2, U_3]$

U_1 : Macroscopic controllable variables

U_2 : Reactor geometry variables

U_3 : Deposition procedure and time variables

X = Internal variables

$Y = [Y_1, Y_2]$ Output variables (performances)

In general:

$$X = f(U)$$

$$Y = g(U, X)$$

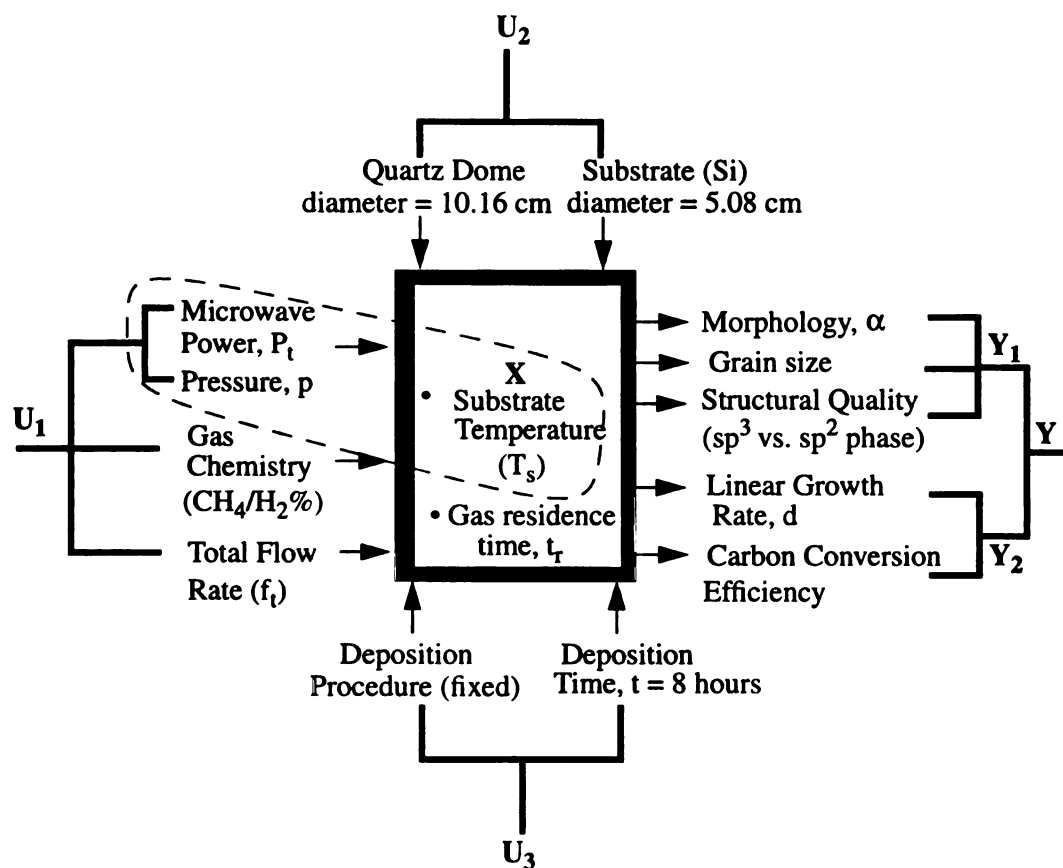


Figure 6.2. Microwave cavity plasma reactor block diagram for the experiments described in this chapter. The dashed curve encircles the T_s , p , and P_t variables indicating that this triad of variables can be considered as a single variable for this investigation.

Table 6.1 Reactor input/internal/output variables studied in this chapter.

Input Variables, U	Macroscopic Controllable Variables, U_1	— Microwave power: $P = 1 - 2.2$ KW — Operating pressure: $p = 20 - 60$ torr - Total gas flow rate: $f_t = 60 - 400$ sccm - Gas chemistry: $CH_4/H_2 = 0.50 - 3.0\%$
	Reactor Geometry Variables, U_2	- Cavity inner diameter = 17.78 cm (fixed) - Quartz dome inner base dia.=10.16 cm (fixed) - Excitation mode = TM_{013} (fixed) - Microwave frequency = 2.45 GHz (fixed) - Substrate Diameter = 5.08 cm ($p<100>$, Si) - Substrate holder = molybdenum under thermally floating configuration (fixed) - Discharge diameter ~ 7.6 cm (fixed)
	Deposition Procedure Variables, U_3	- Deposition time, $t = 8$ hours (fixed) - Substrate Seeding = A mixture of 0.1 micron diamond powder-photoresist solution (fixed) - Start-up and shut-down procedure (fixed)
Internal Variables, X		— Substrate temperature: $T_s = 700 - 1000$ °C
Output Variables, Y		Y_1 — - Surface morphology and grain size — - Structural quality (Raman) Y_2 — - Linear growth rate, d — - Carbon conversion efficiency

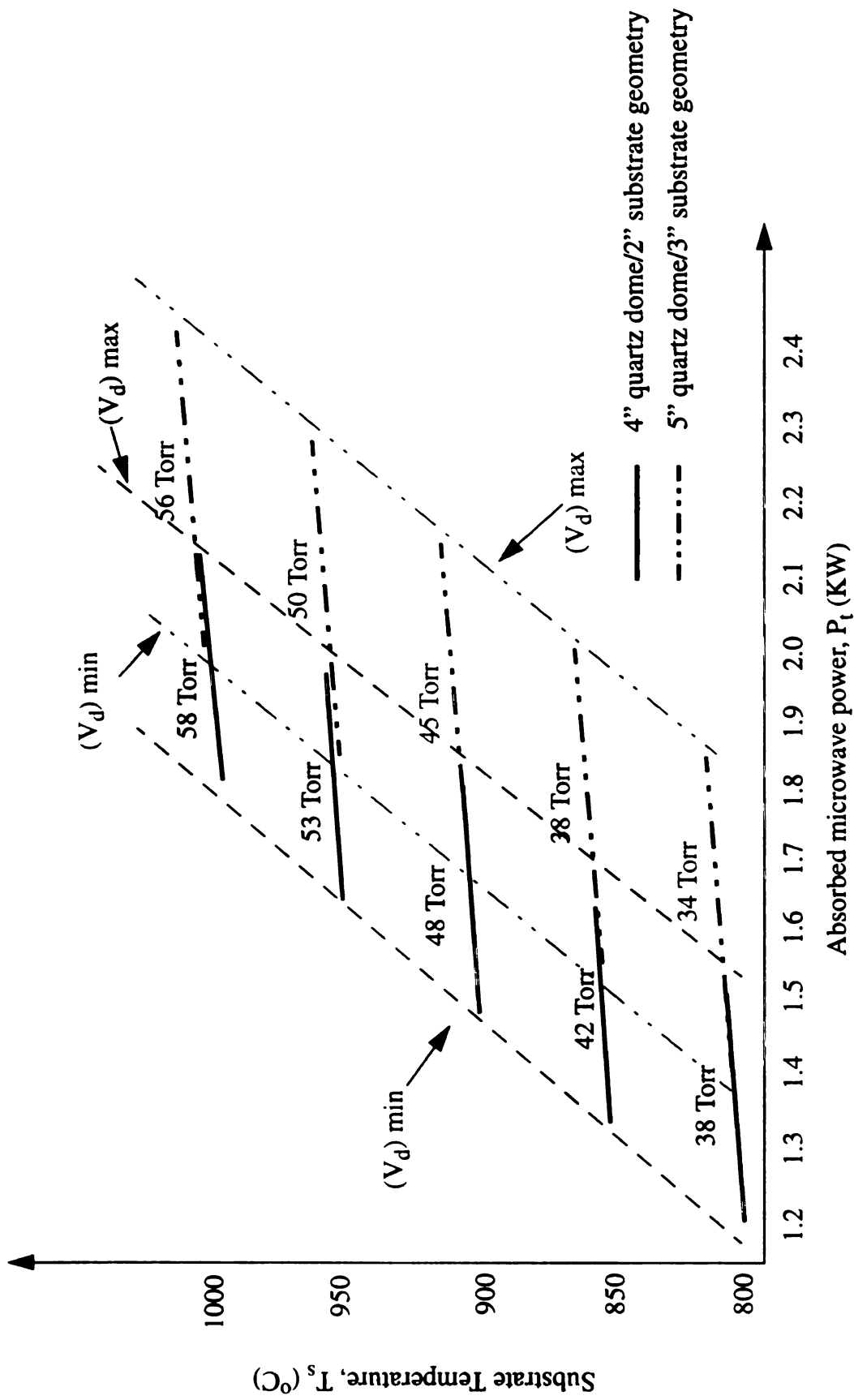


Figure 6.3. Operating road maps of the two reactor configurations under thermally floating arrangement.

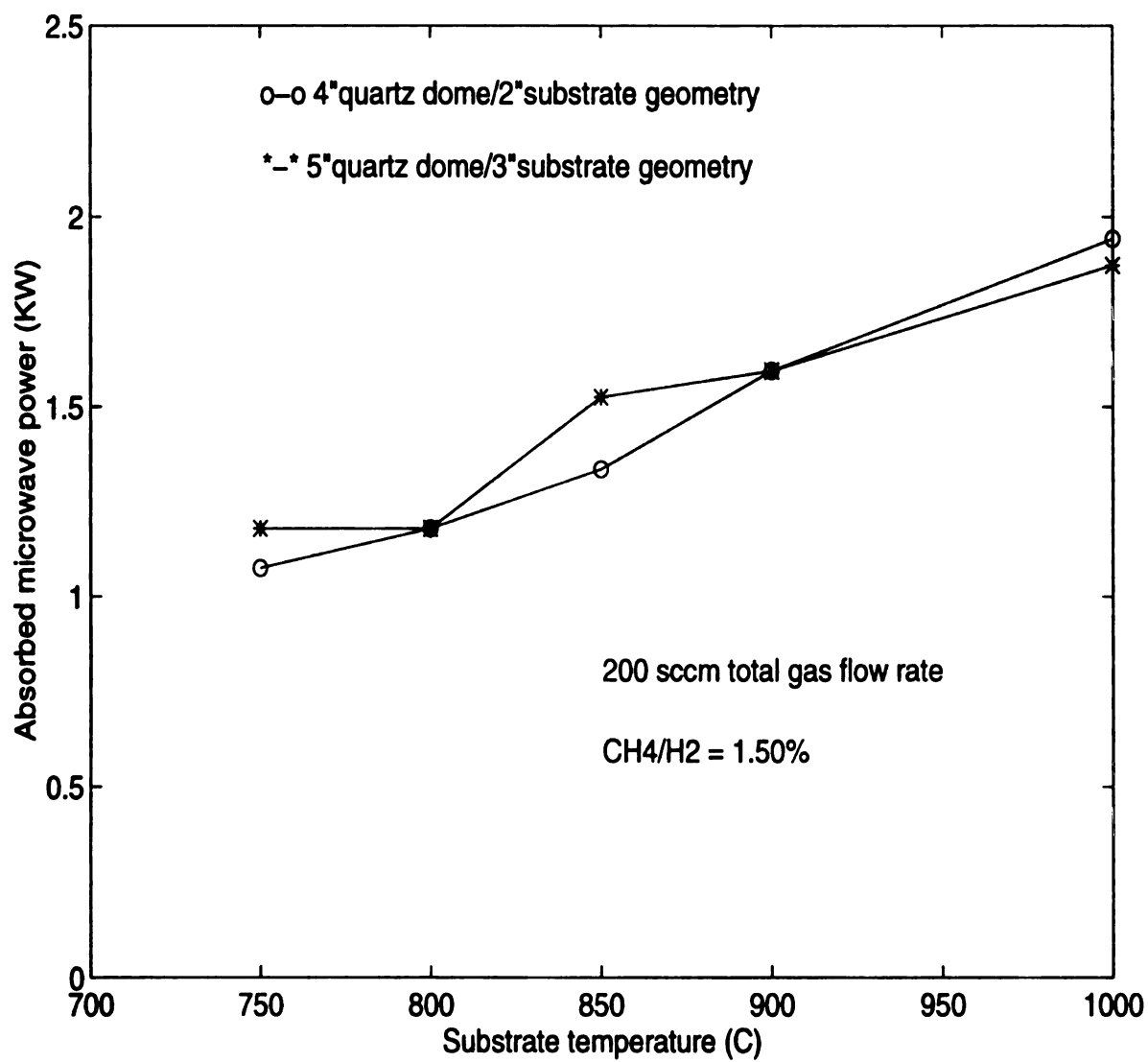


Figure 6.4. Absorbed microwave power vs. substrate temperature for the two different reactor geometries.

volume power d
C
2002
Micro

Figure 6
Factor ge

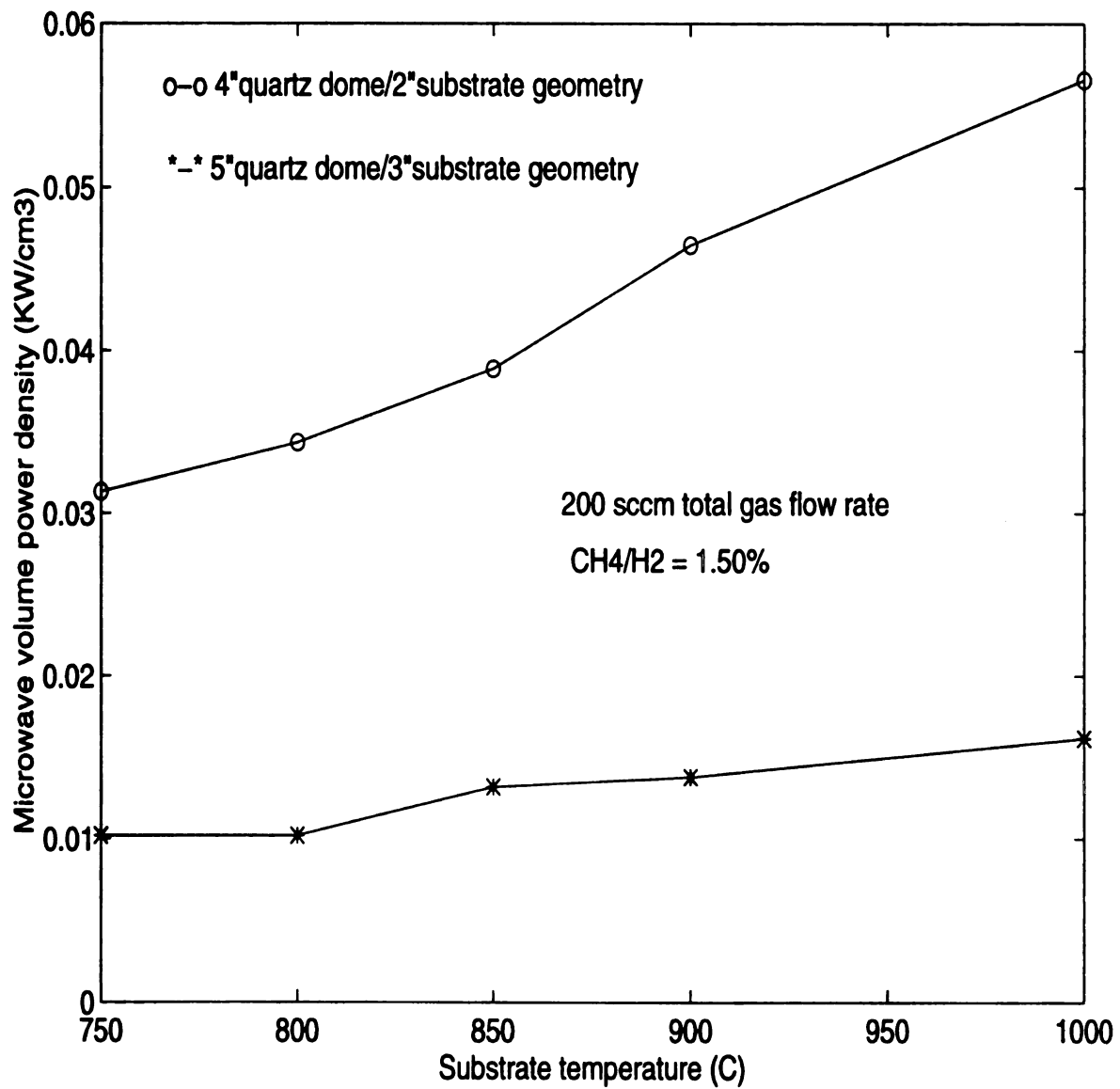


Figure 6.5. Microwave volume power density vs. substrate temperature for two different reactor geometries.

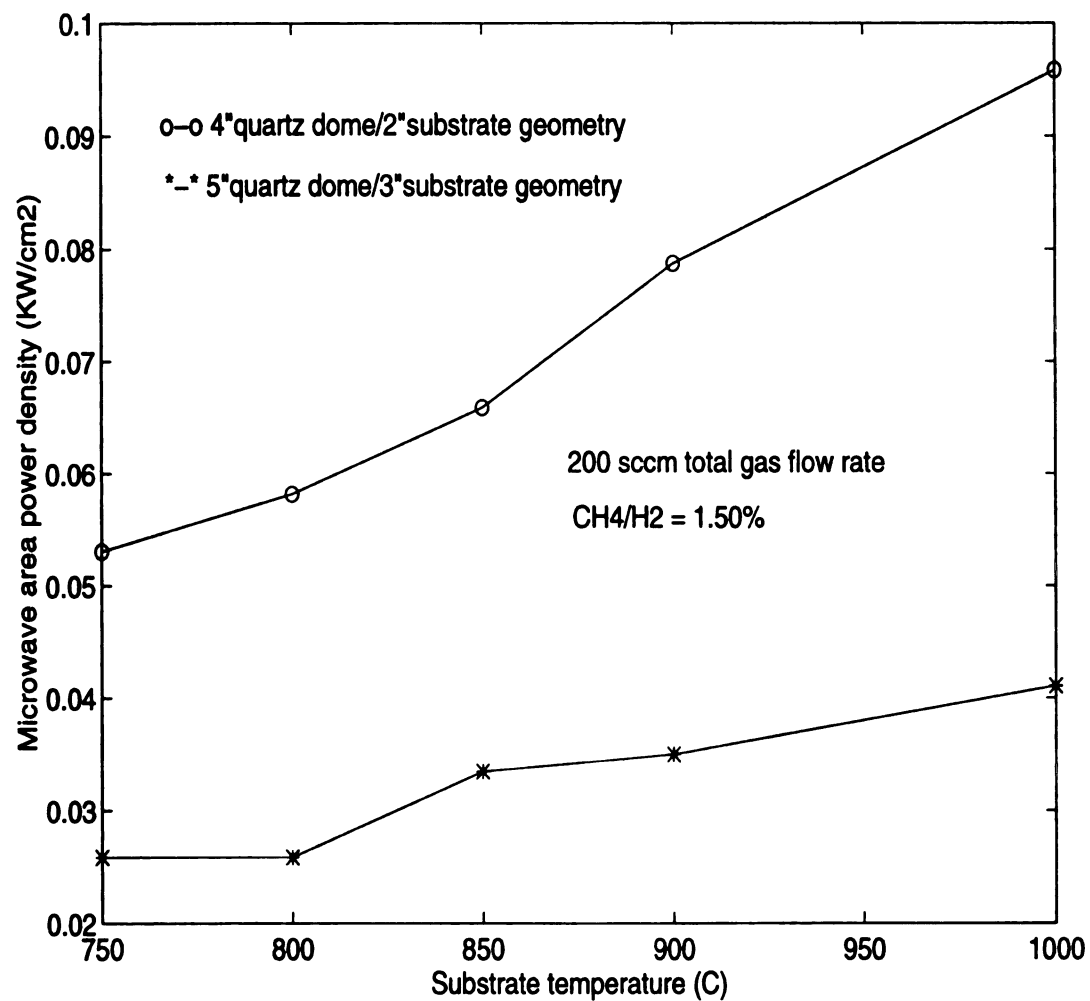


Figure 6.6. Microwave area power density vs. substrate temperature for two different reactor geometries.

The ranges of operating pressure, microwave power, substrate temperature, methane concentration CH_4/H_2 , and total gas flow rate were limited by a number of experimental conditions as depicted in table 6.1. As shown in Figure 6.7 the methane concentrations were within the well-defined diamond zone of the Bachmann diagram.

An investigation of diamond deposition vs. input and internal variables for a fixed deposition time is described in Section 6.2. In this section, output film properties $\mathbf{Y}_1$ (i.e., morphology, grain size, and structural quality) and reactor performance variables $\mathbf{Y}_2$ (i.e., linear growth rate, d and carbon conversion efficiency) are presented vs. variations of the input variables CH_4/H_2 and the triad of substrate temperature-pressure-input microwave power for the total gas flow rate held constant at 400, 200, and 60 sccm. Deposition time is held constant at eight hours for all experiments. It is shown that in addition to methane concentration and the triad of substrate temperature-pressure-microwave power, the total gas flow rate plays an important role in determining film properties. Deposition maps are constructed from the empirical data displaying the morphology (as expressed by the growth parameter α) vs. methane concentration and the triad of substrate temperature-pressure-microwave power for each total gas flow rate. As will be seen in the subsequent sections, the growth parameter α does not precisely explain all details (i.e., twinning, etc.) about the film morphology but it is a useful tool to describe various crystal habits that are observed in the deposited polycrystalline films such as cubic, cubo-octahedron, octahedron, etc. in terms of the growth velocities in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions (see Chapter 3)

Throughout this chapter whenever morphology (i.e., α) vs. substrate temperature is

discussed, for the sake of brevity, only one methane concentration will be selected for SEM picture illustrations. Likewise, to illustrate the dependence of film morphology on methane concentration, only one substrate temperature will be selected for SEM picture illustrations. To make the comparison of output film properties of the two reactor geometries (the 4" quartz dome/2" substrate geometry of this chapter and the 5" quartz dome/3" substrate geometry of Chapter 5) possible, a fixed methane concentration of 1.50% and a fixed substrate temperature of 850°C are chosen for SEM picture illustration for every flow rate discussed. The same principle applies to the illustration of Raman spectra (i.e., structural quality) vs. substrate temperature and methane concentration. For the reader's convenience the data points chosen for SEM and Raman spectra are specified by an + on the morphology field summary maps.

A summary of the effects of total gas flow rate on various film properties are provided in Section 6.3. In Section 6.4 the output film properties (Y_1) and reactor performance (Y_2) of the two reactor geometries (i.e., 4" quartz dome/2" substrate geometry of this chapter and the 5" quartz dome/3" substrate geometry of Chapter 5) utilized in this thesis are compared. The discussion and summary of the results of the experiments discussed in this chapter are presented in Sections 6.5 and 6.6, respectively.

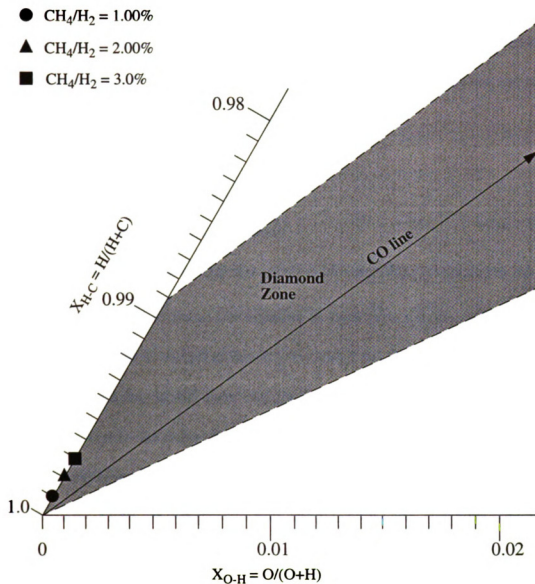


Figure 6.7. Locations of various methane gas concentrations investigated in this chapter on the C-H-O Bachmann phase diagram.

6.2 Film deposition vs. input and internal variables

6.2.1 Film properties (Y_1) vs. various input variables

In what follows, morphology (expressed by the growth parameter α), grain size, and structural quality of the CVD diamond films vs. methane concentration and substrate temperature for various flow rates are investigated.

6.2.1.1 Morphology and grain size

6.2.1.1.1 Total gas flow rate, $f_t = 400$ sccm

For $f_t = 400$ sccm a field map that related field morphology (expressed by the growth parameter α) to the methane concentration in hydrogen, CH_4/H_2 , and the substrate temperature, T_s , was developed as shown in Figure 6.8 (a). Figure 6.8 (b) summarizes the morphology field map of 400 sccm total gas flow rate. At this flow rate films displayed $\{100\}$ (i.e., $\alpha \cong 1 - 2.5$) and $\{111\}$ (i.e., $\alpha \cong 3$) facets when CH_4/H_2 was kept below 2.0%. At and beyond $\text{CH}_4/\text{H}_2 = 2.0\%$ films showed predominately cauliflower structure. Films with $\{100\}$ morphology were deposited at low substrate temperatures ($700 \leq T_s \leq 800^\circ\text{C}$) and mainly in $0.6 \leq \text{CH}_4/\text{H}_2 < 2.0\%$ regime. Films with $\{111\}$ morphology grew at the same methane concentration range (i.e., $0.6 \leq \text{CH}_4/\text{H}_2 < 2.0\%$) but at a higher substrate temperature regime ($850 \leq T_s \leq 1000^\circ\text{C}$). The growth parameter α experienced an abrupt change from $\alpha \cong 1$ (i.e., $\{100\}$ morphology) to $\alpha \cong 3$ (i.e., $\{111\}$ morphology) as the substrate temperature was increased from 800°C to 850°C . The $\{111\}$ (i.e., $\alpha \cong 3$) morphology was predominant for higher substrate temperatures (i.e.,

$T_s > 850^\circ\text{C}$).

Figure 6.

fixed at 1.50°

(i.e., $\alpha \equiv 1 -$

and untwinn

Figure

fixed at 0° .

(i.e., $\alpha \equiv$

morpholo

Figure 6.

for CH_4/A

associated

to $\alpha \equiv 1$

increased

faceted cry

Figure

fixed at 850°

heavily twinn

cauliflower stru

The average gra

increased with CH

$T_s > 850^\circ\text{C}$).

Figure 6.9 displays the SEM pictures of film surface morphology vs. T_s for CH_4/H_2 fixed at 1.50%. For $T_s \in [700, 800]^\circ\text{C}$ the surface morphology of the films was $\{100\}$ (i.e., $\alpha \cong 1 - 2.5$) and no twinning was observed on the crystals. For $T_s > 800^\circ\text{C}$ twinned and untwinned $\{111\}$ and cauliflower/small aggregate morphologies were favored.

Figure 6.10 shows the SEM pictures of film surface morphology vs. T_s for CH_4/H_2 fixed at 0.60%. For $T_s \in [700, 800]^\circ\text{C}$ the surface morphology of the films was $\{100\}$ (i.e., $\alpha \cong 1 - 2.5$) and no twinning was observed on the crystals. For $T_s > 800^\circ\text{C}$ $\{111\}$ morphology was favored. The twin concentration on $\{111\}$ facets decreased with T_s . Figure 6.11 illustrates variation of the growth parameter α with the substrate temperature for $\text{CH}_4/\text{H}_2 = 0.60\%$. As shown, the growth parameter decreased from $\alpha \cong 2.5$ which is associated with crystals with small $\{100\}$ top face and sloped side faces (Figure 6.10 (a)) to $\alpha \cong 1$ (crystals with cubic structure) (Figure 6.10 (b)) as substrate temperature was increased from 700°C to 800°C and experienced an abrupt increase to $\alpha \cong 3$ (i.e., $\{111\}$ faceted crystals) as the substrate temperature was further increased to $T_s \geq 850^\circ\text{C}$.

Figure 6.12 shows the SEM pictures of film surface morphology vs. CH_4/H_2 for T_s fixed at 850°C . The surface morphology changed from moderately twinned $\{111\}$ to heavily twinned $\{111\}$ as CH_4/H_2 changed from 0.60% to 1.00% and 1.50%. The cauliflower structure became dominant as CH_4/H_2 was increased from 1.50% to 2.0%. The average grain size decreased sharply with $\text{CH}_4/\text{H}_2\%$. The twinning concentration increased with $\text{CH}_4/\text{H}_2\%$.

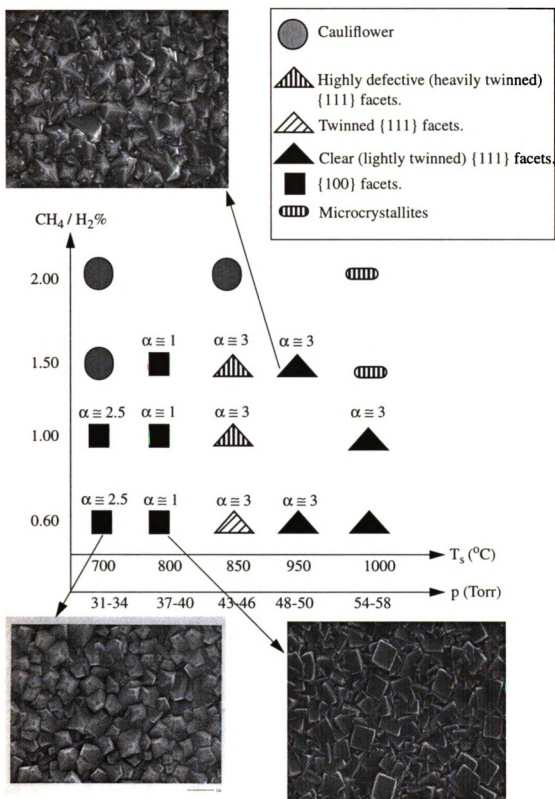
The plo

Chapter 4) vs

size experie

decreased a

The plot of average grain size determined by the method of linear intercept (see Chapter 4) vs. T_s for CH_4/H_2 fixed at 0.60% is shown in Figure 6.13. The average grain size experienced an increase with the substrate temperature up to $T_s = 950^\circ\text{C}$ and decreased as the substrate temperature was further increased to 1000°C .



CH

2

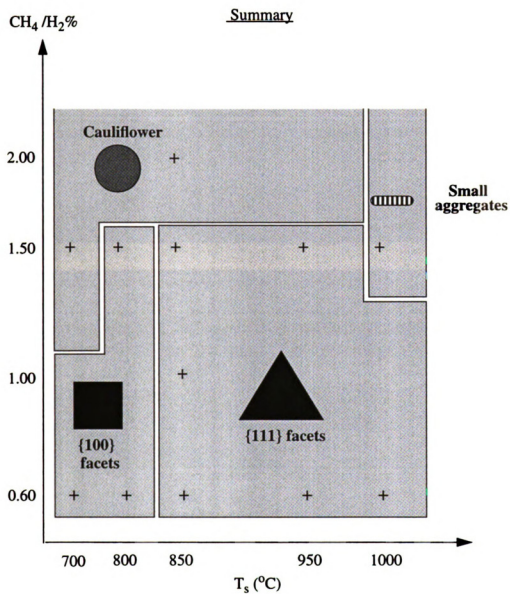


Figure 6.8 (b). Summary of morphology field map for $f_t = 400$ sccm

Figure
and (a)

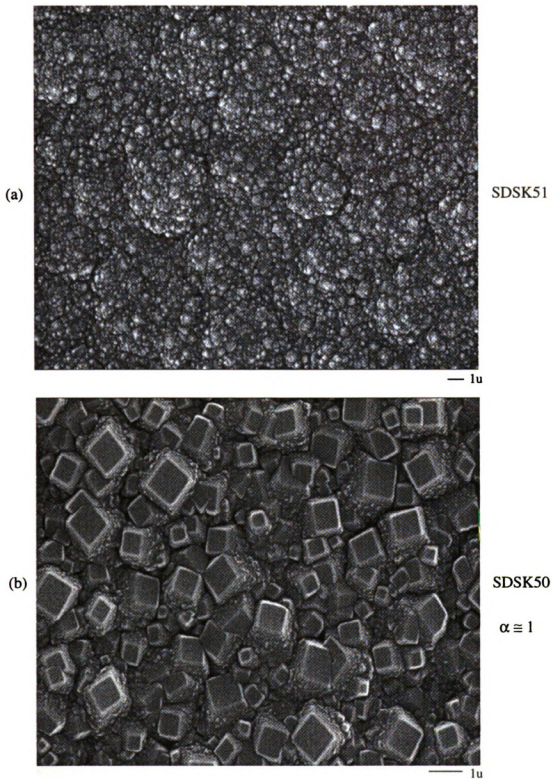


Figure 6.9. SEM pictures of the samples deposited at $f_l = 400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 950^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$.

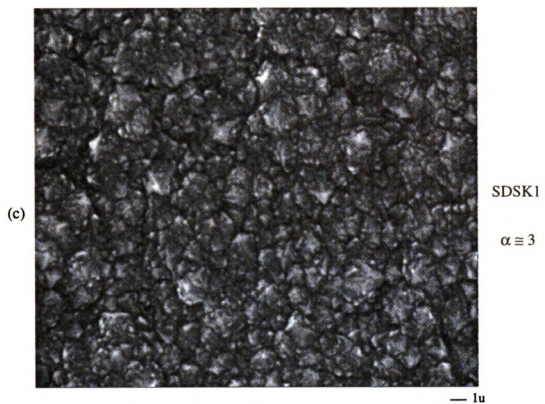


Figure 6.9. Continued

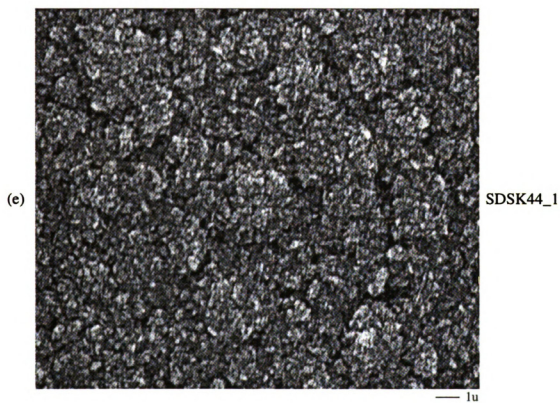


Figure 6.9. Continued

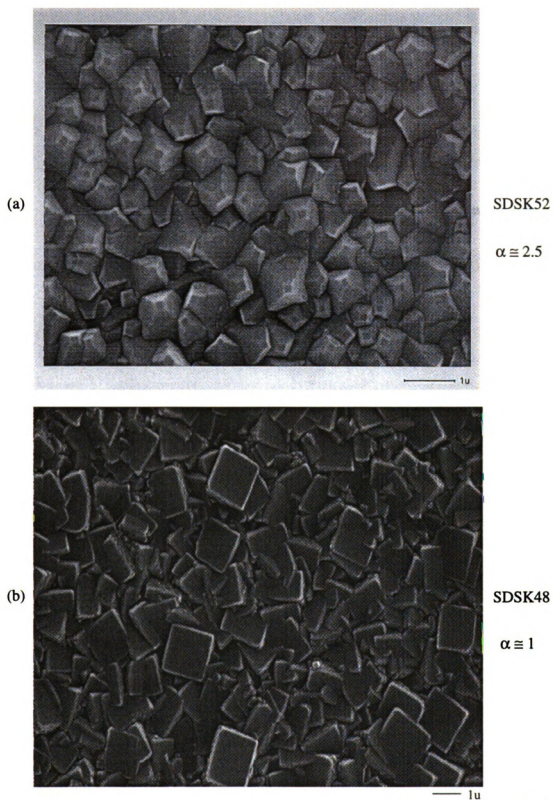
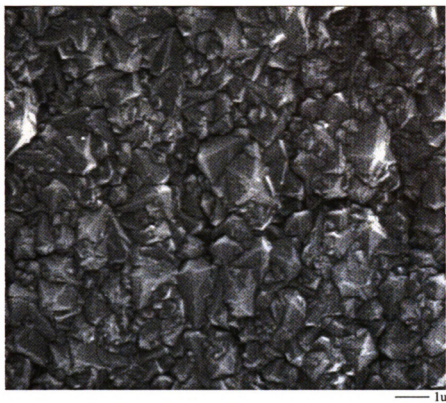


Figure 6.10. SEM pictures of the samples deposited at $f_t = 400$ sccm, $\text{CH}_4/\text{H}_2 = 0.60\%$, and (a) $T_s = 700^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 950^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$.

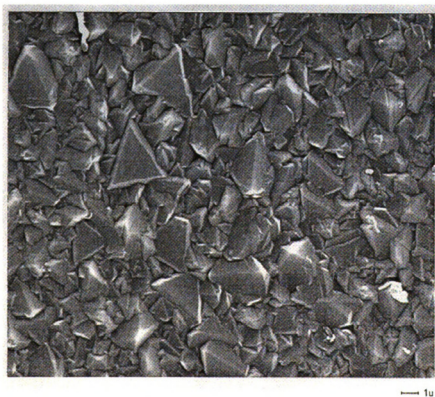
(c)



SDSK2

 $\alpha \equiv 3$

(d)



SDSK3

 $\alpha \equiv 3$

Figure 6.10. Continued.

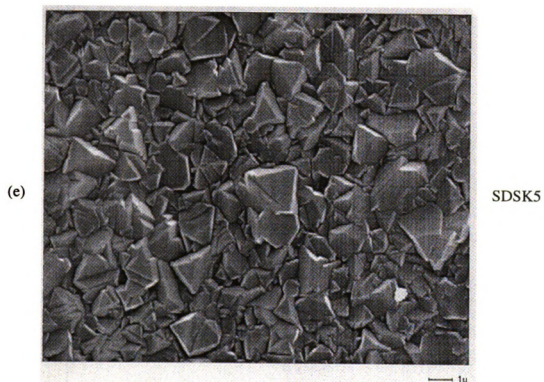


Figure 6.10. Continued.

$$\alpha = \frac{V_{100} \sqrt{3}}{V_{111}}$$

Figure 6.
deposited

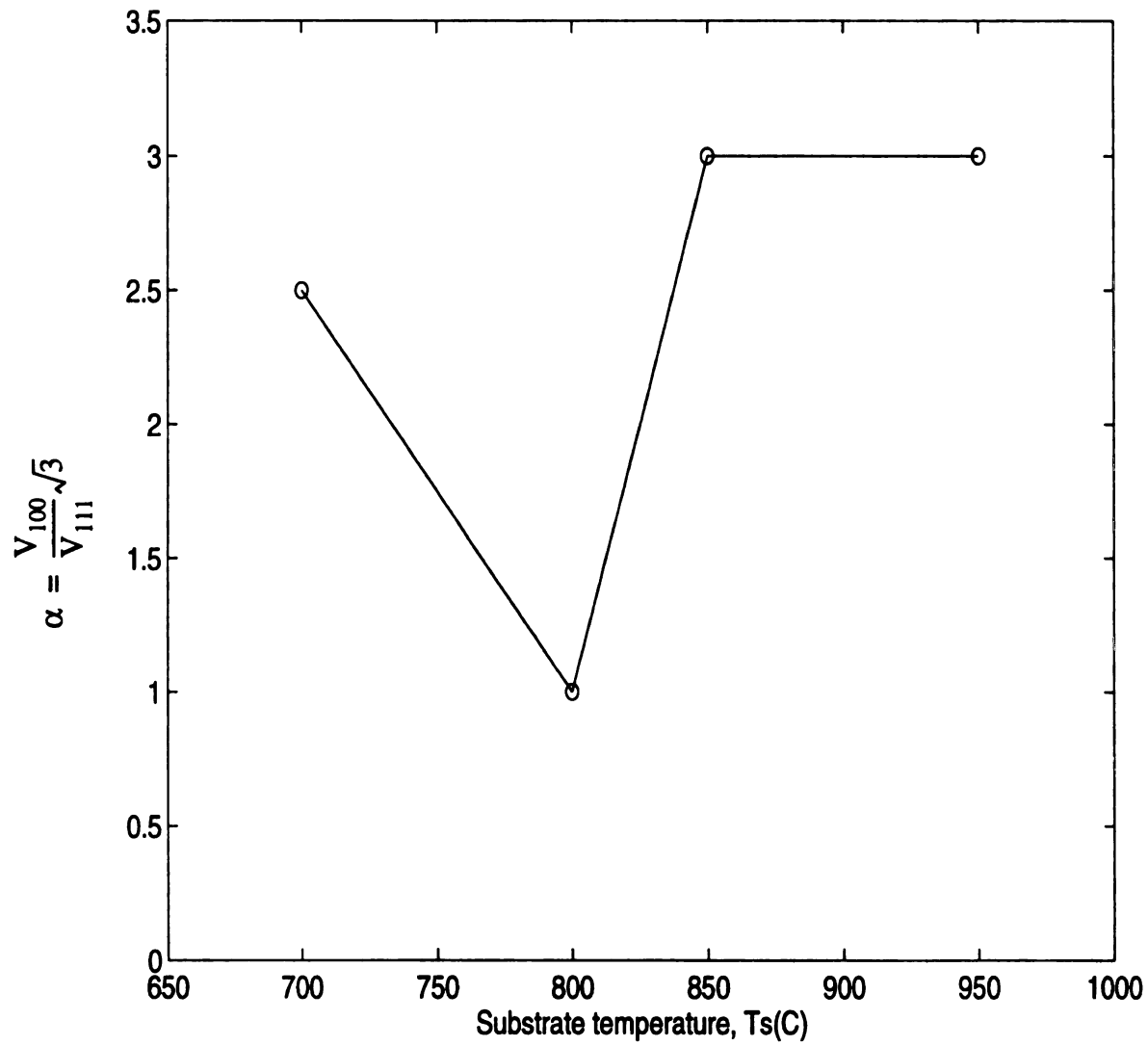


Figure 6.11. Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 400$ sccm and $\text{CH}_4/\text{H}_2 = 0.60\%$.

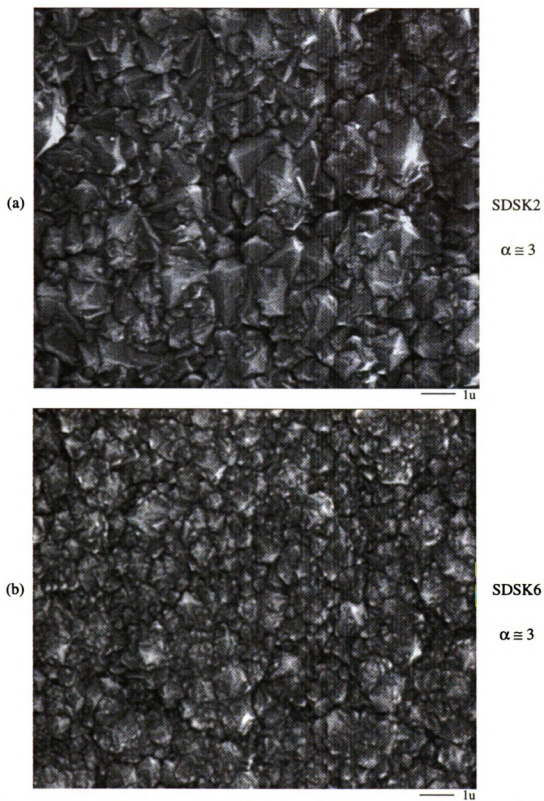
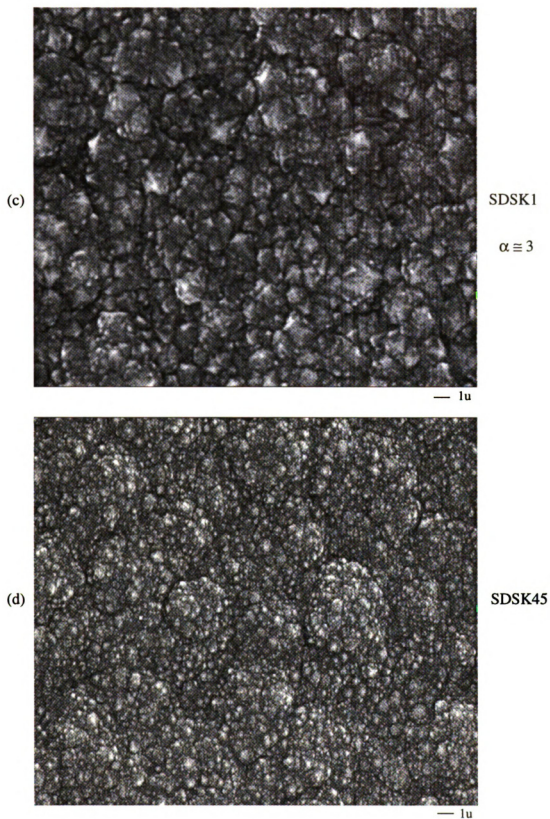


Figure 6.12. SEM pictures of the samples deposited at $f_t = 400$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 0.60\%$, (b) $\text{CH}_4/\text{H}_2 = 1.0\%$, (c) $\text{CH}_4/\text{H}_2 = 1.50\%$, and (d) $\text{CH}_4/\text{H}_2 = 2.0\%$.

(c)

(d)



3

2.5

Grain size (micron)

2

1.5

1

0.5

70x

Figure 6

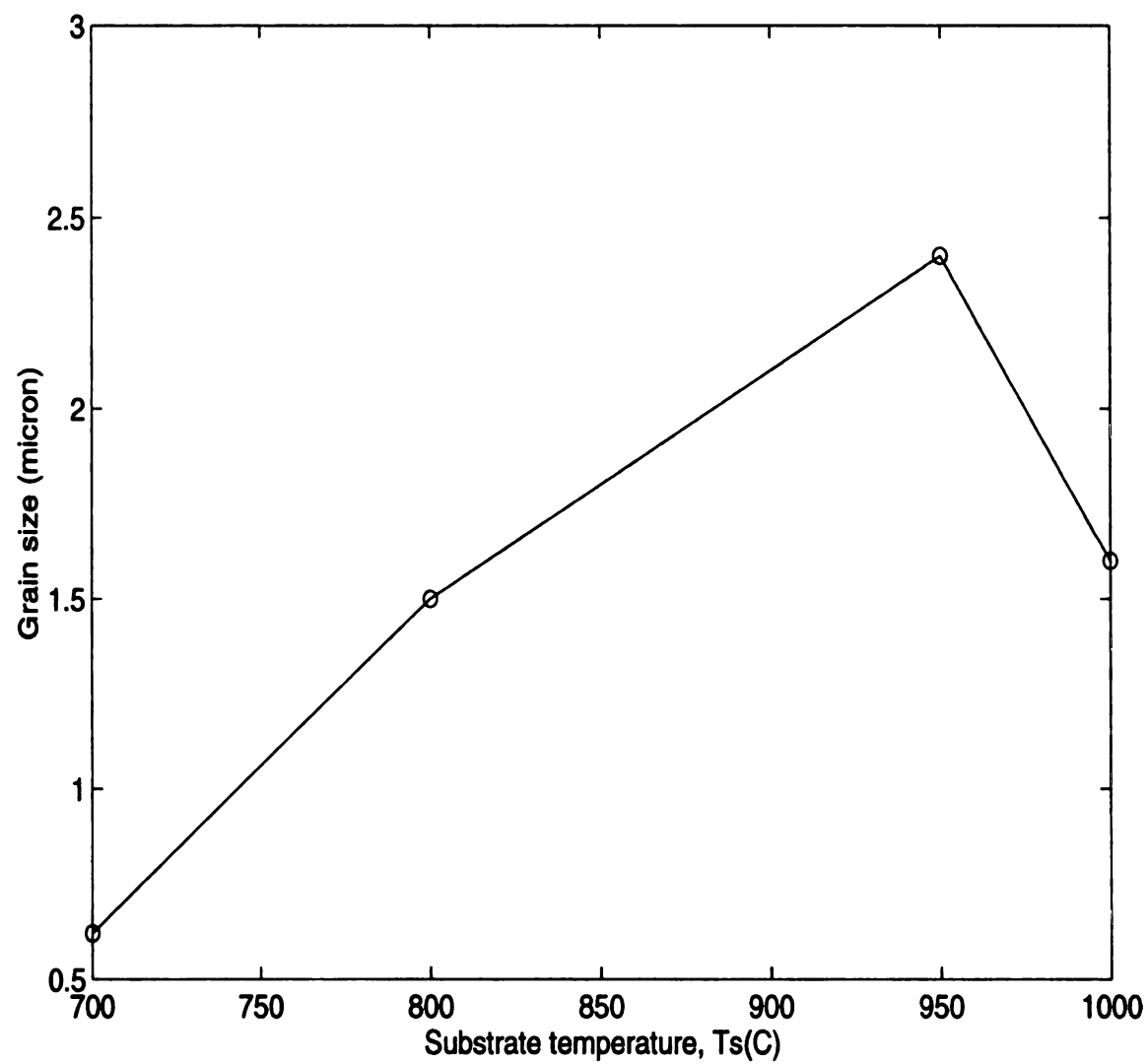


Figure 6.13. Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 0.60\%$ and $f_t = 400$ sccm.

0

r

a

s

c

fi

c

H

co

mo

75

2.0

res

at 1

$\alpha \equiv$

and

twin.

fixed

6.2.1.1.2 Total gas flow rate, $f_t = 200$ sccm

For $f_t = 200$ sccm a field map that related film morphology (expressed by α) to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s , was developed as shown in Figure 6.14 (a). Figure 6.14 (b) summarizes the morphology field map of 200 sccm total gas flow rate. At this flow rate films showed $\{100\}$ (i.e., $\alpha \equiv 1$) and $\{111\}$ (i.e., $\alpha \equiv 3$) facets mainly when CH_4/H_2 was kept below 2.0%. At and beyond $\text{CH}_4/\text{H}_2 = 2.0\%$ films showed predominately cauliflower structure. Films with $\{100\}$ morphology (i.e., $\alpha \equiv 1$) were deposited at substrate temperature range of $800 \leq T_s \leq 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.50\%$. Films with $\{111\}$ morphology (i.e., $\alpha \equiv 3$) grew at the methane concentration range of $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. At $\text{CH}_4/\text{H}_2 = 1.0\%$, the $\{111\}$ morphology was dominant over the entire substrate temperature range of $750 \leq T_s \leq 1000^\circ\text{C}$. At higher methane concentrations of $\text{CH}_4/\text{H}_2 = 1.50\%$ and $\text{CH}_4/\text{H}_2 = 2.0\%$ the $\{111\}$ morphology was favored at $900 \leq T_s \leq 1000^\circ\text{C}$ and $T_s = 1000^\circ\text{C}$, respectively.

Figure 6.15 shows SEM pictures of film surface morphology vs. T_s for CH_4/H_2 fixed at 1.50%. For $T_s \in [800, 850]^\circ\text{C}$ the surface morphology of the films was $\{100\}$ (i.e., $\alpha \equiv 1$) and no twinning was observed on the crystals. For $T_s = 750^\circ\text{C}$ cauliflower structure and for $T_s > 850^\circ\text{C}$ $\{111\}$ (i.e., $\alpha \equiv 3$) morphology were favored and the crystals were twinned.

Figure 6.16 illustrates SEM pictures of film surface morphology vs. CH_4/H_2 for T_s fixed at 850°C . For $\text{CH}_4/\text{H}_2 = 1.0\%$ the film consisted of twinned $\{111\}$ (i.e., $\alpha \equiv 3$)

which c

and 2.0

F

fixed C

with 1

assoc

1.0 p

which changed to {100} (i.e., $\alpha \cong 1$) and cauliflower as CH_4/H_2 was increased to 1.50% and 2.0%, respectively.

Figure 6.17 illustrates the plot average grain size vs. the substrate temperature for a fixed CH_4/H_2 (i.e., $\text{CH}_4/\text{H}_2 = 1.50\%$). The average grain size monotonically increased with T_s . For the substrate temperature fixed at $T_s = 850^\circ\text{C}$, the average grain sizes associated with $\text{CH}_4/\text{H}_2 = 1.0\%$ and $\text{CH}_4/\text{H}_2 = 1.50\%$ were approximately $1.33\ \mu\text{m}$ and $1.0\ \mu\text{m}$, respectively.

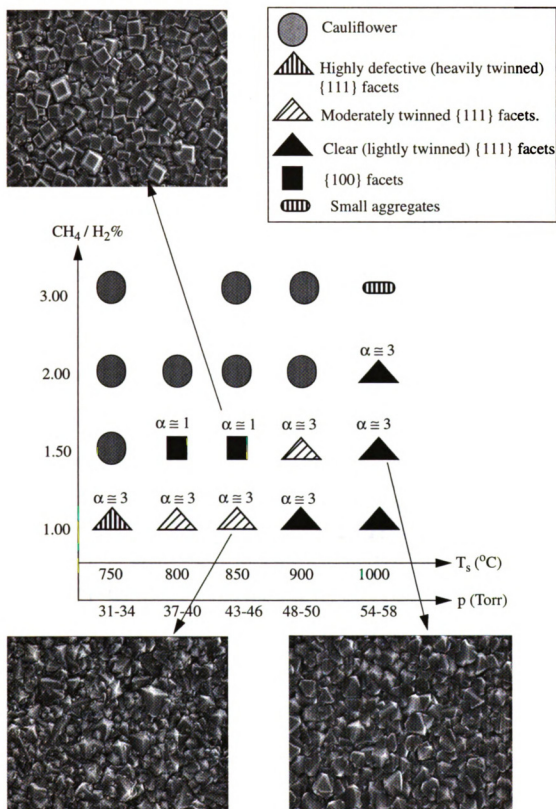


Figure 6.14 (a). Morphology field map for total flow rate $f_t = 200$ sccm.

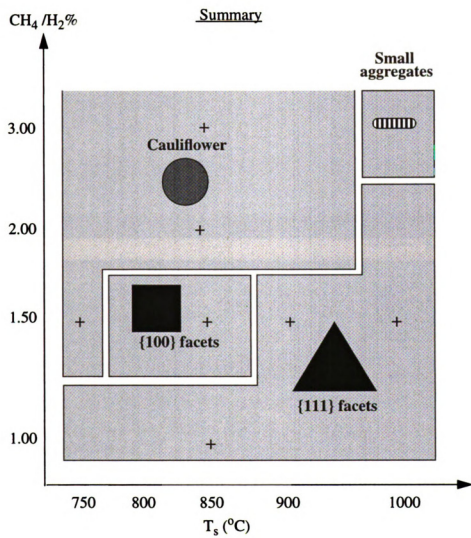


Figure 6.14 (b). Summary of morphology field map for $f_t = 200$ sccm.

(a)

(b)

Figure
and (a)

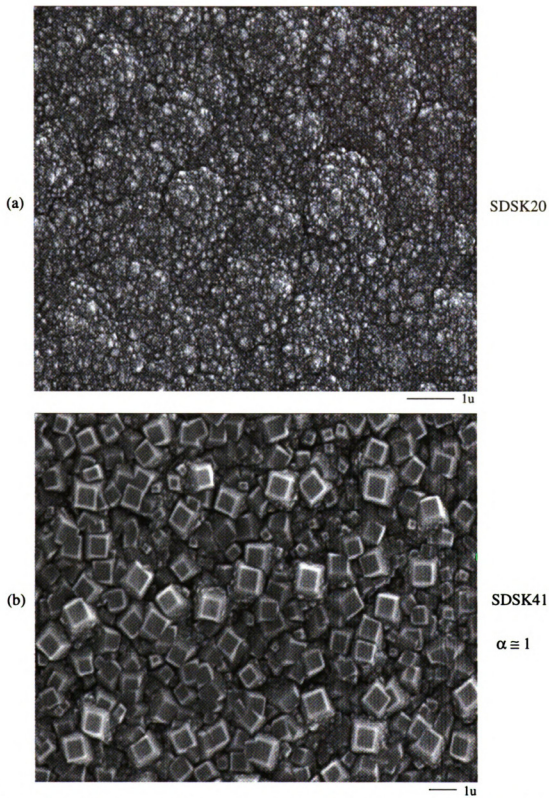


Figure 6.15. SEM pictures of the samples deposited at $f_t = 200$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 750^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 900^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$.

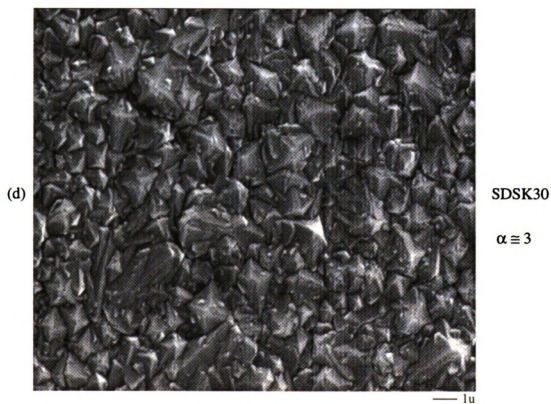
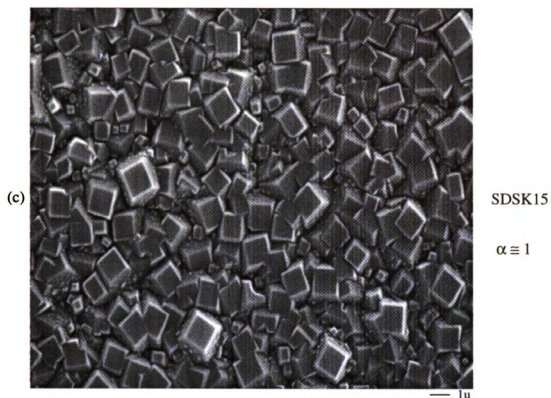


Figure 6.15. Continued.

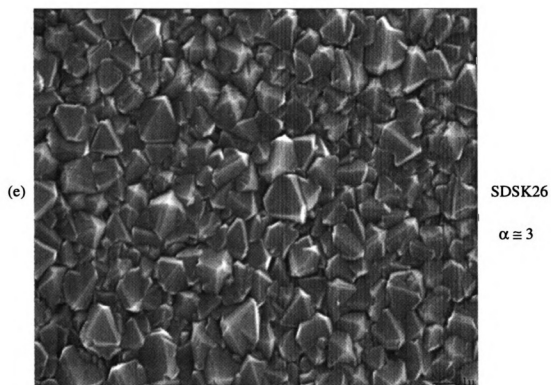


Figure 6.15. Continued.

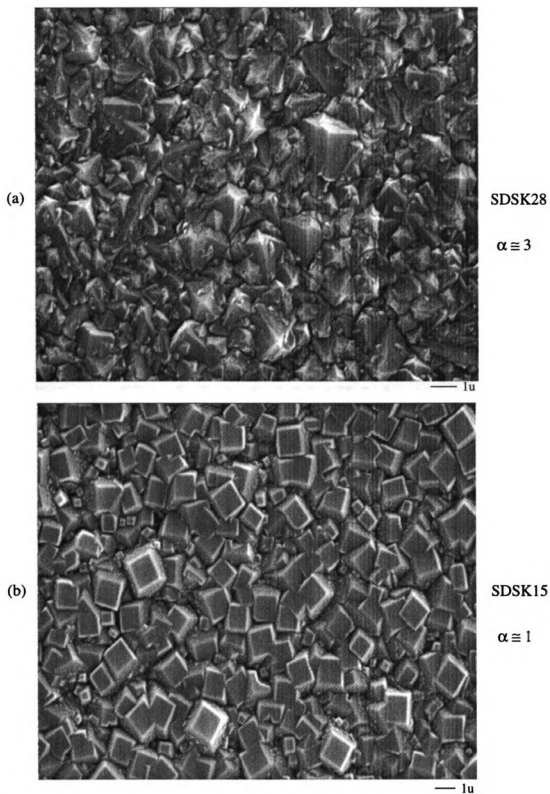


Figure 6.16. SEM pictures of the samples deposited at $f_t = 200$ sccm, $T_s = 850^\circ\text{C}$, and (a) $\text{CH}_4/\text{H}_2 = 1.0\%$, (b) $\text{CH}_4/\text{H}_2 = 1.50\%$, and (c) $\text{CH}_4/\text{H}_2 = 2.0\%$.

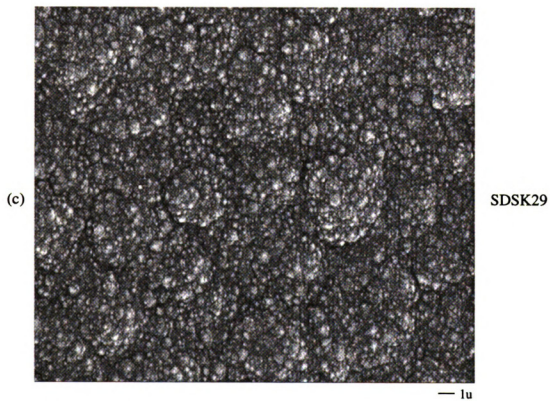


Figure 6.16. Continued.

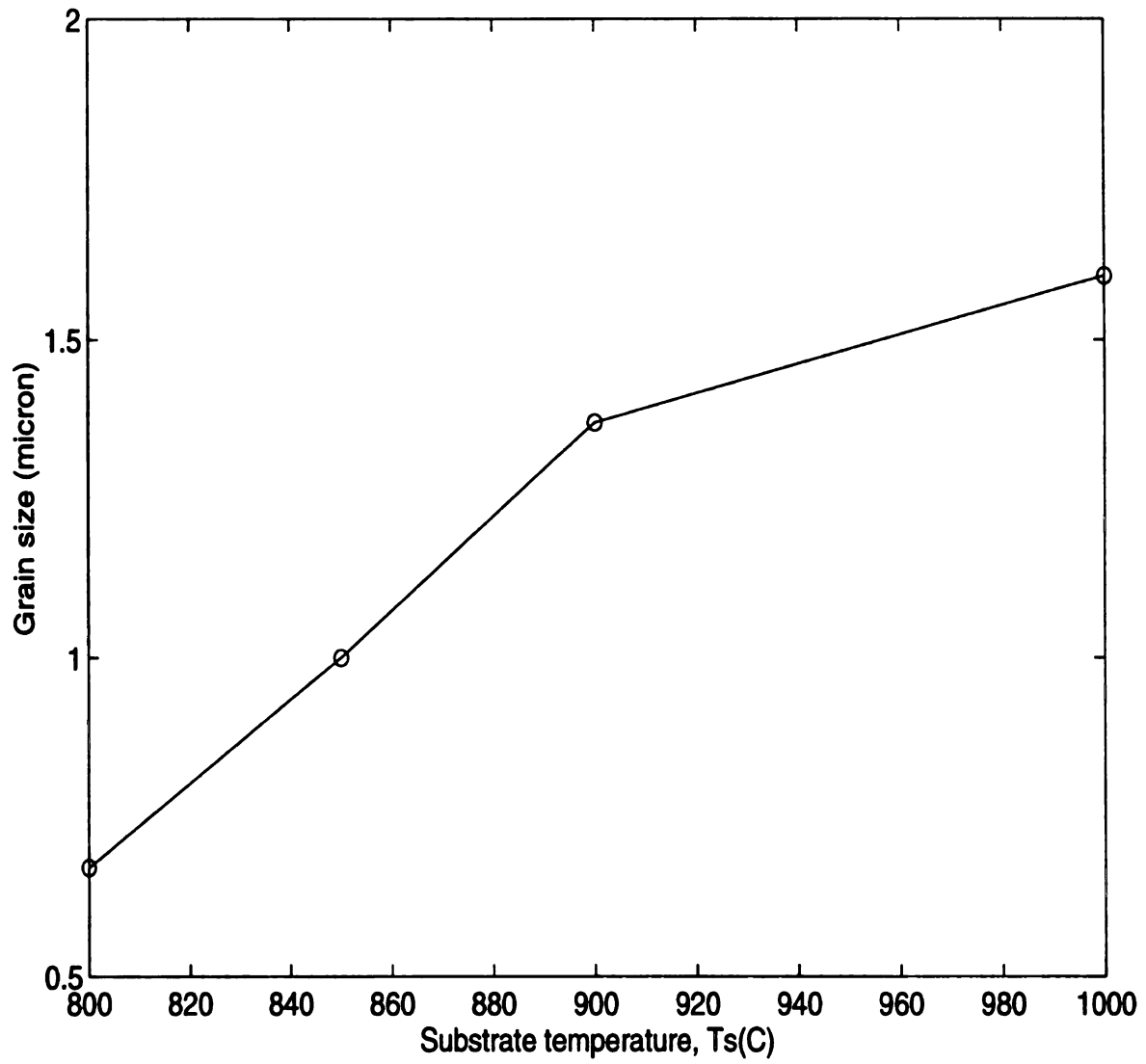


Figure 6.17. Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 200$ sccm.

6.2.1.1.3 Total gas flow rate, $f_t = 60$ sccm

For $f_t = 60$ sccm a field map that related field morphology (expressed by the growth parameter α) to methane concentration in hydrogen, CH_4/H_2 , and substrate temperature, T_s , was developed as shown in Figure 6.18 (a). Figure 6.18 (b) summarizes the morphology field map of 60 sccm total gas flow rate. At this flow rate films with $\{100\}$ morphology (i.e., $\alpha \cong 1 - 2.5$) were deposited at substrate temperature range of $750 \leq T_s \leq 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.0\%$, at $T_s = 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.50\%$, and at $850 \leq T_s \leq 900^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 2.0\%$. Films with $\{111\}$ morphology (i.e., $\alpha \cong 3$) grew at the substrate range of $900 \leq T_s \leq 1000^\circ\text{C}$ when $1.0 \leq \text{CH}_4/\text{H}_2 \leq 1.50\%$ and at $T_s = 1000^\circ\text{C}$ when $2.0 \leq \text{CH}_4/\text{H}_2 \leq 3.0\%$.

Figure 6.19 shows the variation of film surface morphology with T_s for CH_4/H_2 fixed at 1.50%. For $750 \leq T_s \leq 800^\circ\text{C}$ the cauliflower structure was favored. For $T_s = 850^\circ\text{C}$ the surface morphology of the film was $\{100\}$ (i.e., $\alpha \cong 1$) and no twinning was observed on the crystals. For $900 \leq T_s \leq 1000^\circ\text{C}$ $\{111\}$ (i.e., $\alpha \cong 3$) morphology was predominant and the crystals were twinned and had rough surfaces.

Figure 6.20 illustrates the plot of the growth parameter α vs. substrate temperature for $\text{CH}_4/\text{H}_2 = 1.0\%$. The α parameter decreased sharply from $\alpha \cong 2.5$ (i.e., crystals with small $\{100\}$ top face and sloped side faces) to $\alpha \cong 1$ (i.e., cubic crystals) as the substrate temperature increased from 750°C to 800°C . It experienced an abrupt increase to $\alpha \cong 3$ as the substrate temperature increased from 850°C to 900°C .

Figure 6.21 illustrates the variation of film morphology with CH_4/H_2 for T_s fixed at 850°C . For $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$ the surface morphology was $\{100\}$ (i.e., $\alpha \equiv 1$) which changed to cauliflower as CH_4/H_2 was increased to 3.0% .

It should be noted that the $\{100\}$ films that were assigned the same α value were not identical in appearance. Some had rough (jagged) edges (Figure 6.22) and majority had smooth edges (Figure 6.19 (c)). The $\{111\}$ films which were assigned $\alpha \equiv 3$ did not look identical, either. Some were twinned and some did not have a significant twinning population. Furthermore, some $\{111\}$ films had rough faces and some had smooth faces (Figure 6.23). This means that the α parameter though useful in describing various crystal habits in the crystal CVD process, did not explain all details about the film morphology.

For CH_4/H_2 fixed at 1.50% the average grain size increased from $1.1\ \mu\text{m}$ for $T_s = 850^\circ\text{C}$ to $2.2\ \mu\text{m}$ for $T_s = 900^\circ\text{C}$ and decreased to $\sim 1.80\ \mu\text{m}$ for $T_s = 1000^\circ\text{C}$ as shown in Figure 6.24.

The variation of the average grain size with the methane gas concentration for $T_s = 850^\circ\text{C}$ is shown in Figure 6.25. The average grain size decreased from $\sim 1.3\ \mu\text{m}$ to $1.10\ \mu\text{m}$ as CH_4/H_2 was increased from 1.0% to 1.50% and increased to $1.70\ \mu\text{m}$ as CH_4/H_2 was further increased to 2.0% .

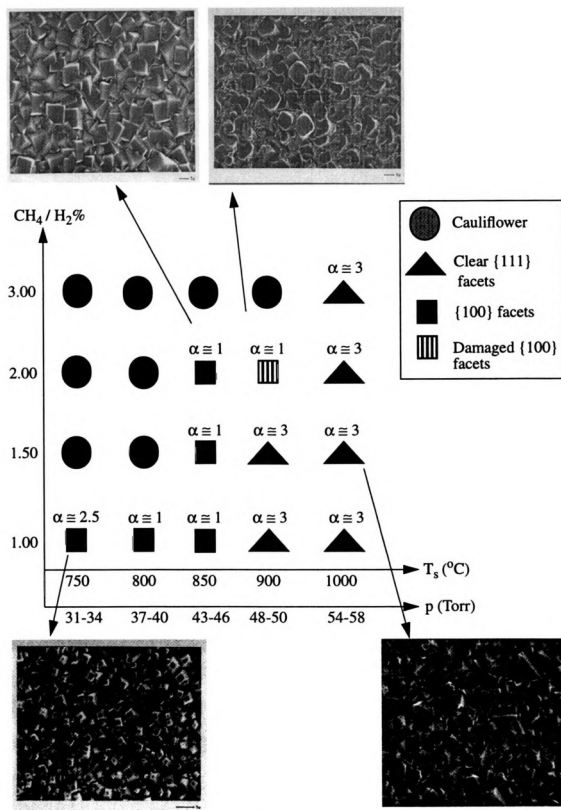


Figure 6.18. (a). Morphology field map for total flow rate $f_t = 60$ sccm.

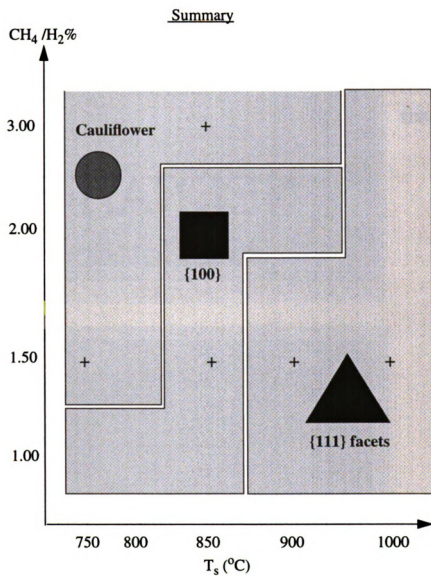


Figure 6.18 (b). Summary of morphology field map for $f_t = 60$ sccm.

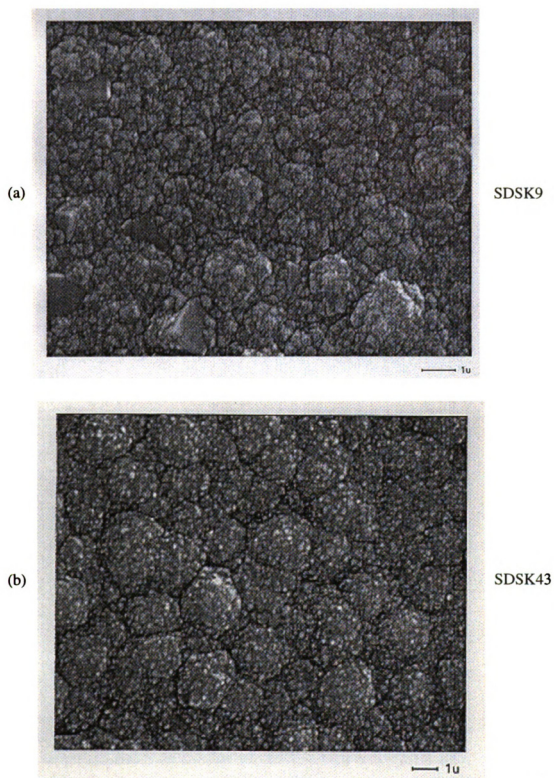
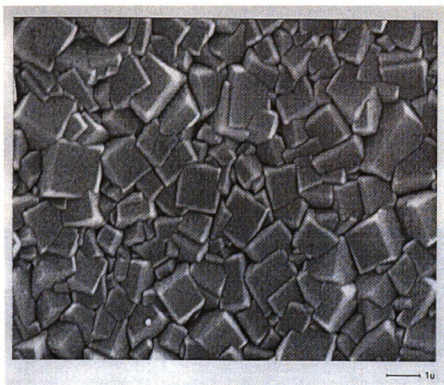


Figure 6.19. SEM pictures of the samples deposited at $f_t = 60$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and (a) $T_s = 750^\circ\text{C}$, (b) $T_s = 800^\circ\text{C}$, (c) $T_s = 850^\circ\text{C}$, (d) $T_s = 900^\circ\text{C}$, and (e) $T_s = 1000^\circ\text{C}$.

(c)



SDSK7r

 $\alpha \equiv 1$

(d)



SDSK12

 $\alpha \equiv 3$

Figure 6.19. Continued.

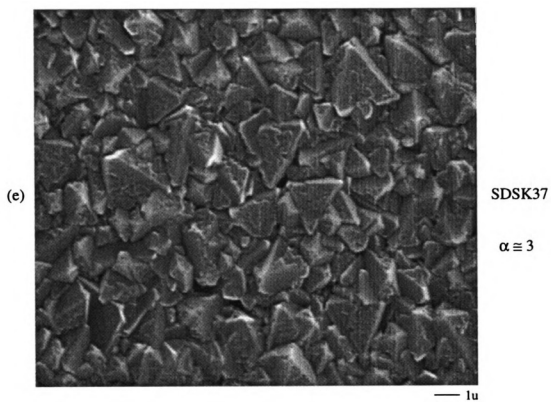


Figure 6.19. Continued.

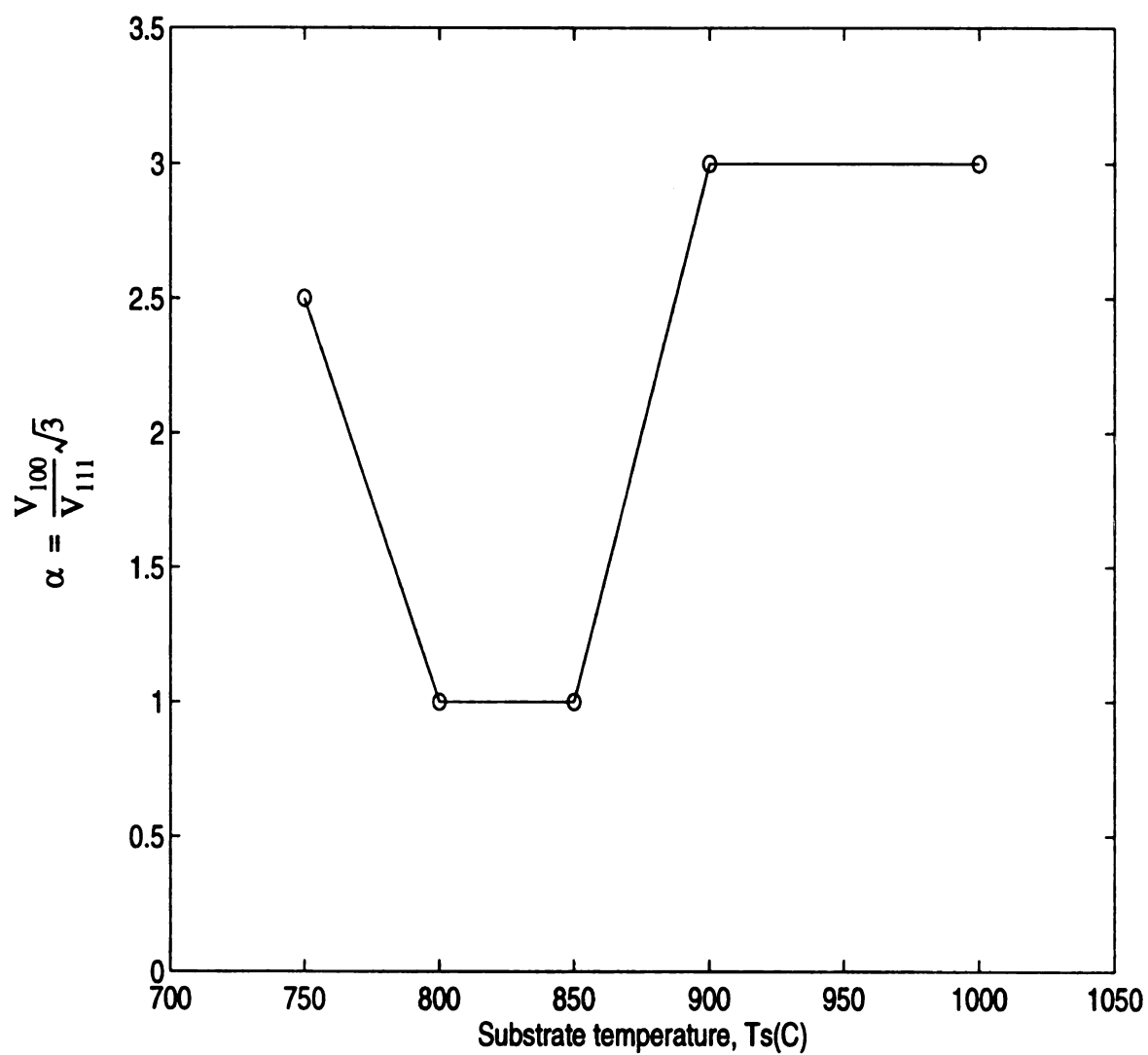


Figure 6.20. Variation of the growth parameter with substrate temperature for samples deposited at $f_t = 60$ sccm and $\text{CH}_4/\text{H}_2 = 1.0\%$.

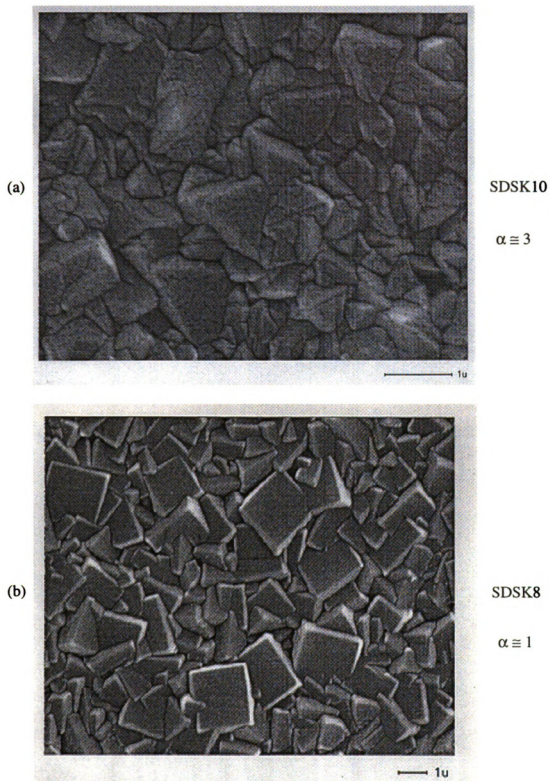
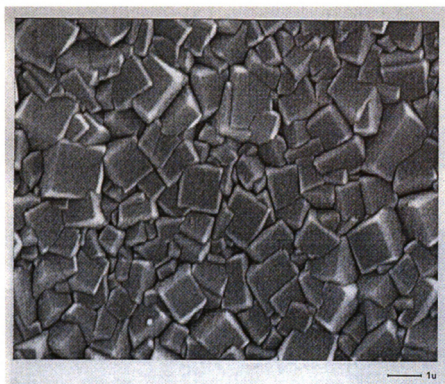


Figure 6.21. SEM pictures of the samples deposited at $f_t = 60$ sccm, $T_s = 850^\circ\text{C}$, and $\text{CH}_4/\text{H}_2 =$ (a) 0.50%, (b) 1.0%, (c) 1.50%, (d) 2.0%, and (e) 3.0%.

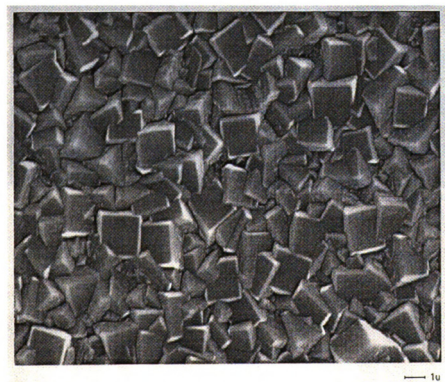
(c)



SDSK7r

 $\alpha \cong 1$

(d)



SDSK11

 $\alpha \cong 1$

Figure 6.21. Continued.

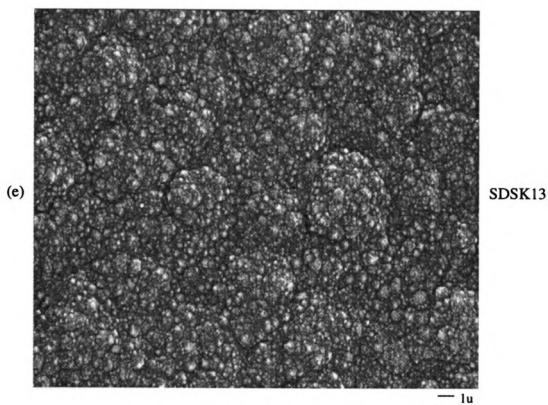
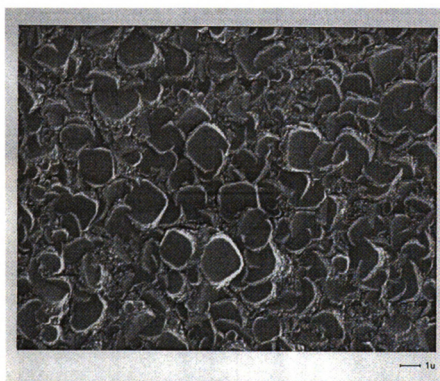


Figure 6.21. Continued.



SDSK19

 $\alpha \cong 1$

Figure 6.22. SEM picture of a $\{100\}$ film with rough (jagged) edges.

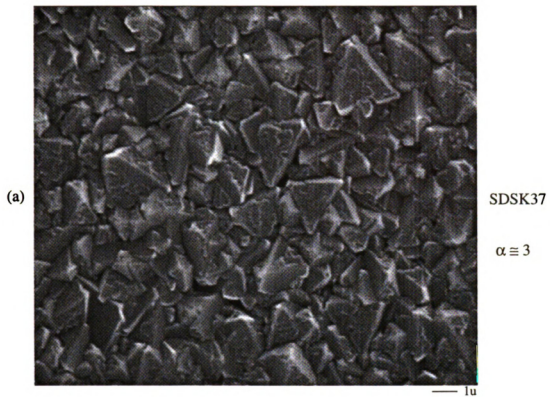


Figure 6.23. SEM pictures of $\{111\}$ films with (a) rough faces and (b) smooth faces.

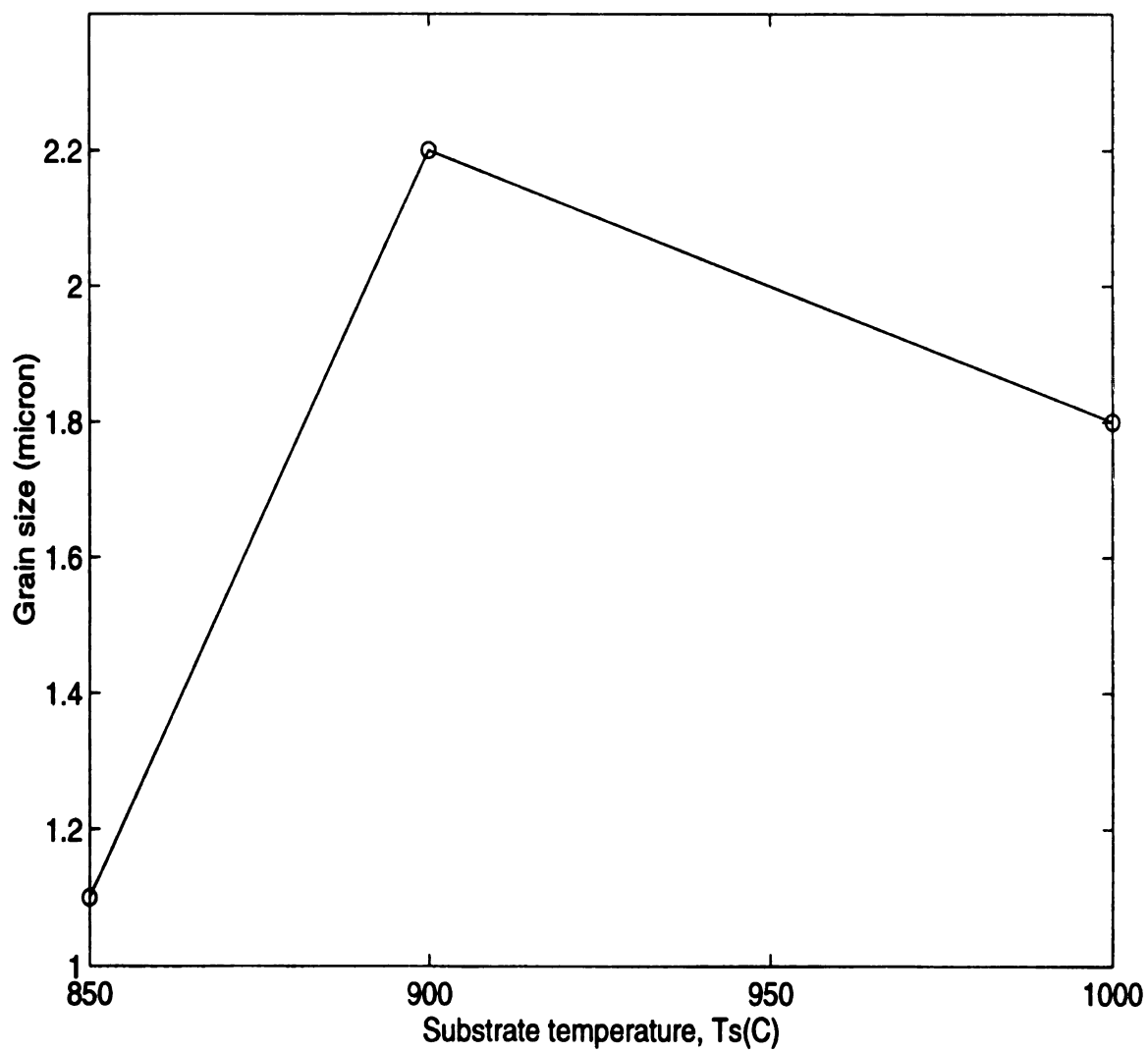


Figure 6.24. Plot of average grain size vs. T_s for $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 60$ sccm.

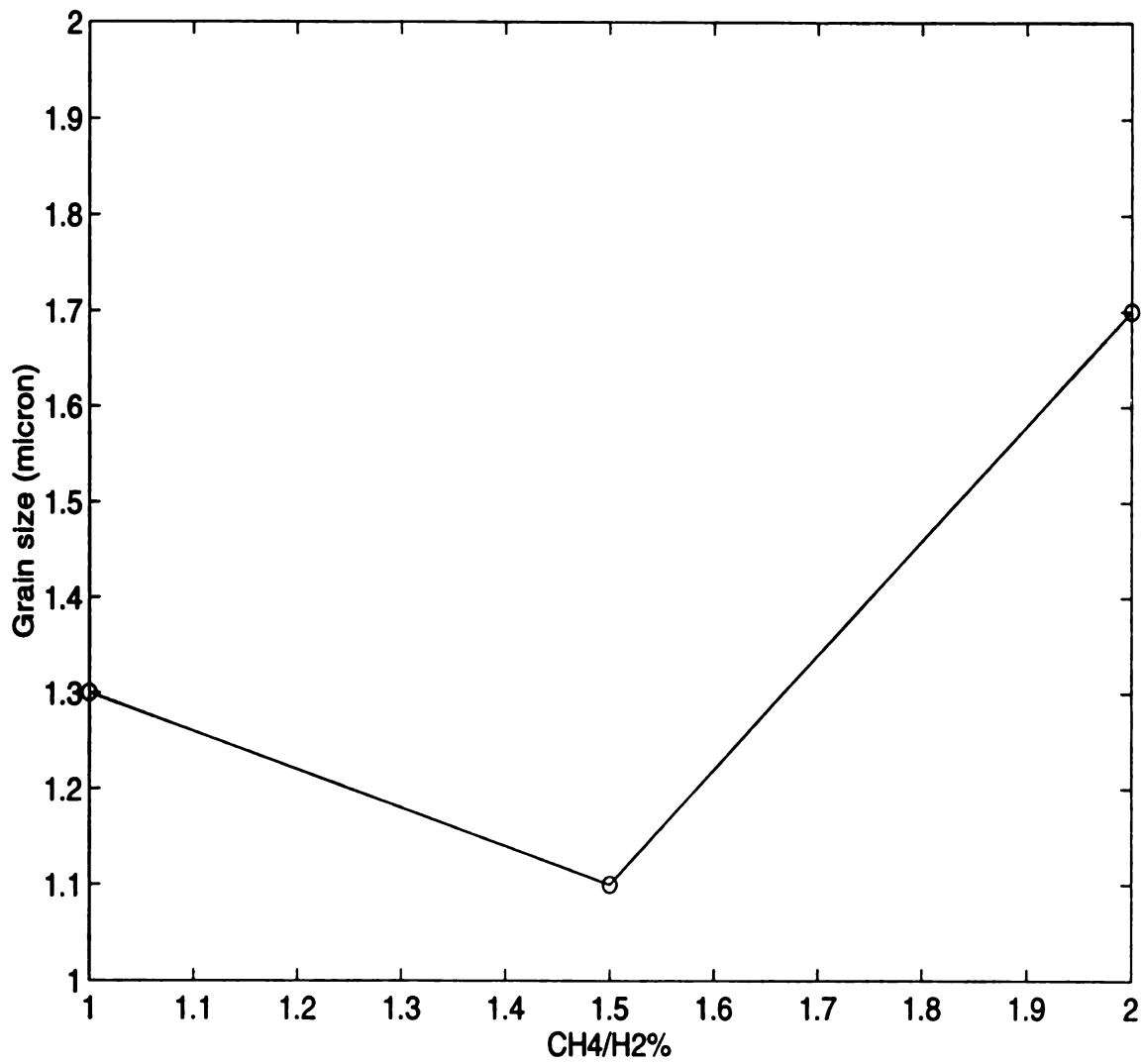


Figure 6.25. Plot of average grain size vs. $\text{CH}_4/\text{H}_2\%$ for $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm.

6.2.1.2 Structural quality

6.2.1.2.1 Total gas flow rate, $f_t = 400$ sccm

Figure 6.26 shows the dependence of the film structural quality on the substrate temperature (hence pressure and power) for the total gas flow rate fixed at 400 sccm. The Figure shows the Raman spectra of the samples deposited at $\text{CH}_4/\text{H}_2=1.50\%$ and $f_t=400$ sccm with $T_s \in [700, 1000]^\circ\text{C}$. Figure 6.27 shows the variation of FWHM with the substrate temperature. As shown, the FWHM decreased with T_s (i.e., film structural quality improved with T_s) in its respected range of $T_s \in [700, 1000]^\circ\text{C}$.

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is apparent from Figure 6.28 which shows Raman spectra of the CVD diamond films deposited at a fixed substrate temperature of 850°C and a fixed total gas flow rate of $f_t=400$ sccm with CH_4/H_2 varying between 1.0% and 2.0%. The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ is shown in Figure 6.29. The FWHM increased sharply with methane concentration in hydrogen. The graphitic content of the diamond films also increased with methane concentration. This is evident from the broad peaks around 1550 cm^{-1} in the Raman spectra of Figure 6.28.

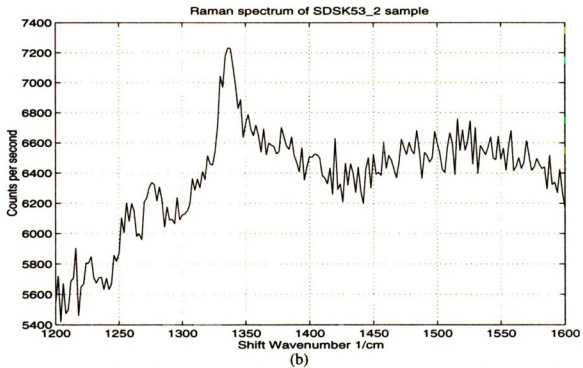
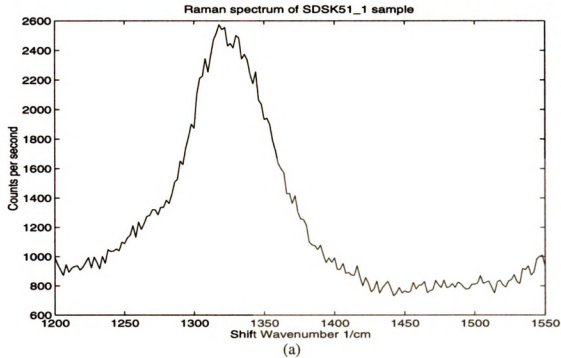


Figure 6.26. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_1 = 400$ sccm with $T_s =$ (a) 700°C , (b) 850°C , and (c) 1000°C .

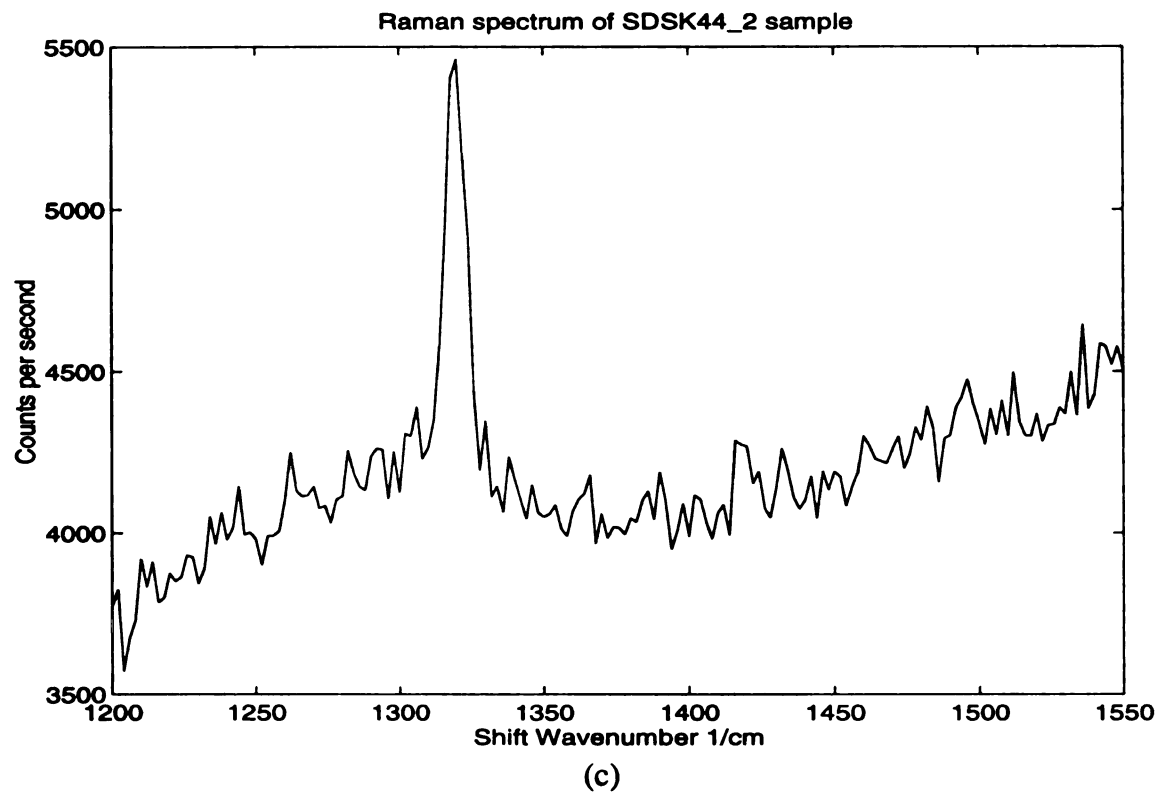
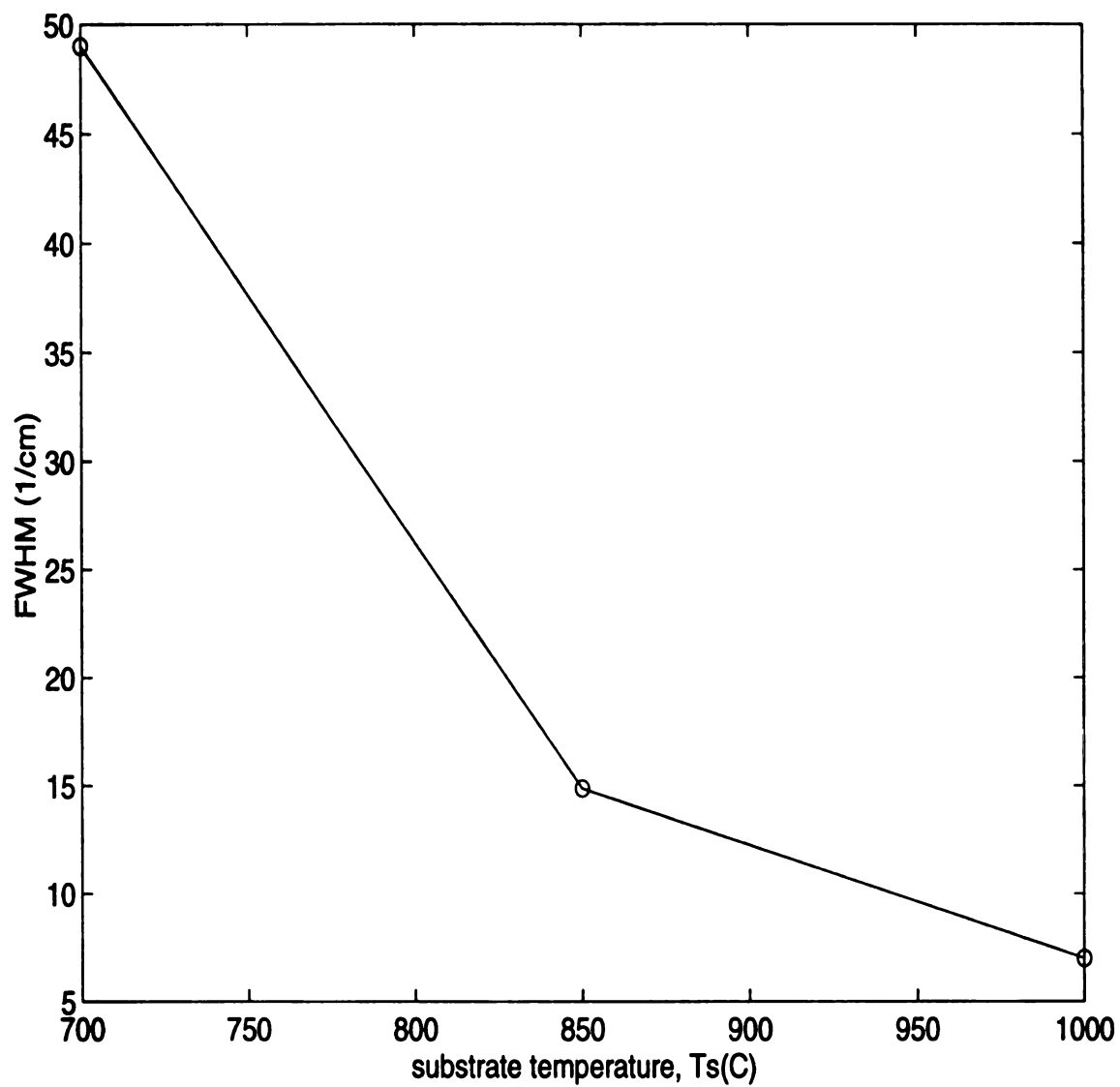


Figure 6.26. Continued.



Sample	T_s (°C)	FWHM (1/cm)
SDSK51_1	700	49
SDSK53_2	850	14.87
SDSK44_2	1000	7.0

Figure 6.27. FWHM vs. substrate temperature for diamond films deposited at $f_t = 400$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

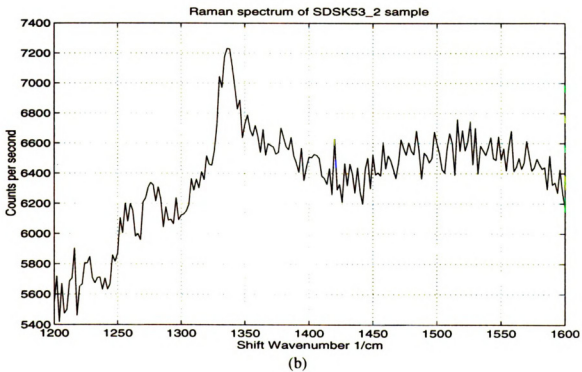
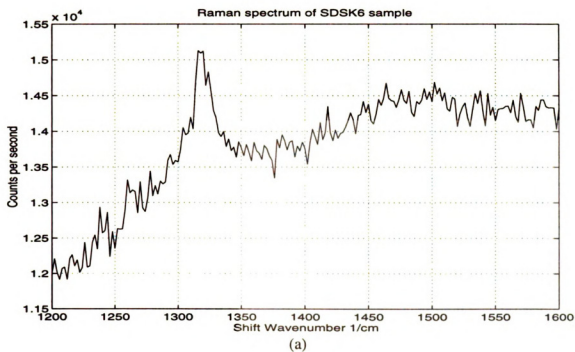


Figure 6.28. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 400$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 2.00%.

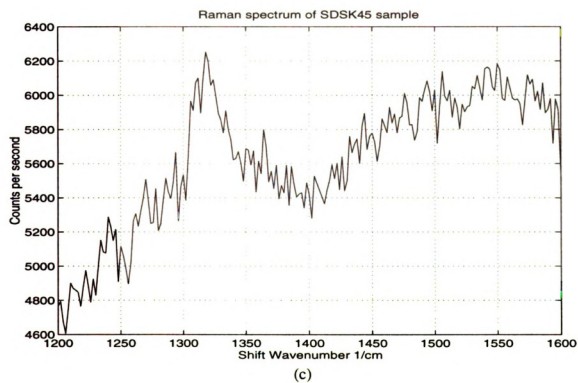
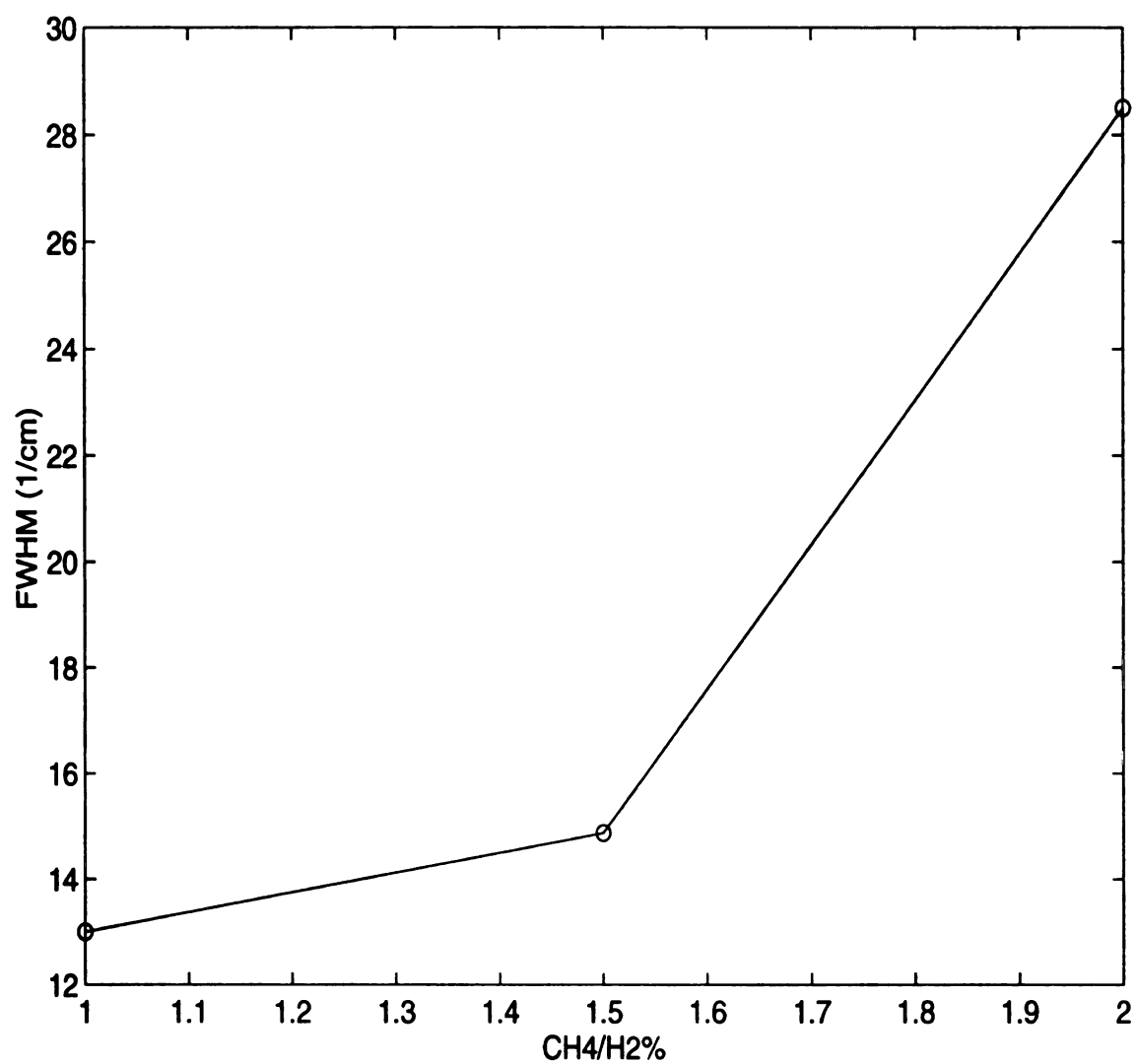


Figure 6.28. Continued.



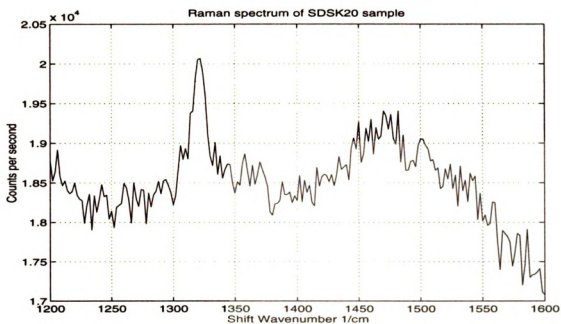
Sample	$\text{CH}_4/\text{H}_2\%$	FWHM ($1/\text{cm}$)
SDSK6	1.00	13.00
SDSK53_2	1.50	14.87
SDSK45	2.00	28.50

Figure 6.29. FWHM vs. $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $f_t = 400$ sccm and $T_s = 850^\circ\text{C}$.

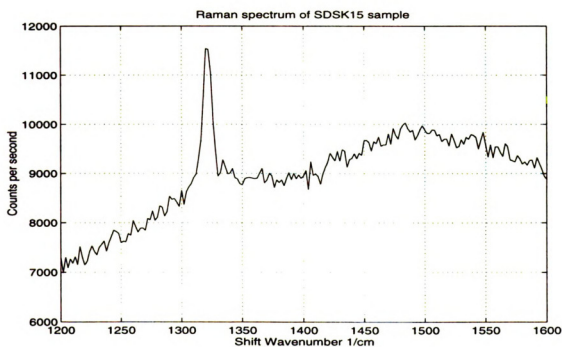
6.2.1.2.2 Total gas flow rate, $f_t = 200$ sccm

Figure 6.30 shows the dependence of the film structural quality on the substrate temperature (hence pressure and power) for the total gas flow rate fixed at 200 sccm. The Figure shows the Raman spectra of the samples deposited at $\text{CH}_4/\text{H}_2=1.50\%$ and $f_t=200$ sccm with $T_s = 750^\circ\text{C} - 1000^\circ\text{C}$. The minimum FWHM of 7.53 cm^{-1} occurred at $T_s = 850^\circ\text{C}$ as shown in Figure 6.31.

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is apparent from Figure 6.32 which shows Raman spectra of the CVD diamond films deposited at a fixed substrate temperature of 850°C and a fixed total gas flow rate of $f_t=200$ sccm with CH_4/H_2 varying between 1.0% and 3.0%. The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ is shown in Figure 6.33. The FWHM was minimum (i.e., 7.53 cm^{-1}) for $\text{CH}_4/\text{H}_2 = 1.50\%$. The FWHM experienced a sharp increase for $\text{CH}_4/\text{H}_2 > 1.50\%$ indicating that for $T_s = 850^\circ\text{C}$ the graphitic content of the diamond films sharply increased when CH_4/H_2 exceeded 1.50%.



(a)



(b)

Figure 6.30. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_1 = 200$ sccm with $T_s =$ (a) 750°C , (b) 850°C , and (c) 1000°C .

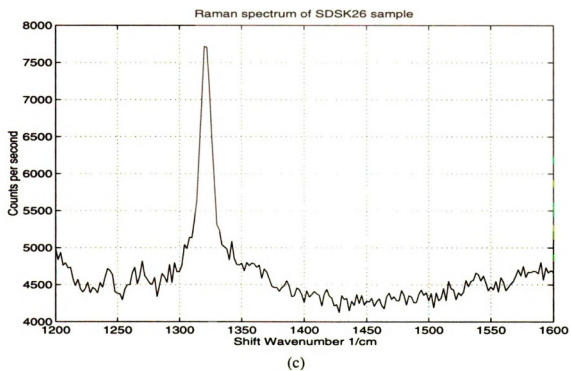
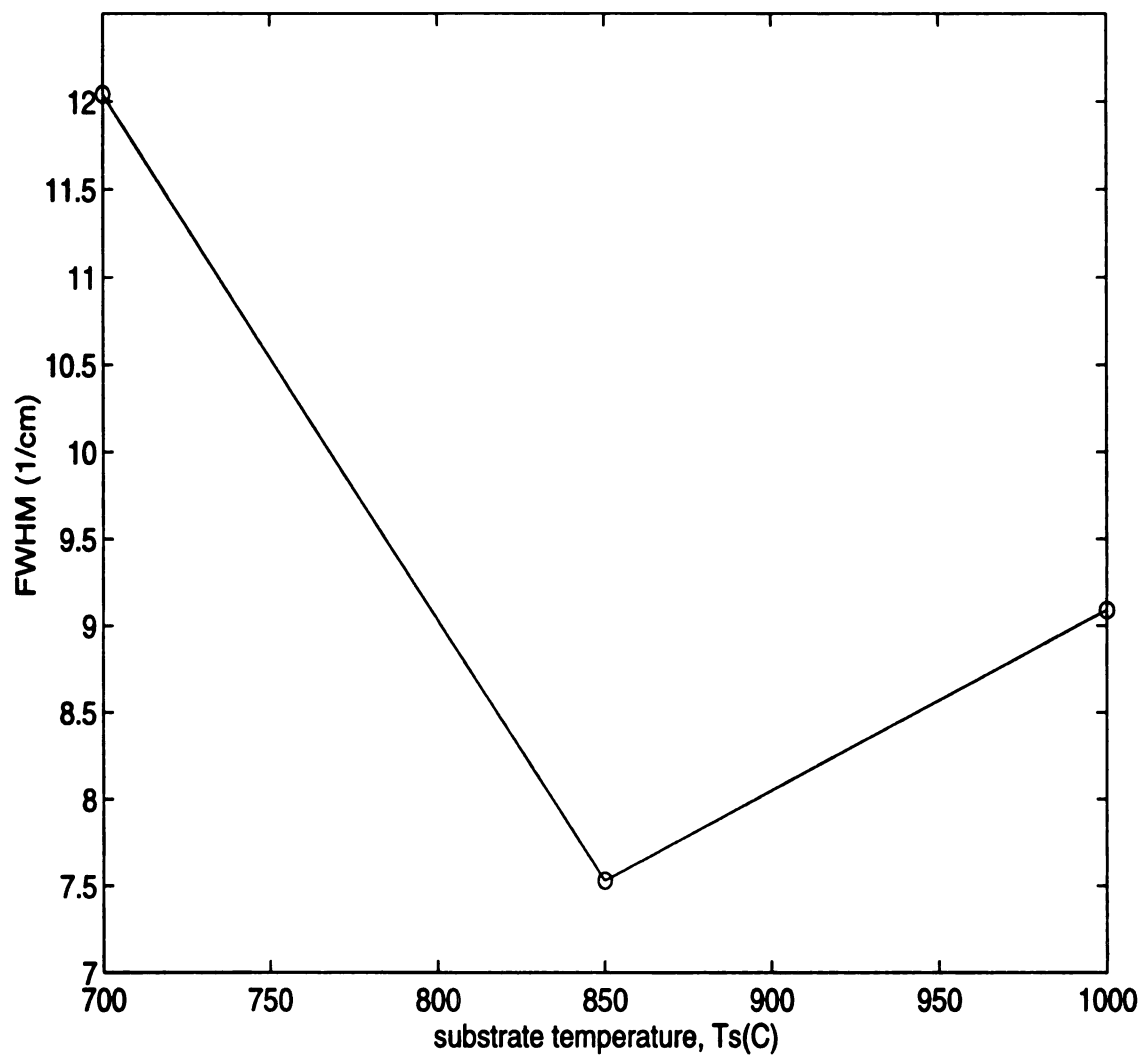


Figure 6.30. Continued.



Sample	T_s (°C)	FWHM (1/cm)
SDSK20	750	12.04
SDSK15	850	7.53
SDSK26	1000	9.09

Figure 6.31. FWHM vs. substrate temperature for diamond films deposited at $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$.

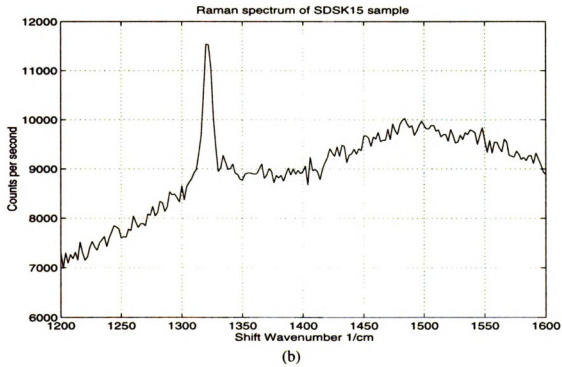
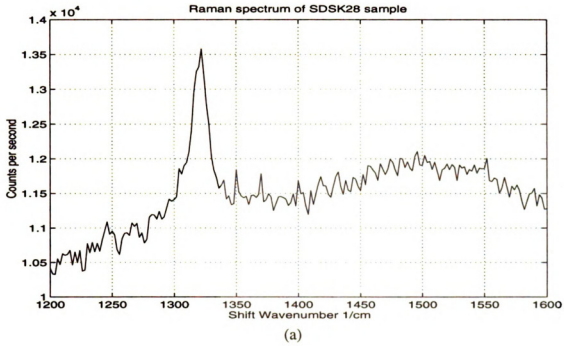


Figure 6.32. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 200$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 3.00%.

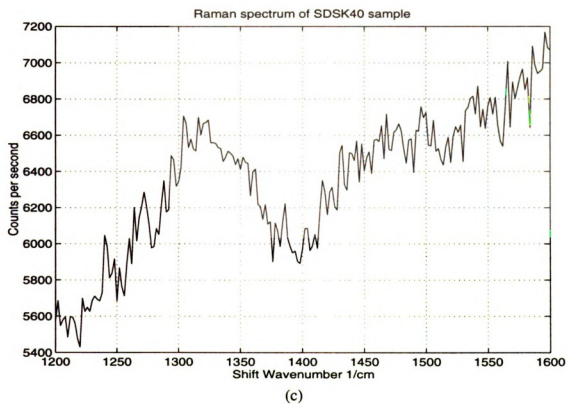
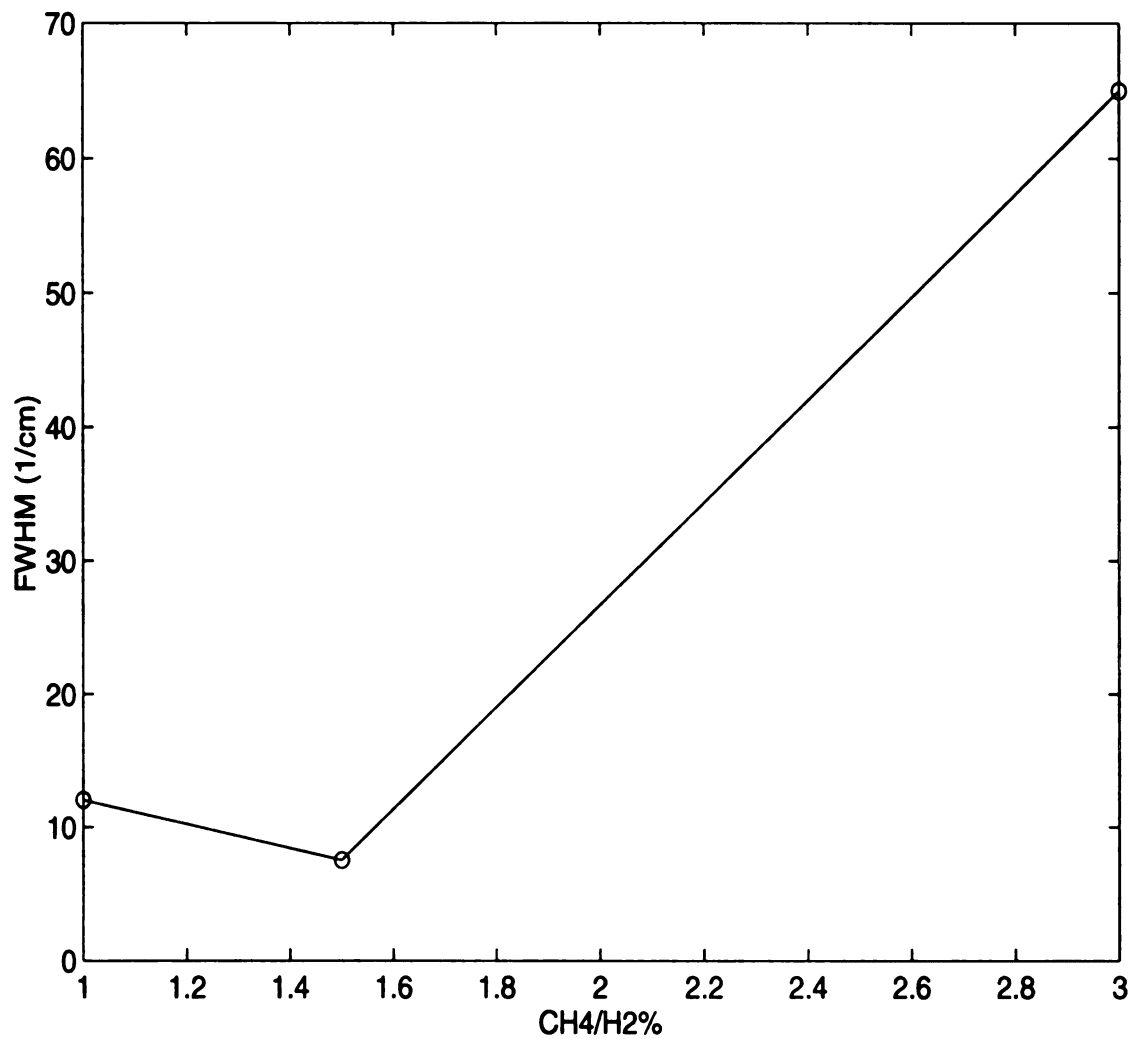


Figure 6.32. Continued.



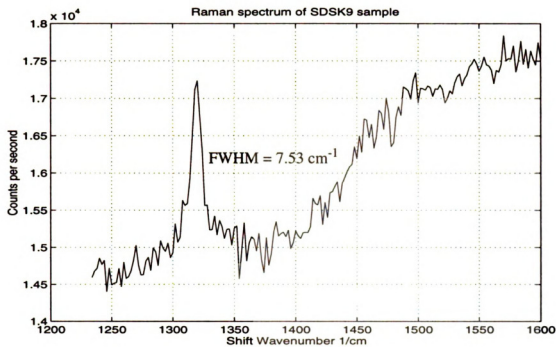
Sample	CH ₄ /H ₂ %	FWHM (1/cm)
SDSK28	1.00	12.04
SDSK15	1.50	7.53
SDSK40	3.00	65.0

Figure 6.33. FWHM vs. CH₄/H₂% for diamond films deposited at $f_t = 200$ sccm and $T_s = 850^\circ\text{C}$.

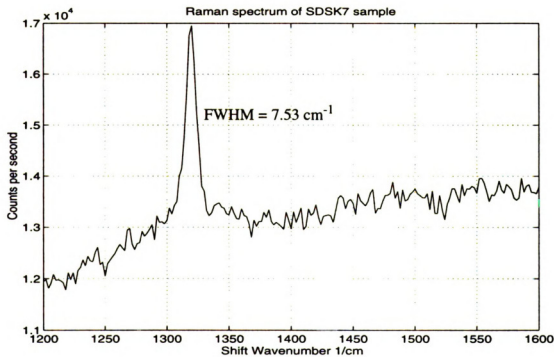
6.2.1.2.3 Total gas flow rate, $f_t = 60$ sccm

Figure 6.34 shows the variation of the Raman spectra (i.e., structural quality) of the samples with the substrate temperature for a fixed methane concentration of $\text{CH}_4/\text{H}_2 = 1.50\%$ and a fixed flow rate of 60 sccm. The FWHM was measured to be 7.53 cm^{-1} for the three samples deposited at $T_s = 750^\circ\text{C}$, $T_s = 850^\circ\text{C}$, and $T_s = 1000^\circ\text{C}$ indicating that the diamond film structural quality did not vary with the substrate temperature when CH_4/H_2 was fixed at 1.50%. The graphitic content of the diamond films, however, decreased with the substrate temperature. This is evident from the broad peak about 1550 cm^{-1} of the Raman spectra of Figure 6.34.

The effect of methane concentration in hydrogen, $\text{CH}_4/\text{H}_2\%$, on the film structural quality is apparent from Figure 6.35 which shows Raman spectra of the CVD diamond films deposited at a fixed substrate temperature of 850°C with CH_4/H_2 varying between 1.0% and 3.50%. The plot of FWHM vs. $\text{CH}_4/\text{H}_2\%$ is shown in Figure 6.36. The FWHM decreased from 8.32 cm^{-1} for $\text{CH}_4/\text{H}_2 = 1.0\%$ to 7.53 cm^{-1} for $\text{CH}_4/\text{H}_2 = 1.50\%$ and increased sharply to 49.7 cm^{-1} for $\text{CH}_4/\text{H}_2 = 3.50\%$.



(a)



(b)

Figure 6.34. Raman spectra for diamond films deposited at $\text{CH}_4/\text{H}_2=1.50\%$ and $f_t = 60$ with $T_s =$ (a) 750°C , (b) 850°C , and (c) 1000°C .

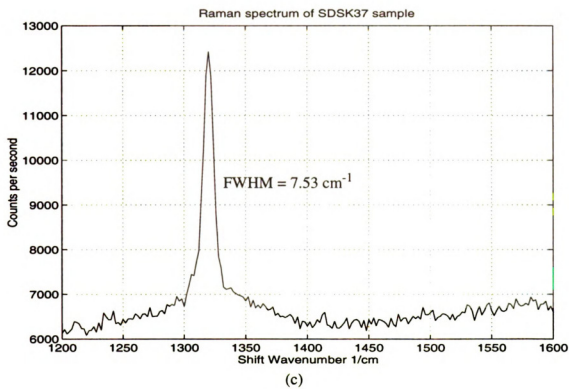


Figure 6.34. Continued.

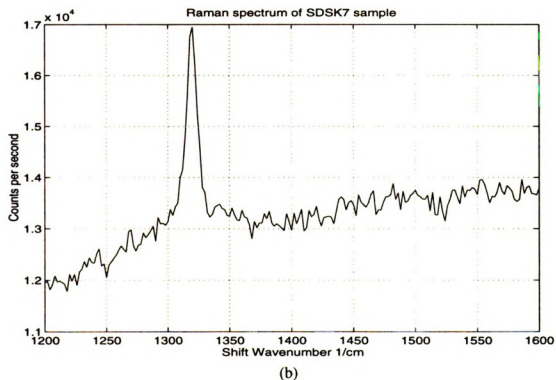
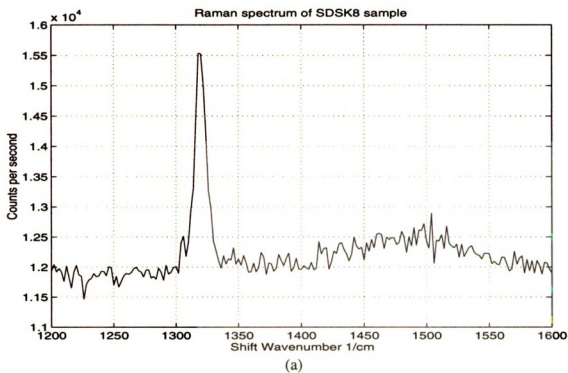


Figure 6.35. Raman spectra for diamond films deposited at $T_s = 850^\circ\text{C}$ and $f_t = 60$ sccm with $\text{CH}_4/\text{H}_2 =$ (a) 1.00%, (b) 1.50%, and (c) 3.50%.

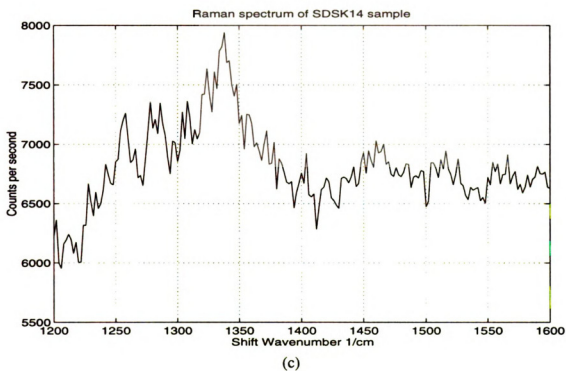
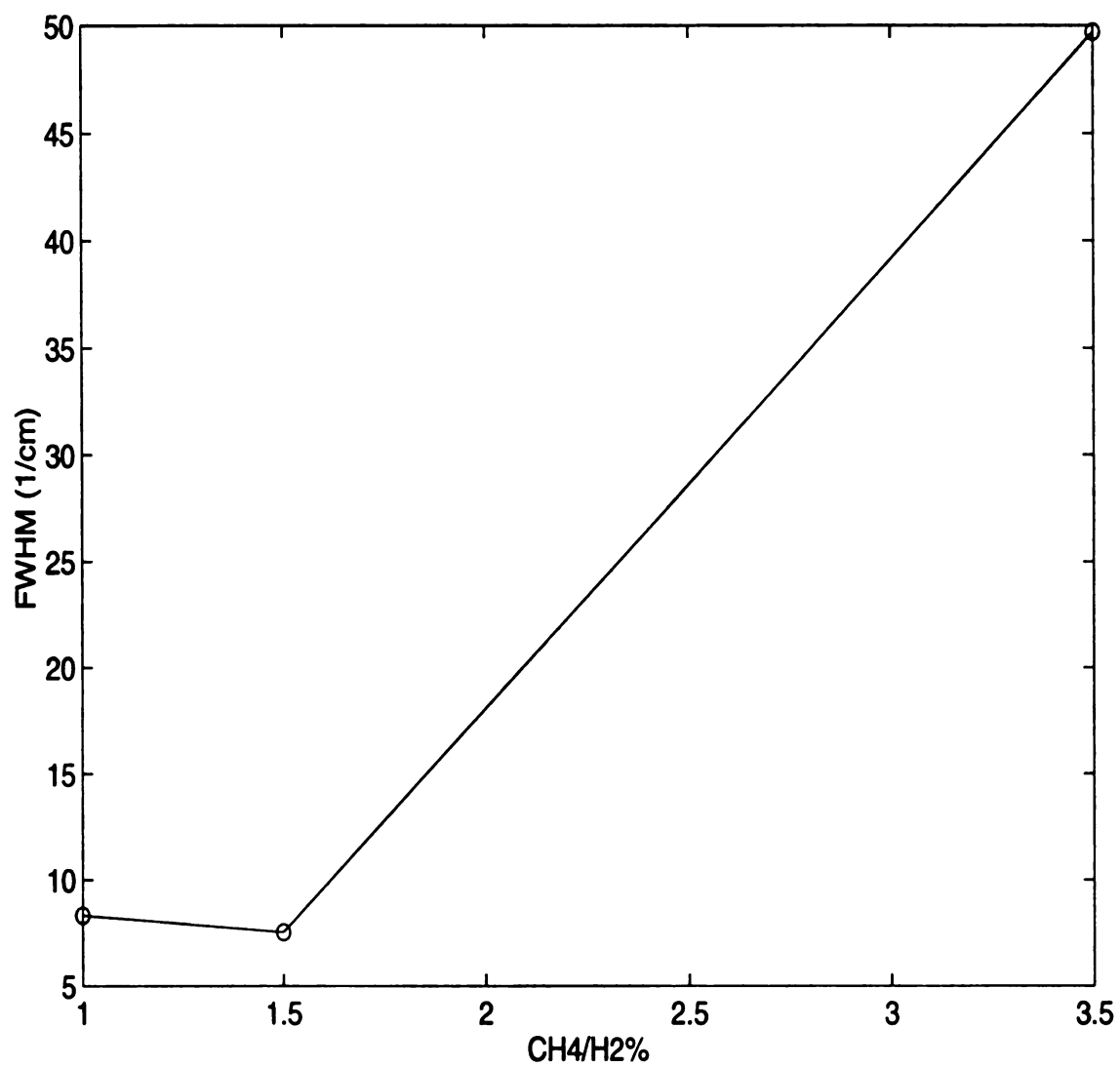


Figure 6.35. Continued.



Sample	CH ₄ /H ₂ %	FWHM (1/cm)
SDSK8	1.00	8.32
SDSK7	1.50	7.53
SDSK14	3.00	49.7

Figure 6.36. FWHM vs. CH₄/H₂% for diamond films deposited at $f_t = 60$ sccm and $T_s = 850^\circ\text{C}$.

6.2.2 Reactor performance (Y_2) vs. various input variables

In what follows, linear growth rate and carbon conversion efficiency vs. methane concentration and substrate temperature for various flow rates are investigated.

6.2.2.1 Linear growth rate

6.2.2.1.1 Total gas flow rate, $f_t = 400$ sccm

Film linear growth rates have been calculated via the method described in Section 4.5.4 (eq. 4.1.). This measurement method determines the average film growth rate over the substrate surface. Figure 6.37 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s with the flow rate fixed at 400 sccm. The value of growth parameter α is included in Figure 6.37. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 6.37. The linear growth rate increased with the substrate temperature up to $T_s = 950^\circ\text{C}$ and dropped beyond this substrate temperature. The linear growth rate exhibited a similar behavior with respect to CH_4/H_2 . It increased with CH_4/H_2 up to $\text{CH}_4/\text{H}_2 = 1.50\%$ and decreased as the methane concentration exceeded this value. For $f_t = 400$ sccm the deposition condition $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 950^\circ\text{C}$ resulted in the maximum linear growth rate of $0.665 \mu\text{m/hr}$ where $\alpha \cong 3$.

6.2.2.1.2 Total gas flow rate, $f_t = 200$ sccm

Figure 6.38 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s with the flow rate fixed at 200 sccm. The value of growth parameter α is included in Figure 6.38. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are

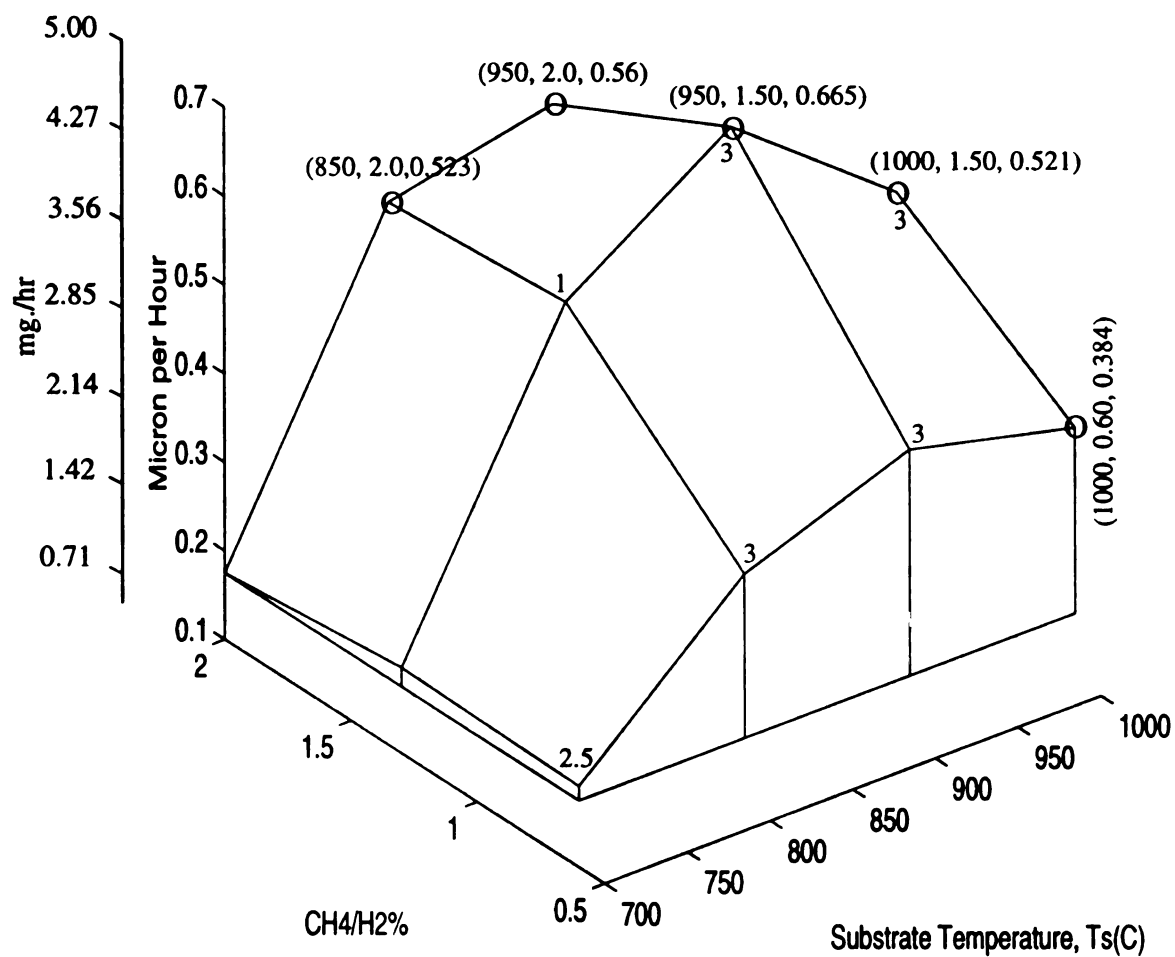


Figure 6.37. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 400 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates.

also included in Figure 6.38. The linear growth rate increased with the substrate temperature up to $T_s = 900^\circ\text{C}$ and dropped beyond this substrate temperature. The linear growth rate exhibited a similar trend with respect to CH_4/H_2 . It increased with CH_4/H_2 up to $\text{CH}_4/\text{H}_2 = 2.0\%$ and decreased for higher methane concentrations. For $f_t = 200$ sccm the deposition condition $\text{CH}_4/\text{H}_2 = 2.0\%$ and $T_s = 900^\circ\text{C}$ resulted in the maximum linear growth rate of $0.54 \mu\text{m/hr}$.

6.2.2.1.3 Total gas flow rate, $f_t = 60$ sccm

Figure 6.39 illustrates the dependence of the linear growth rate on CH_4/H_2 and T_s with the total gas flow rate fixed at 60 sccm. The value of growth parameter α is included in Figure 6.39. The $(T_s, \text{CH}_4/\text{H}_2, \mu\text{m/hr})$ coordinates of some points (specified by O) are also included in Figure 6.39. From this Figure it is seen that with the exception of $\text{CH}_4/\text{H}_2 = 3.0\%$ which showed a monotonic increase of the linear growth rate with T_s , the linear growth rate increased with substrate temperature up to $T_s = 900^\circ\text{C}$ and dropped beyond this substrate temperature. With respect to CH_4/H_2 the linear growth rate increased up to $\text{CH}_4/\text{H}_2 = 2.0\%$ and decreased for higher methane concentrations. For $f_t = 60$ sccm the deposition condition $\text{CH}_4/\text{H}_2 = 2.0\%$ and $T_s = 900^\circ\text{C}$ resulted in the maximum linear growth rate of $0.635 \mu\text{m/hr}$. This deposition condition resulted in a $\{100\}$ film (i.e., $\alpha \cong 1$) with rough (jagged) edges.

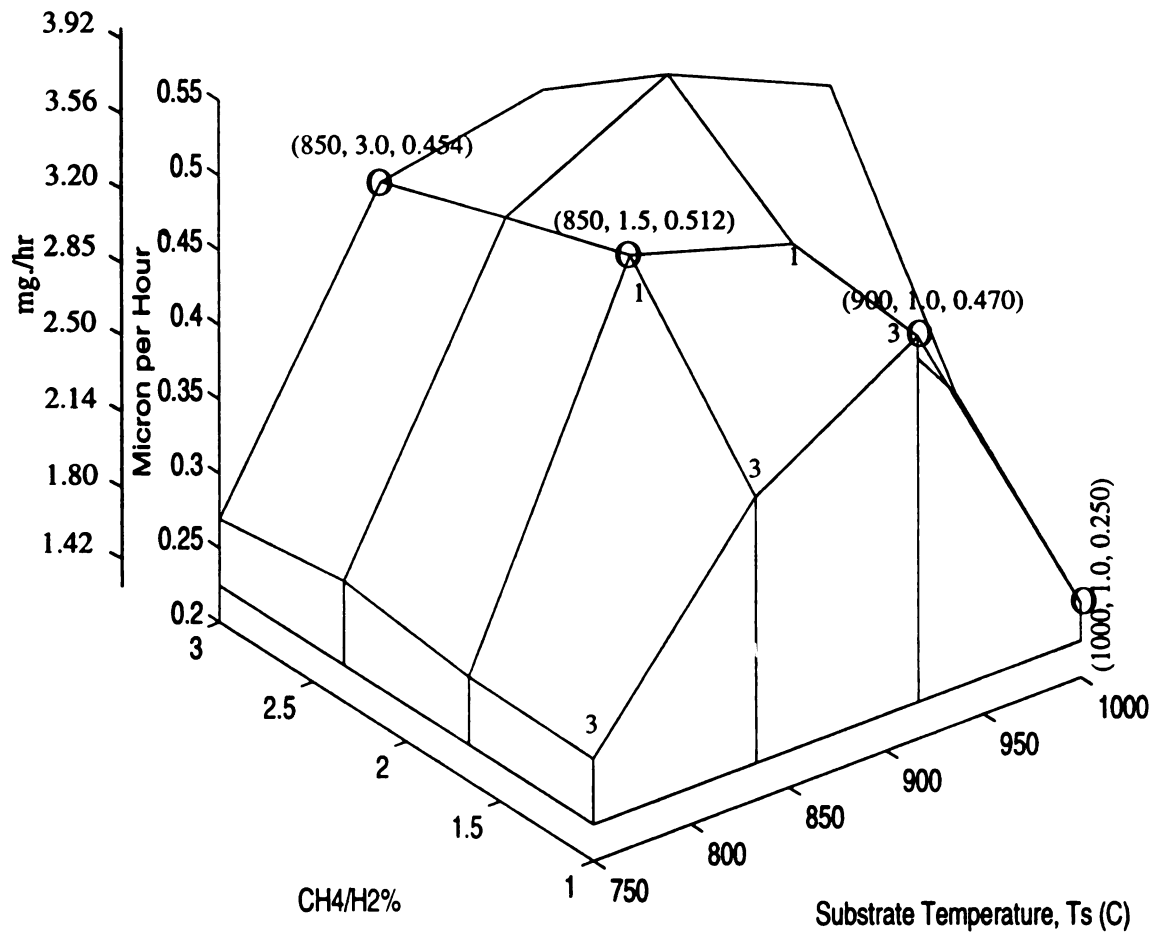


Figure 6.38. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 200 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, um/hr) coordinates.

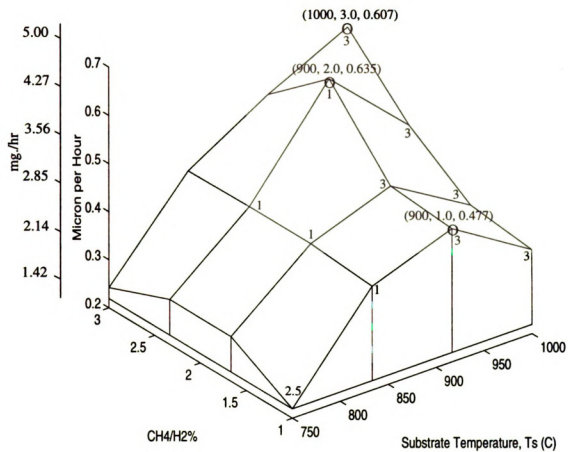


Figure 6.39. Linear growth rate vs. substrate temperature and $\text{CH}_4/\text{H}_2\%$ for 60 sccm total gas flow rate. The coordinate numbers represent the α values. O represents the (T_s , $\text{CH}_4/\text{H}_2\%$, $\mu\text{m/hr}$) coordinates.

6.2.2.2 Carbon conversion efficiency

6.2.2.2.1 Total gas flow rate, $f_t = 400$ sccm

For the flow rate, f_t , fixed at 400 sccm, Figure 6.40 shows the dependence of carbon conversion efficiency on substrate temperature and methane gas concentration in hydrogen. As shown, the carbon conversion efficiency increased with the substrate temperature up to $T_s = 950^\circ\text{C}$ and dropped beyond this substrate temperature (i.e., consistent with the growth rate trend). The carbon conversion efficiency decreased monotonically with the methane gas concentration indicating that although up to a certain point the film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

6.2.2.2.2 Total gas flow rate, $f_t = 200$ sccm

For the flow rate, f_t , fixed at 200 sccm, Figure 6.41 shows the dependence of carbon conversion efficiency on substrate temperature and methane gas concentration in hydrogen. From Figure 6.41 it is seen that with the exception of $T_s = 1000^\circ\text{C}$ which exhibits that the carbon conversion efficiency was larger for $\text{CH}_4/\text{H}_2 = 2.0\%$ than for $\text{CH}_4/\text{H}_2 = 1.50\%$, the carbon conversion efficiency decreased monotonically with the methane gas concentration. This indicates that although up to a certain point the film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

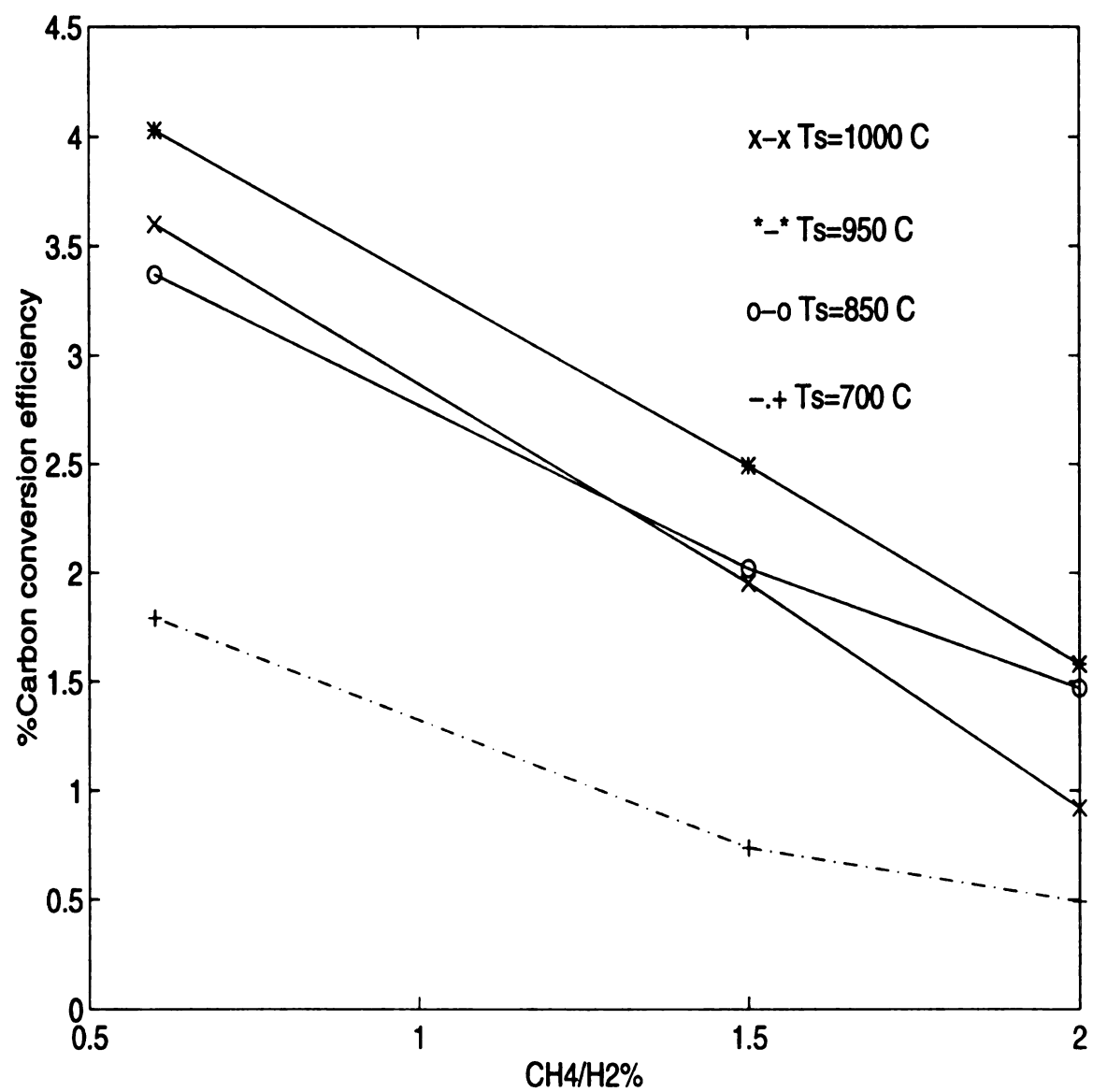


Figure 6.40. Carbon conversion efficiency vs. substrate temperature and CH_4/H_2 for $f_t = 400\text{ sccm}$.

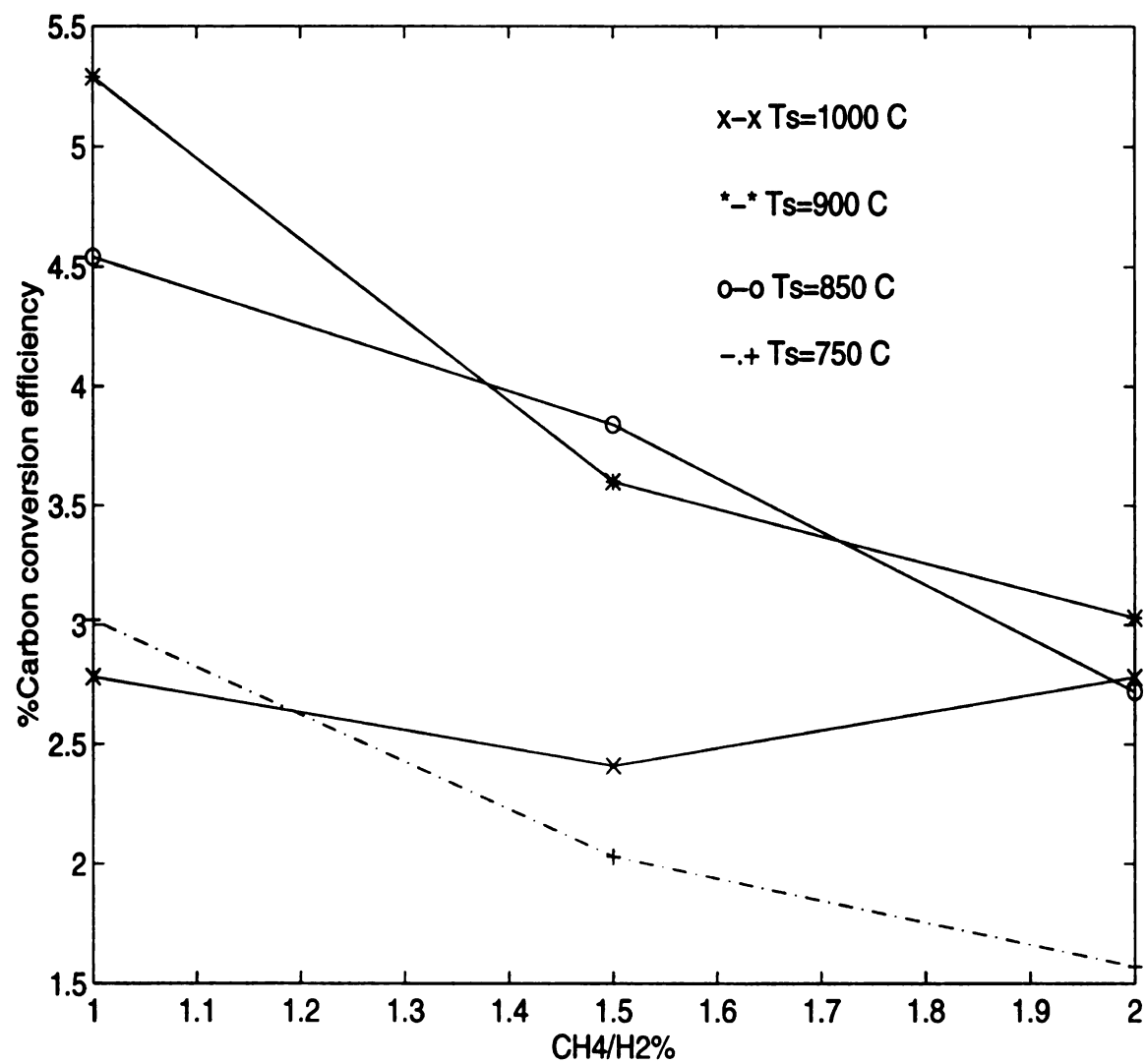


Figure 6.41. Carbon conversion efficiency vs. substrate temperature and CH₄/H₂ for $f_t = 200$ sccm.

6.2.2.2.3 Total gas flow rate, $f_t = 60$ sccm

For the flow rate, f_t , fixed at 60 sccm, Figure 6.42 shows the dependence of carbon conversion efficiency on substrate temperature and methane gas concentration in hydrogen. From Figure 6.42 it is seen that the carbon conversion efficiency decreased monotonically with the methane gas concentration. This indicates that although up to a certain point the film growth rate increased with methane concentration in hydrogen, only a small amount of additional supplied carbon was added to the film so the denominator in equation 4.4 grew faster than the numerator in this equation.

6.3 Summary of the effect of total gas flow rate on output variables

The preceding sections dealt with a detailed analysis of the Microwave Cavity Plasma Reactor output film properties (Y_1) and reactor performance variables (Y_2) vs. the CH_4/H_2 gas chemistry and the substrate temperature (hence operating pressure and microwave power) for the total flow rates of 400, 200, and 60 sccm. An examination of the output variables $Y = [Y_1, Y_2]$ at each of these flow rates revealed the dependence of these variables on the total gas flow rate, as well. In this section a summary of the effect of the total gas flow rate on output variables Y is provided. The data provided in this section were taken from the previous sections.

6.3.1 Film properties (Y_1) vs. total gas flow rate

6.3.1.1 Film morphology

Figure 6.43 illustrates the dependence of film morphology (expressed by the growth parameter α) on the total gas flow rate for various $CH_4/H_2\%$ for a fixed substrate

temperature of $T_s = 850^\circ\text{C}$. Figure 6.44 shows the variation of the film morphology with the total gas flow rate for $\text{CH}_4/\text{H}_2\% = 1.50\%$ and $T_s = 850^\circ\text{C}$. The films displayed $\{100\}$ morphology (i.e., $\alpha \cong 1$) for $f_t = 60$ sccm and 200 sccm. The film morphology changed to the heavily twinned $\{111\}$ (i.e., $\alpha \cong 3$) as the total gas flow rate was increased to $f_t = 400$ sccm.

6.3.1.2 Structural quality

In addition to being dependent upon methane gas concentration and substrate temperature, the film structural quality was dependent upon gas total flow rate. Figure 6.45 shows the Raman spectra of the diamond films deposited at the total gas flow rates of 60, 200, and 400 sccm with CH_4/H_2 and T_s fixed at 1.50% and 850°C , respectively. The diamond peak (i.e., around 1332 cm^{-1}) was weaker for $f_t = 400$ sccm than for $f_t = 60$ sccm and 200 sccm. Furthermore, the diamond peak associated with $f_t = 400$ sccm spectrum was shifted to the right with respect to the 1332 cm^{-1} line. This was an indication of a compressive stress in the corresponding film. The plot of FWHM vs. total gas flow rate is shown in Figure 6.46. The film deposited at $f_t = 400$ sccm was of a poorer quality than those deposited at $f_t = 60$ and $f_t = 200$ sccm.

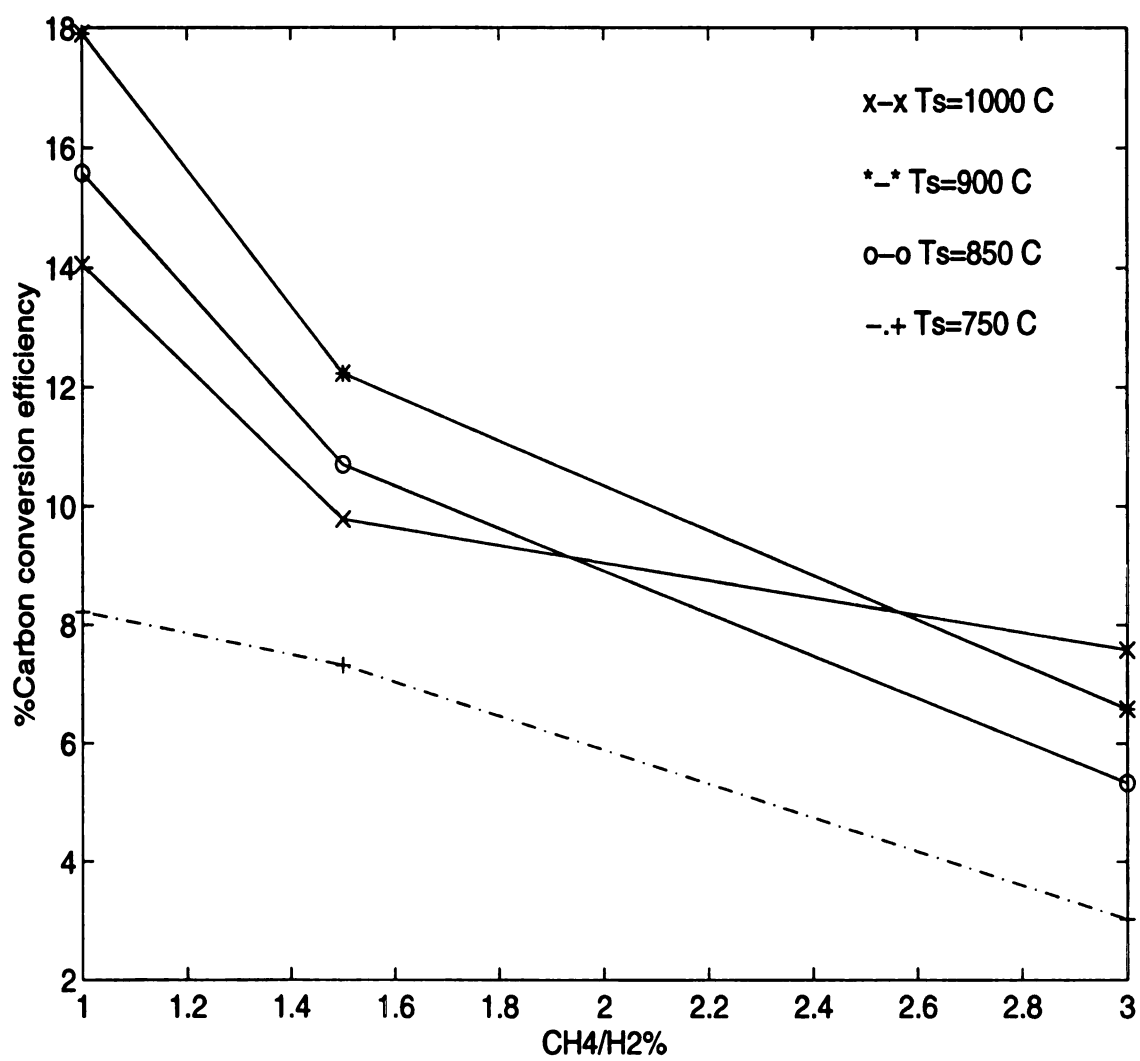


Figure 6.42. Carbon conversion efficiency vs. substrate temperature and CH_4/H_2 for $f_t = 60\text{ sccm}$.

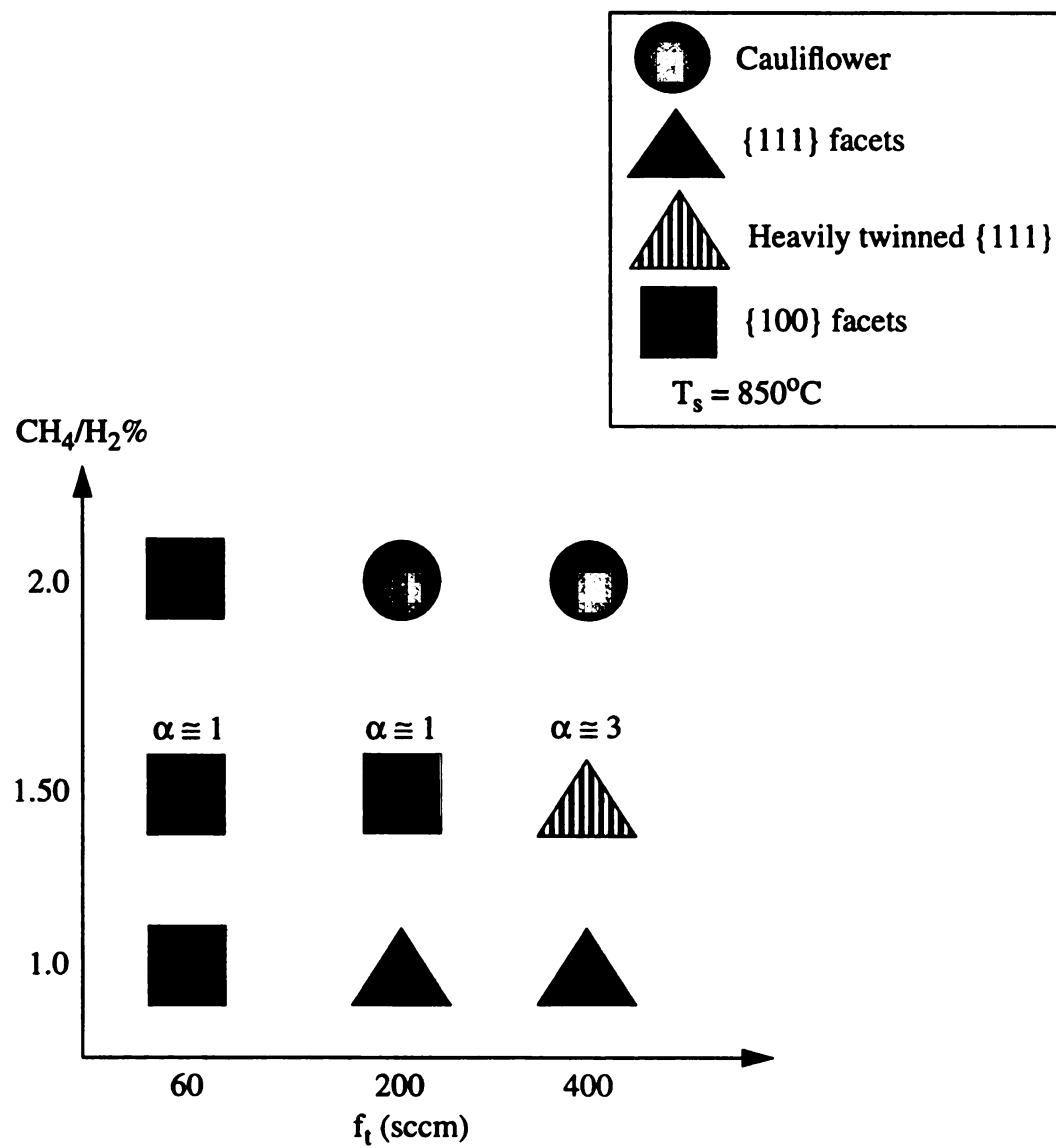


Figure 6.43. Morphology vs. total flow rate for substrate temperature fixed at 850°C .

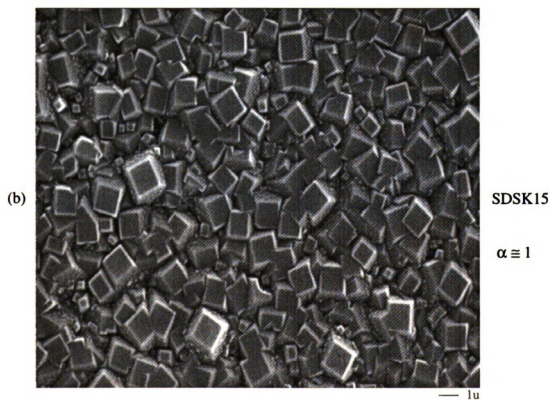
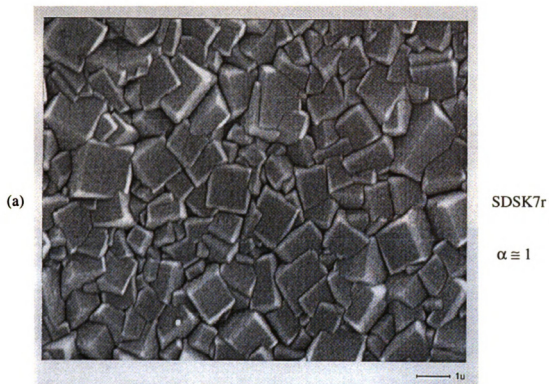


Figure 6.44. SEM pictures diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$, $T_s = 850^\circ\text{C}$, and (a) $f_t = 60$ sccm, (b) $f_t = 200$ sccm, and (c) $f_t = 400$ sccm.

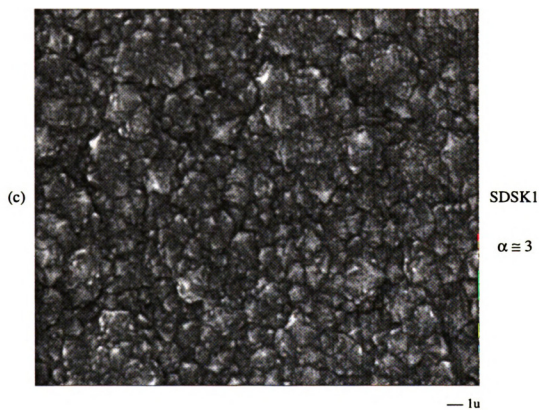


Figure 6.44. Continued.

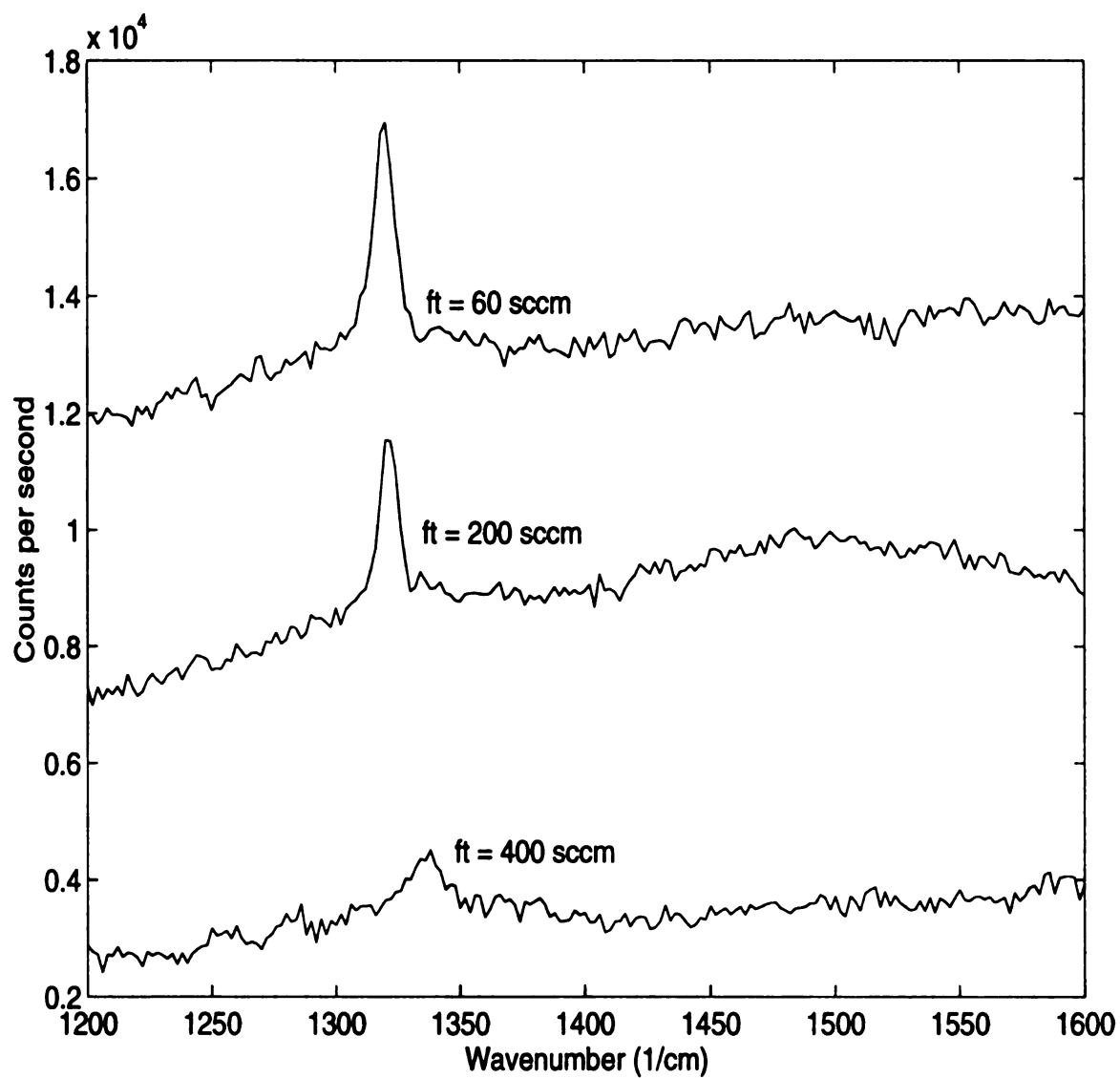


Figure 6.45. Structural quality vs. total gas flow rate with substrate temperature fixed at 850°C and $\text{CH}_4/\text{H}_2=1.50\%$.

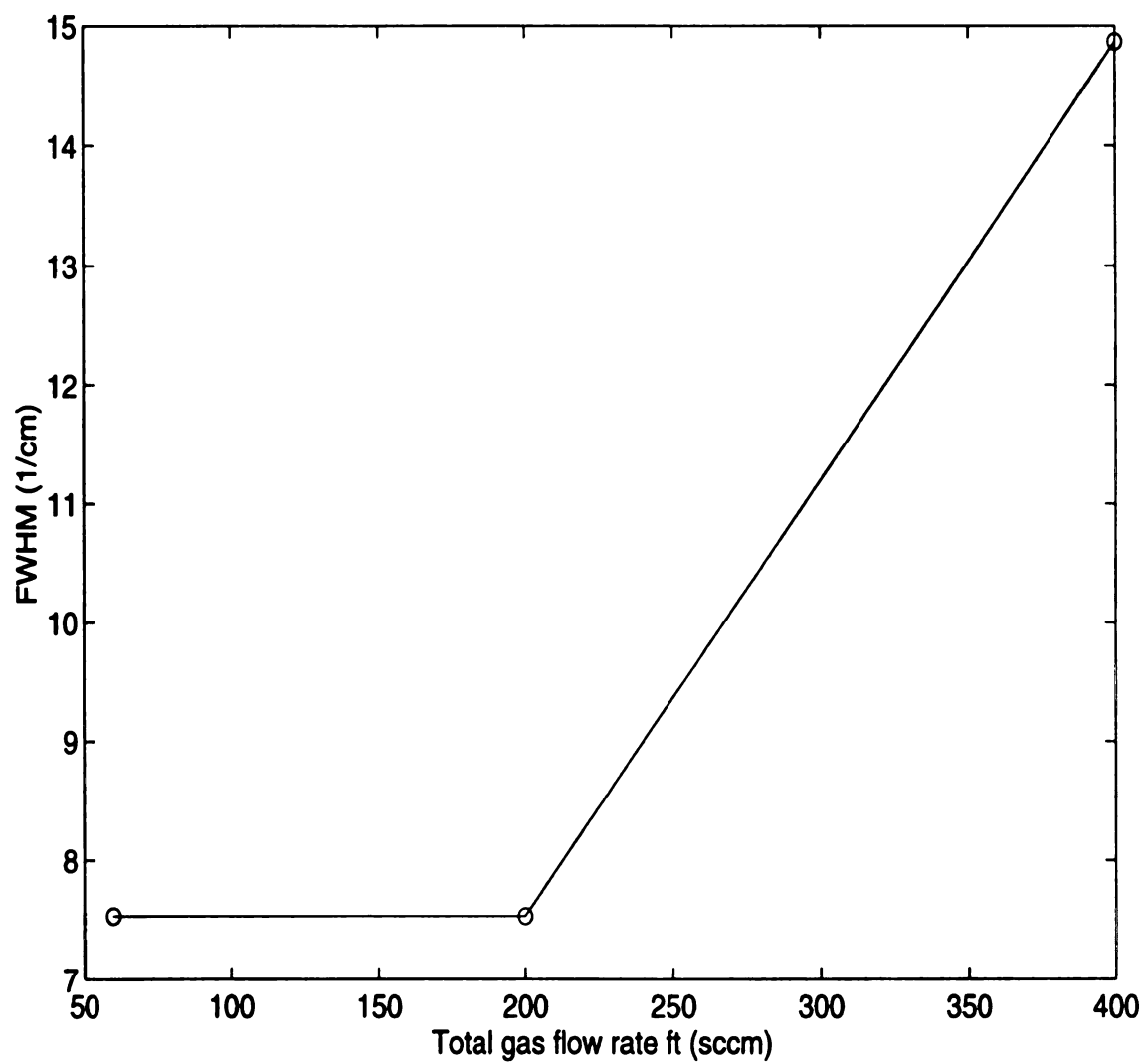


Figure 6.46. Plot of FWHM vs. total gas flow rate for diamond films deposited at $\text{CH}_4/\text{H}_2 = 1.50\%$ and $T_s = 850^\circ\text{C}$.

6.3.2 Reactor performance (Y_2) vs. total gas flow rate

6.3.2.1 Linear growth rate

Figure 6.47 shows the plot of linear growth rate vs. total gas flow rate for various methane concentrations, CH_4/H_2 for the substrate temperature fixed at $T_s=850^\circ\text{C}$. With the exception of the $\text{CH}_4/\text{H}_2 = 1.0\%$ plot which showed that the linear growth rate associated with $f_t = 200$ sccm was slightly smaller than that associated with $f_t = 60$ sccm, the linear growth rate increased with total gas flow rate in the range of $f_t = 60 - 400$ sccm.

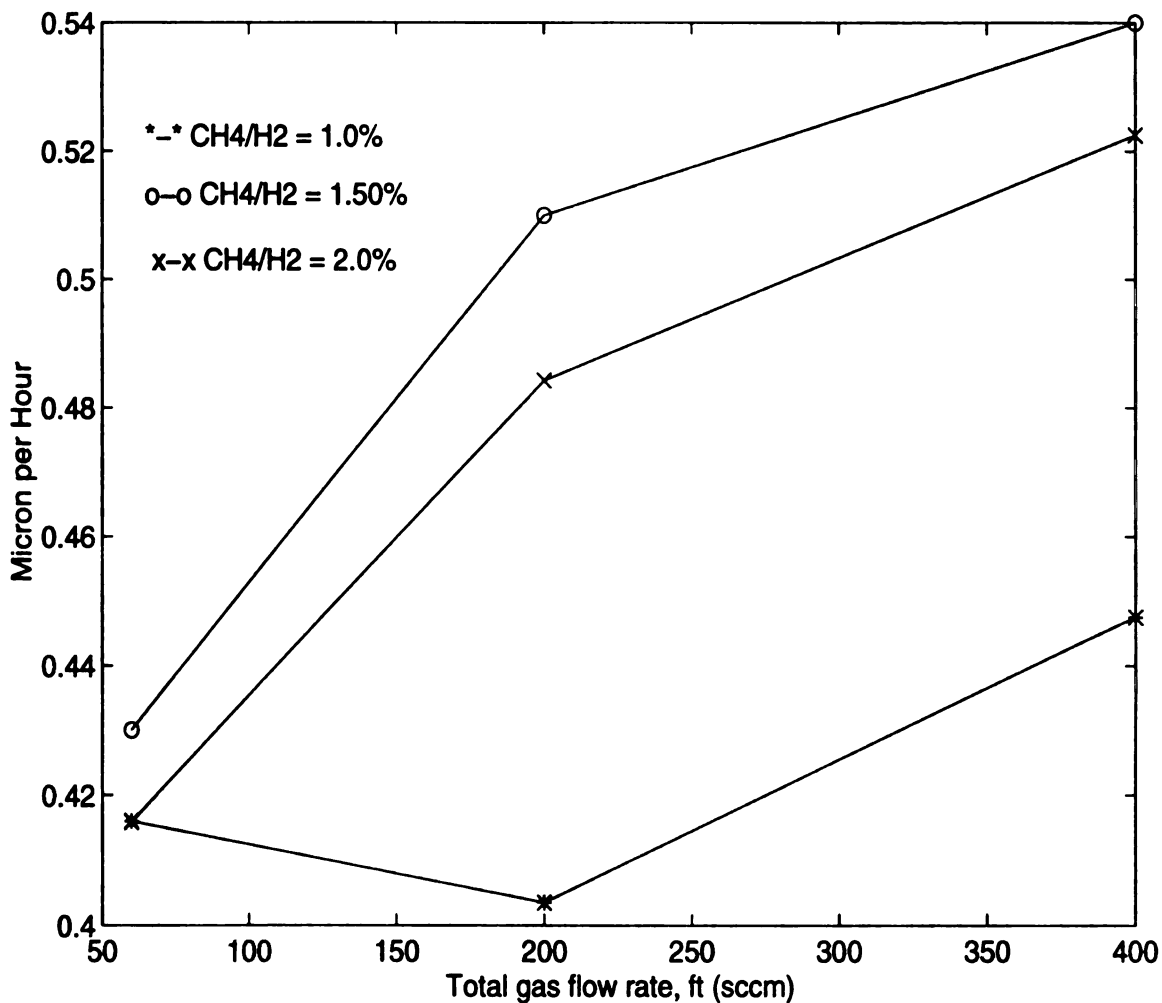


Figure 6.47. Linear growth rate vs. total gas flow rate and $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $T_s = 850^\circ\text{C}$.

6.3.2.2 Carbon conversion efficiency

Carbon conversion efficiency strongly depended on the total gas flow rate. Figure 6.48 shows the variation of carbon conversion efficiency with the total gas flow rate for various methane gas concentrations, CH_4/H_2 for the substrate temperature fixed at 850°C . It shows that carbon conversion efficiency was inversely proportional to the total gas flow rate and decreased sharply as the total gas flow rate increased.

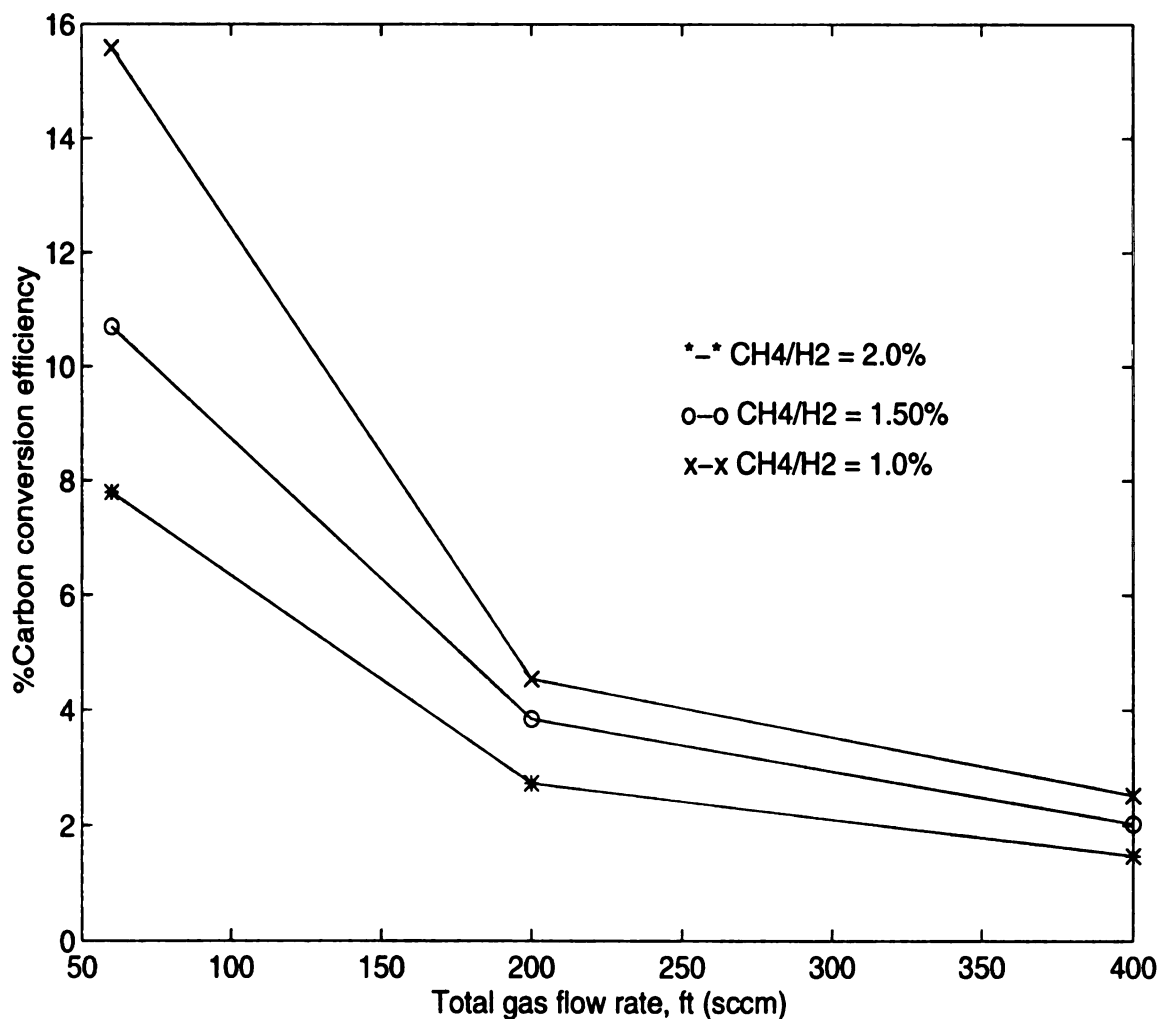


Figure 6.48. %Carbon conversion efficiency vs. total gas flow rate and $\text{CH}_4/\text{H}_2\%$ for diamond films deposited at $T_s = 850^\circ\text{C}$.

6.4 Comparison between the output variables ($Y = [Y_1, Y_2]$) of the 5"quartz dome/3" substrate and the 4" quartz dome/2" substrate reactor geometries.

6.4.1 Diamond film properties (Y_1)

6.4.1.1 Film morphology

Figure 6.49, Figure 6.50, and Figure 6.51 illustrate the effect of reactor geometry on the film morphology for constant flow rates of 400, 200, and 60 sccm, respectively. In these Figures, for each value of CH_4/H_2 there are two rows of figures. First row (i.e., top row) represents film morphology vs. substrate temperature for the 4"quartz dome/2" substrate reactor configuration and the second row (i.e., bottom row) represents film morphology vs. substrate temperature (T_s) for the 5"quartz dome/3" substrate reactor configuration. It is seen that a variation in the reactor geometry had an important influence on the output film morphology, particularly in the lower substrate temperature regime of $T_s \leq 850^\circ C$. Furthermore, the CH_4/H_2 , T_s , f_t variable "volume" to achieve well-faceted films was smaller for the small reactor than for the large reactor. Thus the morphology variations in the small reactor were more sensitive to changes in the input variables than for the large reactor. Nevertheless, the morphology trends of the two reactors were similar; high flow rates, i.e., $f_t = 400$ sccm, produced $\{111\}$ films at substrate temperatures in the range of $T_s \geq 800^\circ C$ and methane concentration in the range of $0.6 < CH_4/H_2 \leq 1.50\%$. Lower flow rates (i.e., $f_t \leq 200$ sccm) produced $\{111\}$ films at high substrate temperatures (i.e., $T_s \geq 850^\circ C$) and $0.60 \leq CH_4/H_2 \leq 2.0\%$ and produced $\{100\}$ films at lower substrate temperatures (i.e., $T_s \leq 850^\circ C$) and $0.60 < CH_4/H_2 \leq 2.0\%$. Well-

faceted {100} and {111} films were produced at $\frac{\text{CH}_4}{\text{H}_2} \leq 2$. Films with cauliflower and

small aggregate morphologies were produced at higher methane concentrations.

A comparison of the diamond grain sizes synthesized by the two geometry configurations is illustrated in Figure 6.52 (a) - (c). This figure compares the grain size vs. substrate temperature for the two reactor geometries for $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 60, 200$, and 400 sccm. For $\text{CH}_4/\text{H}_2 = 1.50\%$, $f_t = 60$ and 200 sccm, the grain sizes were bigger for the 5"quartz dome/3" substrate reactor. For $\text{CH}_4/\text{H}_2 = 1.50\%$ and $f_t = 400$ sccm the 4"quartz dome/2" substrate reactor produced films with bigger grains for $T_s \leq 950^\circ\text{C}$.

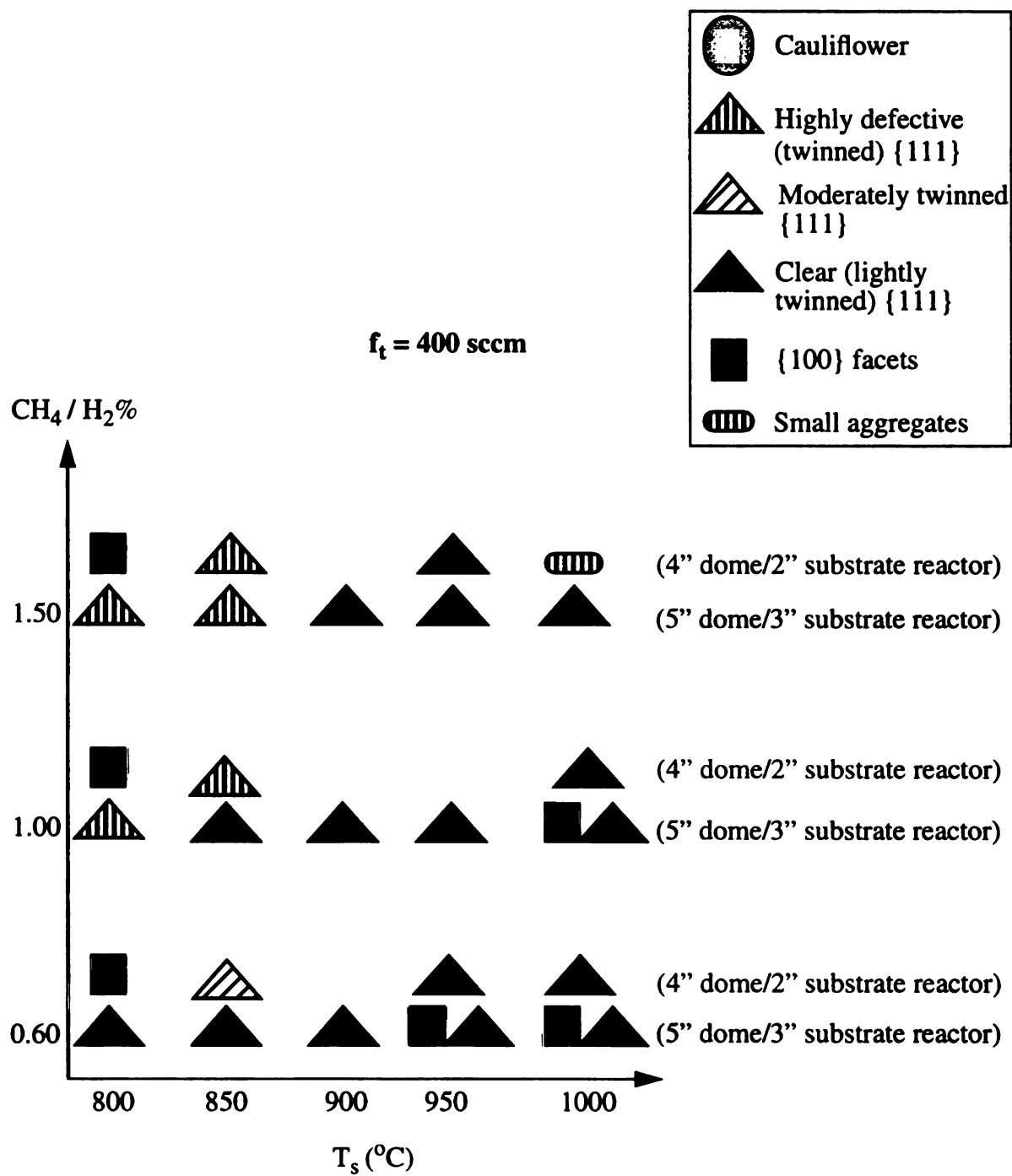


Figure 6.49. Morphology field maps for the 4'' dome/2'' substrate and the 5'' dome/3'' substrate reactor geometry configurations for $f_t = 400 \text{ sccm}$.

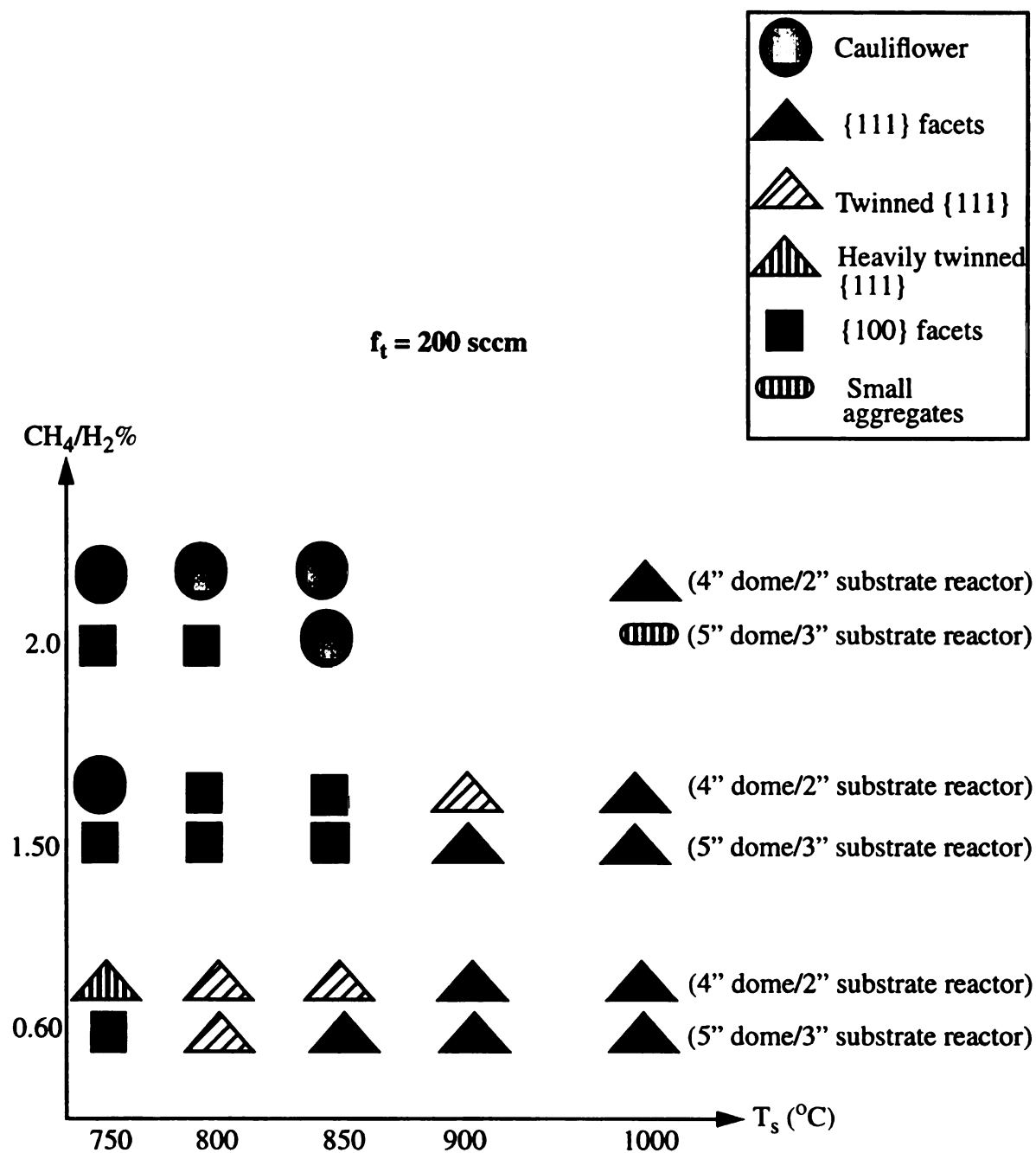


Figure 6.50. Morphology field maps for the 4'' dome/2'' substrate and the 5'' dome/3'' substrate reactor geometry configurations for $f_t = 200 \text{ sccm}$.

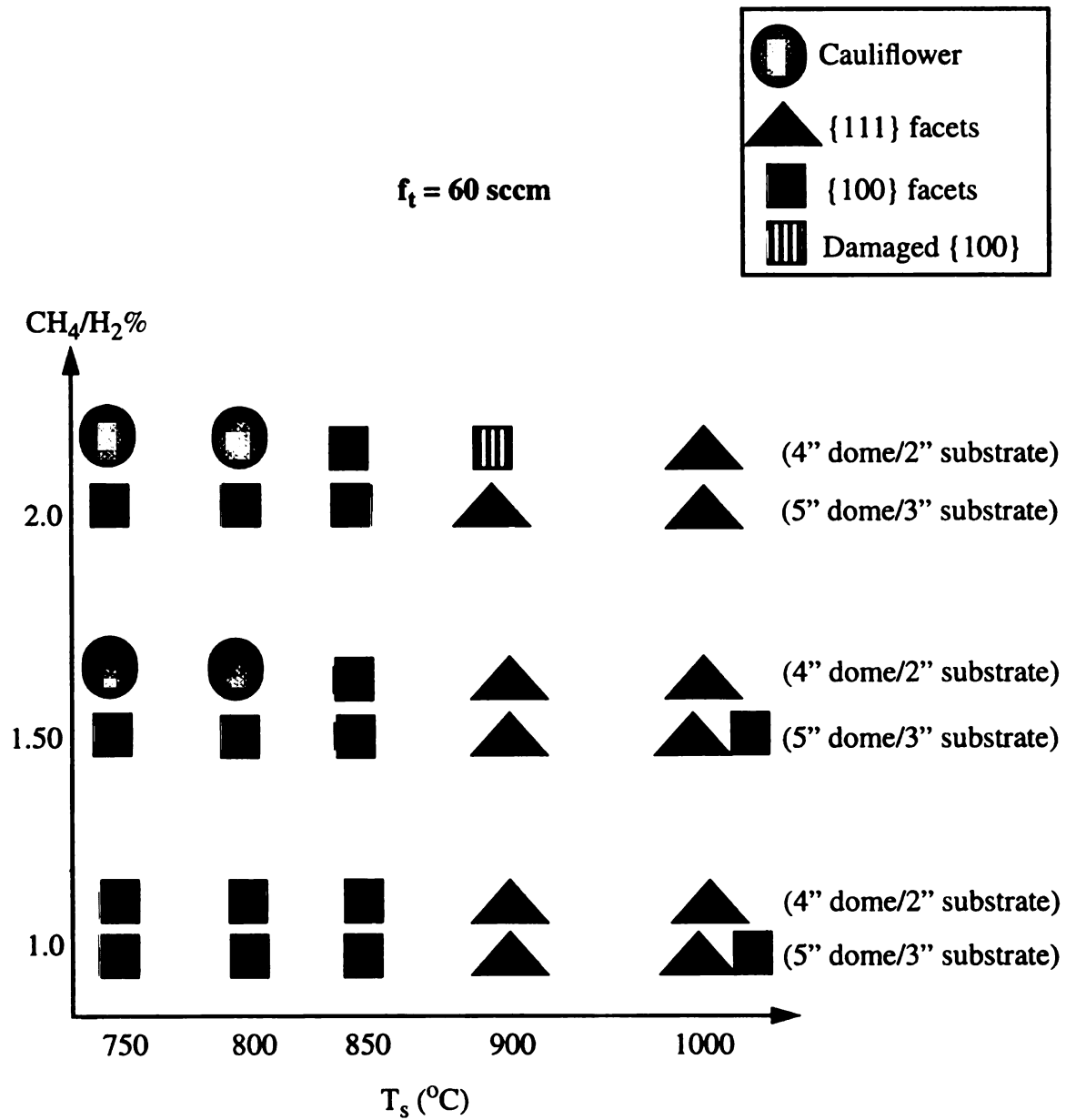


Figure 6.51. Morphology field maps for the 4" dome/2" substrate and the 5" dome/3" substrate reactor geometry configurations for $f_t = 60 \text{ sccm}$.

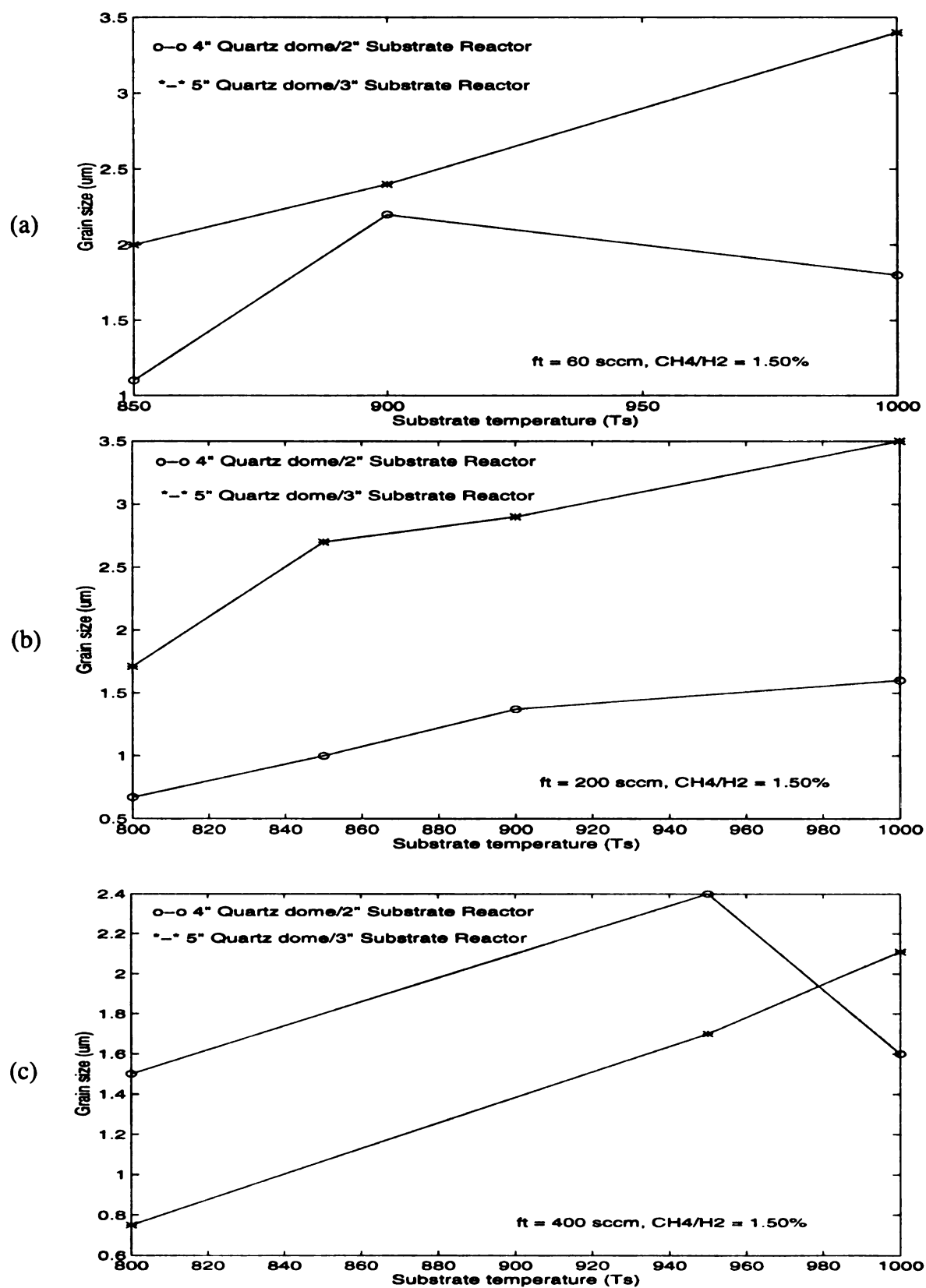


Figure 6.52. Grain size vs. substrate temperature for the two reactor geometries for CH₄/H₂ = 1.50% and (a) $f_t = 60$ sccm, (b) $f_t = 200$ sccm, and (c) $f_t = 400$ sccm.

6.4.1.2 Structural quality

A comparison of the structural qualities (determined by FWHM) of the diamond films synthesized by the two reactor configurations is shown in Table 6.2. This table displays the FWHM values of the films for various flow rates, CH_4/H_2 , and T_s for the 5" dome/3" substrate and the 4" dome/2" substrate reactor geometry configurations. As evident from the table, the variation in the reactor geometry configuration did influence the structural quality (i.e., FWHM) of these films but the effect was not very significant. Highly faceted films showed similar FWHM values in the range of 7 - 11 cm^{-1} while films with cauliflower and small aggregate morphologies displayed larger FWHM values ($\text{FWHM} > 15 \text{ cm}^{-1}$).

Table 6.2. A comparison of the structural qualities (FWHM) of the diamond films synthesized by the two reactor configurations.

f_t (sccm)	% CH_4/H_2	$T_s(^{\circ}\text{C})$	FWHM (cm^{-1}) 5" dome/3" substrate	FWHM (cm^{-1}) 4" dome/2" substrate
400	1.50	850	12.04	14.87
400	1.50	1000	11.2	7.0
200	1.50	850	7.05	7.53
200	1.50	1000	7.05	9.09
60	1.50	850	9.09	7.53
60	1.50	1000	9.62	7.53
400	1.0	850	12.04	13.0
200	3.0	850	> 50	65
60	1.0	850	10.49	8.32
60	3.0	850	40.83	49.7

6.4.2 Reactor performance (Y_2)

6.4.2.1 Linear growth rate, d

A comparison of the weight gain (mg./hr) and linear growth rates of the diamond films synthesized by the two reactor configurations are shown in Figure 6.53 and Figure 6.54, respectively. These figures display the mg./hr and linear growth rates of the films for various flow rates (f_t), substrate temperatures (T_s), and methane concentrations (CH_4/H_2) for the 5" dome/3" substrate and the 4" dome/2" substrate reactor geometry configurations. As evident from these figures, the variation in the reactor geometry configuration did influence the mg./hr and linear growth rates of the films. As shown in Figure 6.53 the variation in the reactor geometry significantly influenced the weight gain (mg./hr). Except for $T_s = 1000^\circ\text{C}$, the effect of the variation in the linear growth rates vs. substrate temperature (i.e., Figure 6.54 (a) - (c)) of the films due to a variation in the reactor geometry was not very significant. For the 5" dome/3" substrate reactor geometry configurations the linear growth rates increased with substrate temperature monotonically and reached their maximum values at $T_s = 1000^\circ\text{C}$ which was the upper limit of the substrate temperature range (see Chapter 5). For the 4" dome/2" substrate reactor geometry configurations the linear growth rates reached their maximum values at $T_s < 1000^\circ\text{C}$. This is the reason for observing a significant difference in the growth rates vs. reactor geometry variation at $T_s = 1000^\circ\text{C}$ in Figure 6.54 (a) - (c). As seen in Figure 6.54 (d) except for $CH_4/H_2 = 1.0\%$, the effect of a variation in the reactor geometry configuration on the linear growth rates vs. CH_4/H_2 was not very significant, either. At $CH_4/H_2 = 1.0\%$, the linear growth rate associated with the 4" dome/2" substrate reactor

geometry configuration was approximately 30% greater than the linear growth rate associated with the 5" dome/3" substrate reactor geometry configuration.

6.4.2.2 Carbon conversion efficiency

The variation of the percent carbon conversion efficiency and the normalized percent carbon conversion efficiency (i.e., % carbon conversion efficiency/substrate area) with the reactor geometry configuration are evident from Figure 6.55 and Figure 6.56 which show the percent carbon conversion efficiency and the normalized percent carbon conversion efficiency vs. CH_4/H_2 for different substrate temperatures and flow rates for the 5" dome/3" substrate and the 4" dome/2" substrate reactor geometry configurations. As shown in Figure 6.55 and Figure 6.56, the variation in the reactor geometry configuration had significant influence on the percent carbon conversion efficiency but its influence on the normalized carbon conversion efficiency was not very significant.

6.4.2.3 Specific yield (KW-hr/g)

Table 6.3 compares the specific yields (i.e., KW-hr/g) of the two reactor geometry configurations for different flow rates, substrate temperatures, and methane concentrations. It is seen that the specific yield was significantly influenced by the variation in the reactor geometry configuration and that for similar deposition conditions, the specific yield associated with the small dome reactor were significantly larger than the specific yields associated with the large dome reactor.

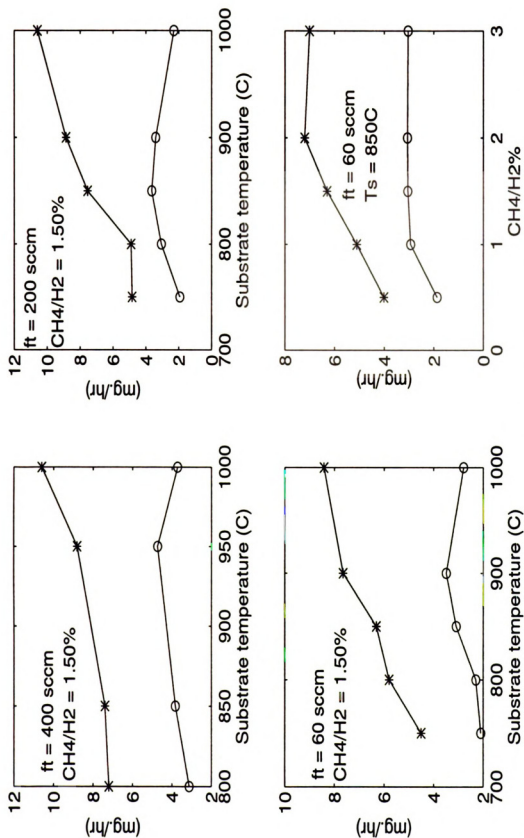


Figure 6.53. Variation of weight gain (mg/hr) with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-.* curves represent the 5" dome/3" substrate reactor configuration.

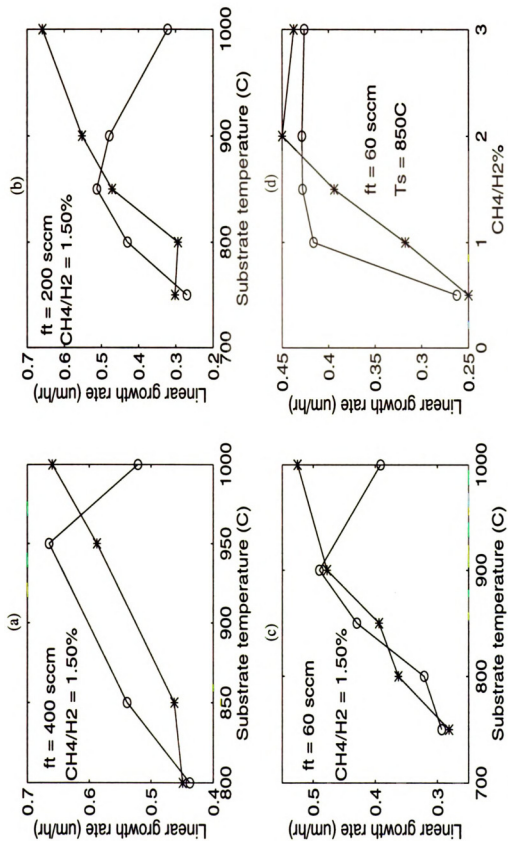


Figure 6.54. Variation of linear growth rate with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.

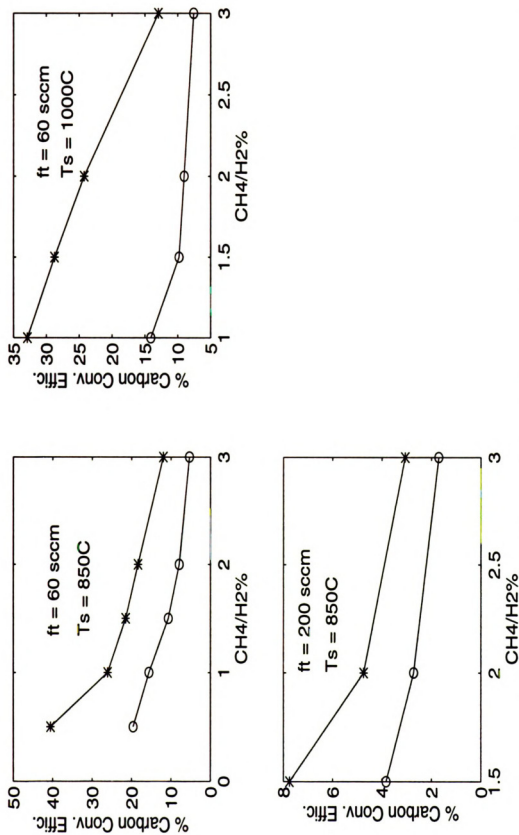


Figure 6.55. Variation of percent carbon conversion efficiency with the reactor geometry configuration. O-O curves represent the 4" dome/2" substrate reactor configuration and *-* curves represent the 5" dome/2" substrate reactor configuration.

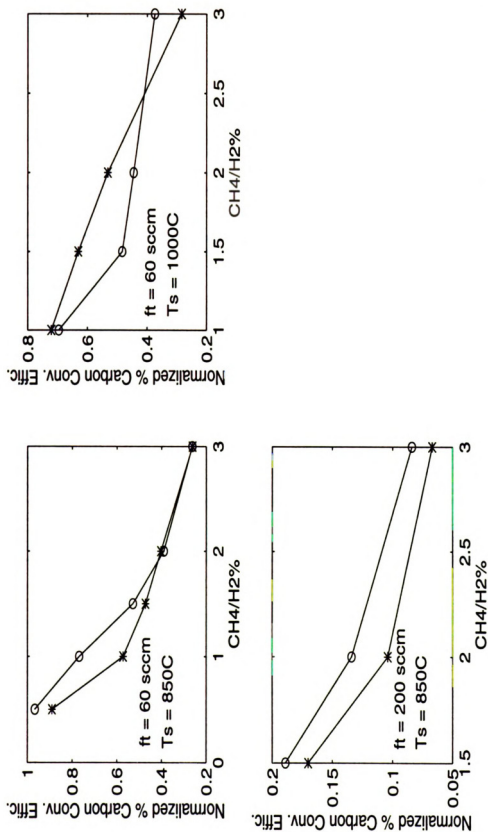


Figure 6.56. Variation of normalized percent carbon conversion efficiency (i.e., % carbon conversion efficiency/substrate area) with the reactor geometry configuration. O-O curves represent the 4" dome/3" substrate reactor configuration and *-* curves represent the 5" dome/3" substrate reactor configuration.

Table 6.3. A comparison of the specific yields associated with the two reactor configurations.

f_t (sccm)	%CH ₄ /H ₂	T _s (°C)	Specific yield (KW-hr/g) 5" dome/3" substrate	Specific yield (KW-hr/g) 4" dome/2" substrate
400	1.50	850	222	307
400	1.50	1000	244	500
200	1.50	850	217	366
200	1.50	1000	183	847
60	1.50	850	282	386
60	1.50	1000	216	735
200	3.0	850	305	407
60	3.0	850	244	474

6.5 Discussion

The variation in the reactor geometry caused significant variations in the microwave volume power density and microwave area power density as shown in Figure 6.5 and Figure 6.6. These figures show that for the same input variables, the microwave volume power density and area power density were significantly larger in the small dome geometry configuration than in the large dome geometry configuration. It is speculated that more species interacted with the walls and were lost to the walls in the small dome reactor so that a larger amount of input power was needed to maintain the discharge in this reactor. Such significant variations are believed to have caused the variations observed in the output variables when the reactor geometry was varied. This phenomenon (i.e., having different microwave power density for different reactor geometries) explains why different microwave reactors deposit films with different properties under similar experimental conditions.

6.6 Summary

The reactor geometry was changed from 5" quartz dome/3" substrate configuration shown in Figure 6.1 (a) which was investigated in Chapter 5 to the 4" quartz dome/2" substrate configuration shown in Figure 6.1 (b). This reactor configuration was experimentally investigated in this chapter. The two reactor configurations were identical except in the sizes of the quartz dome base diameter, substrate, and substrate holder assembly. Such variations in the reactor geometry variables (U_2) resulted in changes in the reactor operating road map, absorbed microwave power vs. substrate temperature, microwave volume and area power densities, and gas residence time. The variation in the

absorbed microwave power vs. temperature was not significant but the microwave volume and area power densities associated with the small (i.e., 4" quartz dome/2" substrate) reactor configuration were significantly larger than those of the large (5" quartz dome/3" substrate) reactor configuration. Furthermore, for constant pressures and flow rates, the gas residence times associated with the small reactor were approximately 3 times smaller than for the large dome reactor.

Under a fixed reactor geometry, film properties (Y_1) and reactor performance (Y_2) depended not only upon gas chemistry (i.e., $\text{CH}_4/\text{H}_2\%$) and pressure but also depended upon total flow rate and deposition time.

For $f_t = 400$ sccm total gas flow rate films with $\{100\}$ morphology were deposited at low substrate temperatures ($700 \leq T_s \leq 800^\circ\text{C}$) and mainly in $0.6 \leq \text{CH}_4/\text{H}_2 < 2.0\%$ zone. Films with $\{111\}$ morphology grew at the same methane concentration range (i.e., $0.6 \leq \text{CH}_4/\text{H}_2 < 2.0\%$) but at a higher substrate temperature regime ($850 \leq T_s \leq 1000^\circ\text{C}$). At this flow rate, films with cauliflower structure were deposited at $\text{CH}_4/\text{H}_2 \geq 2.0\%$.

For $f_t = 200$ sccm total gas flow rate films with $\{100\}$ morphology were deposited at substrate temperature range of $800 \leq T_s \leq 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.50\%$. Films with $\{111\}$ morphology grew at the methane concentration range of $1.0 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$. At $\text{CH}_4/\text{H}_2 = 1.0\%$, the $\{111\}$ morphology was dominant over the entire substrate temperature range of $750 \leq T_s \leq 1000^\circ\text{C}$. At higher methane concentrations of $\text{CH}_4/\text{H}_2 = 1.50\%$ and $\text{CH}_4/\text{H}_2 = 2.0\%$ the $\{111\}$ morphology was favored at $900 \leq T_s \leq 1000^\circ\text{C}$ and

$T_s = 900^\circ\text{C}$, respectively.

For $f_t = 60$ sccm total gas flow rate films with $\{100\}$ morphology were deposited at substrate temperature range of $750 \leq T_s \leq 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.0\%$, at $T_s = 850^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 1.50\%$, and at $850 \leq T_s \leq 900^\circ\text{C}$ when $\text{CH}_4/\text{H}_2 = 2.0\%$. Films with $\{111\}$ morphology grew at the substrate range of $850 \leq T_s \leq 900^\circ\text{C}$ when $1.0 \leq \text{CH}_4/\text{H}_2 \leq 1.50\%$ and at $T_s = 1000^\circ\text{C}$ when $2.0 \leq \text{CH}_4/\text{H}_2 \leq 3.0\%$. At this flow rate, films with cauliflower structure were mainly deposited at $\text{CH}_4/\text{H}_2 \geq 2.0\%$

Films with $\{100\}$ and $\{111\}$ facets showed strong Raman peak around 1332 cm^{-1} which is an indication of having predominantly diamond phase (sp^3 bonds) in the films. Cauliflower films showed wider FWHM (i.e., poorer structural quality) and the graphitic phase (indicated by a broad peak around 1550 cm^{-1}) was more pronounced in the Raman spectra of the films with cauliflower structure. The FWHM was generally improved with the substrate temperature but with respect to the methane concentration it increased sharply at high methane concentrations where cauliflower structure was dominant.

Linear growth rate was shown to improve with substrate temperature up to a certain temperature (i.e., $T_s = 950^\circ\text{C}$ for $f_t = 400$ sccm and $T_s = 900^\circ\text{C}$ for $f_t = 200$ and $f_t = 60$ sccm) and drop beyond this substrate temperature. With respect to CH_4/H_2 the linear growth rate increased up to a certain methane concentration (i.e., $\text{CH}_4/\text{H}_2 = 2.0\%$ for $f_t = 60$ sccm and $f_t = 200$ sccm and $\text{CH}_4/\text{H}_2 = 1.50\%$ for $f_t = 400$ sccm total gas flow rate) and decreased for higher methane concentrations. Table 6.4 lists the maximum growth rate and the corresponding deposition conditions for each total gas flow rate experimentally

investigated in Chapter 6.

Table 6.4. Maximum growth rate and the corresponding deposition conditions for the total gas flow rate experimentally investigated in Chapter 6.

Maximum growth rate $\mu\text{m/hr}$	Total gas flow rate (sccm)	$\text{CH}_4/\text{H}_2\%$	Substrate temperature ($^{\circ}\text{C}$)	Morphology	growth parameter α
0.665	400	1.50	950	{111}	3
0.540	200	2.0	900	Cauliflower	-
0.635	60	2.0	900	Damaged {100}	1

Carbon conversion efficiency is the ratio of carbon added to the film to the total amount of carbon supplied by the input gas. It was found to be inversely proportional to $\text{CH}_4/\text{H}_2\%$ and total gas flow rate. With respect to the substrate temperature the carbon conversion efficiency showed a trend similar to that of the linear growth rate. It increased with T_s as long as the linear growth rate increased with T_s and vice versa.

Finally, a change in the reactor geometry from the 5" quartz dome/3" substrate reactor geometry to the 4" quartz dome/2" substrate geometry influenced the output variables $\mathbf{Y} = [\mathbf{Y}_1, \mathbf{Y}_2]$ of the microwave cavity plasma reactor. The impact of the variation in the reactor geometry ($\mathbf{U}_2$) was significant on the film morphology, particularly at lower temperatures, weight gain (mg./hr), and carbon conversion efficiency. On the other hand, FWHM, linear growth rate (except at $T_s = 1000^{\circ}\text{C}$), and normalized carbon conversion efficiency (i.e., carbon conversion efficiency/substrate area) were not significantly affected

by the reactor geometry variation. The significant variations in the microwave volume and area power densities and gas residence time are believed to have caused the variations observed in the output variables when the reactor geometry was varied.

CHAPTER 7

Diamond CVD with Carbon Monoxide

7.1 Introduction

A series of experiments were carried out to deposit diamond films with carbon monoxide, CO, in hydrogen with no hydrocarbon (i.e., CH₄) present. The intention for depositing diamond with hydrogen and CO was to conduct a preliminary examination of the CO-H₂ diamond deposition (i.e., no CH₄ gas) and compare the output film properties Y_1 (i.e., morphology and structural quality) and reactor performance Y_2 (i.e., linear growth rate and carbon conversion efficiency) with CH₄ - H₂ diamond deposition as carried out in Chapter 5. It was of a particular interest to find out if diamond films with less graphitic content compared to diamond deposited with hydrogen and methane could be deposited this way since atomic oxygen is a strong etchant of the graphite. It should be emphasized that only a limited number of experiments were conducted with CO gas to explore CO-H₂ diamond deposition and the data presented in this chapter reflect only a preliminary exploration of the diamond deposition with CO and H₂ gases.

The 5" quartz dome/3" substrate reactor geometry configuration was used for CO-H₂ diamond film deposition. The input, internal, and output variables under the consideration and their ranges of operation are listed in Table 7.1. Figure 7.1 illustrates the block

diagram of the microwave cavity plasma reactor utilized for CO-H₂ diamond film deposition.

It was observed that unlike CH₄/H₂ concentration which did not have any effect on the substrate temperature-pressure relationship (Figure 4.6), the CO/H₂ concentration did influence the substrate temperature when pressure was fixed at a value. Figure 7.2 illustrates this effect. Substrate temperature increased with CO concentration in hydrogen. The rise in the substrate temperature as CO/H₂ was increased from 2.50% to 50% was 55°C which showed that the substrate temperature experienced a 5.50% increase as CO was increased by a factor of 20. Since substrate temperature was dependent upon the CO/H₂ concentration, in the subsequent sections the pressure instead of the substrate temperature is used as an independent input variable and the output variables Y_1 and Y_2 are mapped into the pressure and CO/H₂ instead of the substrate temperature and CO/H₂.

The ranges of operating pressure, substrate temperature, microwave power, gas chemistry CO/H₂, and hydrogen gas flow rate were limited by a number of experimental conditions. These conditions are described below.

Operating pressure and input microwave power

The first few experiments that were carried out at and below $p = 25$ torr showed that the resulting films were discontinuous and the weight gains (i.e., hence growth rates) were insignificant. For instance, for CO/H₂ = 10%, H₂ = 400 sccm, and $p = 25$ torr (Figure 7.3) the growth rate was only 0.09375 $\mu\text{m/hr}$. Therefore, this pressure was not used for film deposition. Films deposited at 60 torr were discontinuous after 8 hours of deposition (see

Table 7.1. Reactor input/internal/output variables for CO-H₂ diamond film deposition.

Input Variables, U	Macroscopic Controllable Variables, U ₁	— Microwave power: P_t = 1 - 3 KW — Operating pressure: p = 25 - 60 torr - Total gas flow rate: f_t = 400 sccm (fixed) - Gas chemistry: CO/H₂ = 2.5 - 70%
	Reactor Geometry Variables, U ₂	- Cavity inner diameter = 17.78 cm (fixed) - Quartz dome inner base dia. = 12.7 cm (fixed) - Excitation mode = TM₀₁₃ (fixed) - Microwave frequency = 2.45 GHz (fixed) - Substrate Diameter = 3 inches (p<100>, Si) - Substrate holder = molybdenum under thermally floating configuration (fixed) - Discharge diameter ~ 10 cm (fixed)
	Deposition Procedure Variables, U ₃	- Deposition Time, t = 8 hours - Substrate Seeding = A mixture of 0.1 micron diamond powder-photoresist solution (fixed) - Start-up and shut-down procedure (fixed)
Internal Variables, X		— Substrate temperature: T_s = 700 - 1100 °C
Output Variables, Y		- Y₁ — - Surface morphology — - Structural quality - Y₂ — - Linear growth rate — - Carbon conversion efficiency

U = Input variables where $U = [U_1, U_2, U_3]$

U_1 : Macroscopic controllable variables

U_2 : Reactor geometry variables

U_3 : Deposition procedure and time variables

X = Internal variables

Y = Output variables (performances)

In general:

$$X = f(U)$$

$$Y = g(U, X)$$

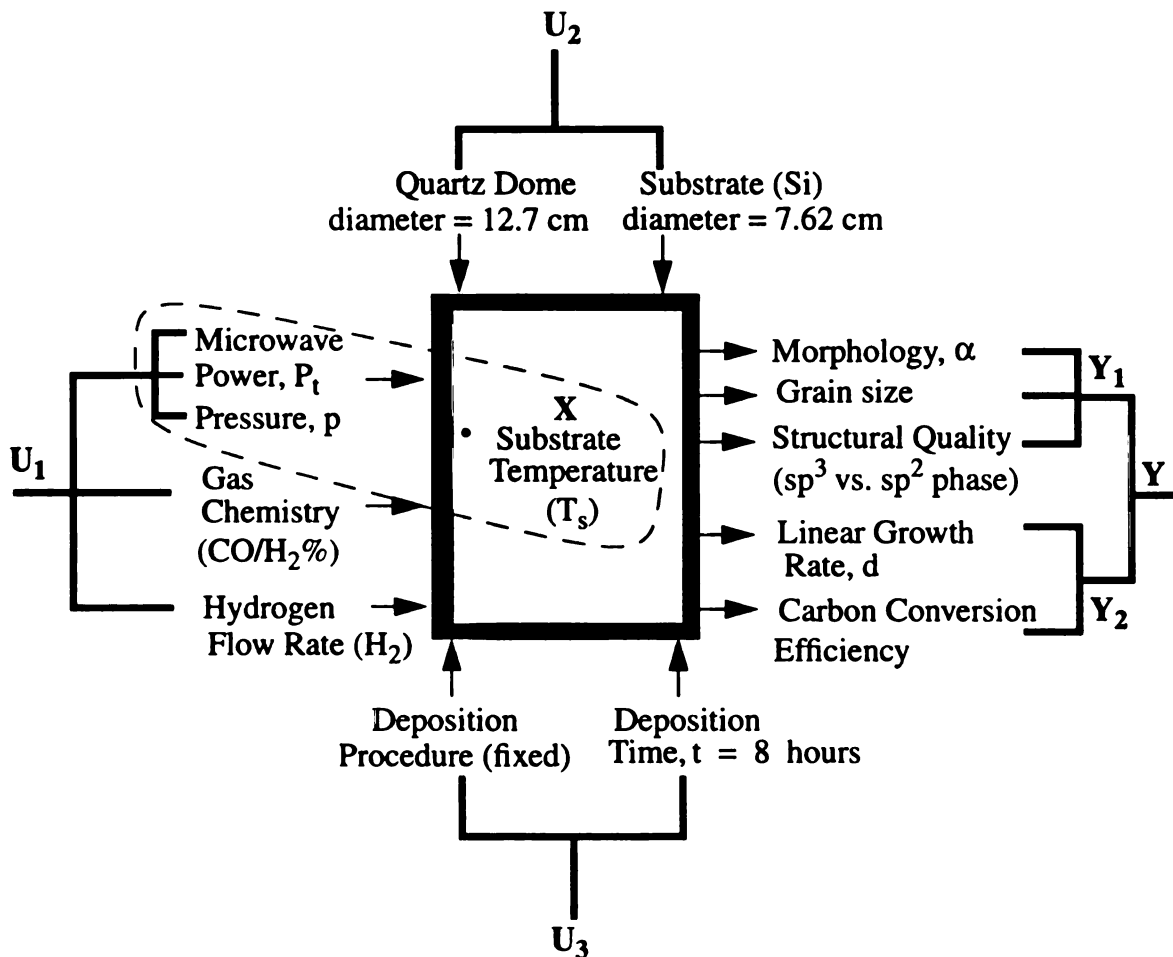


Figure 7.1. Microwave cavity plasma reactor block diagram utilized for CO-H₂ diamond film deposition. The dashed curve encircles the T_s , p , and P_t variables indicating that this triad of variables can be considered as a single input variable for this investigation.

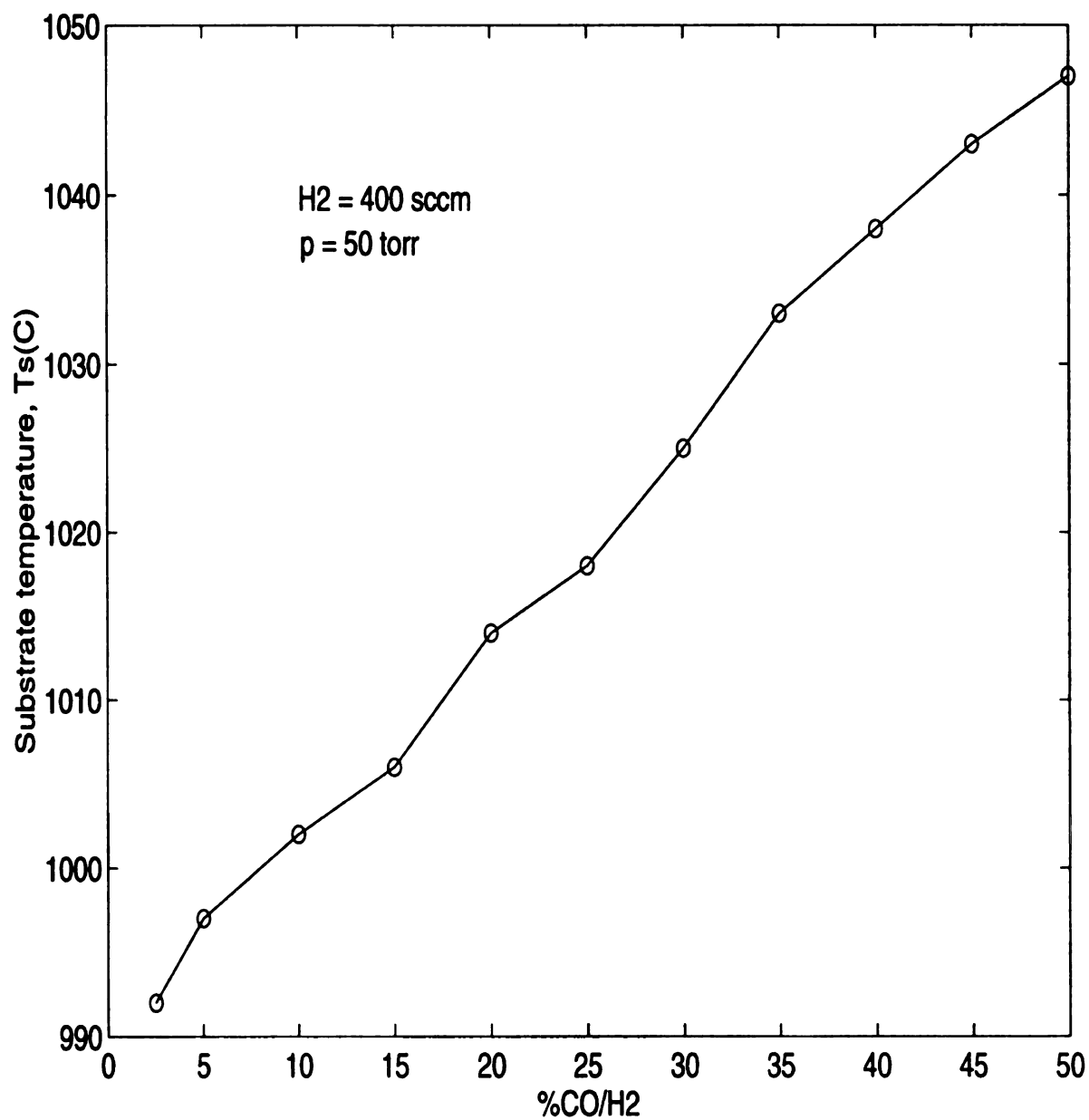


Figure 7.2. Effect of CO concentration on the substrate temperature for $H_2 = 400$ sccm, and $p = 50$ torr.

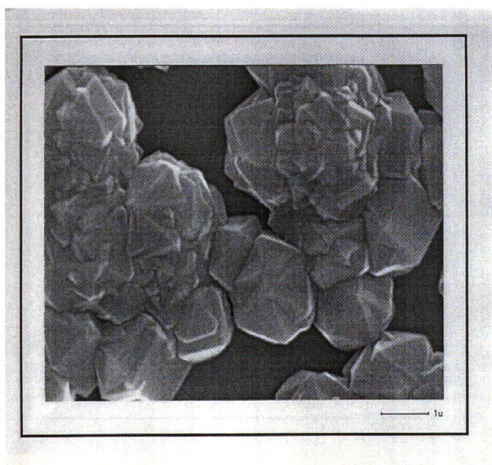
Section 7.2.1.1, Figure 7.8), hence, for most of the experiments reported in this chapter, the pressure range of $p \in [35, 50]$ torr was used. The diamond films in the pressure range of $p \in [35, 50]$ torr were continuous for $\frac{\text{CO}}{\text{H}_2} \in [10, 70]\%$. The range of absorbed input microwave power (1 - 2.5 KW) was determined from the discharge size requirement i.e., discharge size required to cover the substrate surface. It should be noted that since substrate temperature was affected by variations in CO concentrations, the reactor road map of Figure 4.5 could not be utilized to determine the range of absorbed microwave power. Different reactor road maps were needed for different CO concentrations for CO-H₂ diamond deposition experiments. This was beyond the scope of this thesis.

Hydrogen flow rate and CO concentration, CO/H₂

The first few experiments that were carried out at $\text{H}_2 = 100$ sccm with $\text{CO}/\text{H}_2 \leq 10\%$ and $p = 35$ torr resulted in discontinuous films with small growth rates. For instance, at $\text{H}_2 = 100$ sccm, $\text{CO}/\text{H}_2 = 10\%$, and $p = 35$ torr the diamond film was discontinuous as shown in Figure 7.4 and the growth rate was about $0.095 \mu\text{m/hr}$. Under similar CO/H_2 concentration and pressure but $\text{H}_2 = 400$ sccm the resulting film was continuous and the growth rate was about $0.17 \mu\text{m/hr}$ (see Section 7.2.1.1, Figure 7.7 (a)). Therefore, $\text{H}_2 = 400$ sccm was selected for CO-H₂ diamond deposition. It should be noted that since high CO concentrations (compared to methane concentrations) are used in CO-H₂ diamond film deposition, H_2 flow rate (instead of total gas flow rate, f_t) was used as an independent input variable. At $\text{CO}/\text{H}_2 = 2.50\%$, the deposition rate was very small,

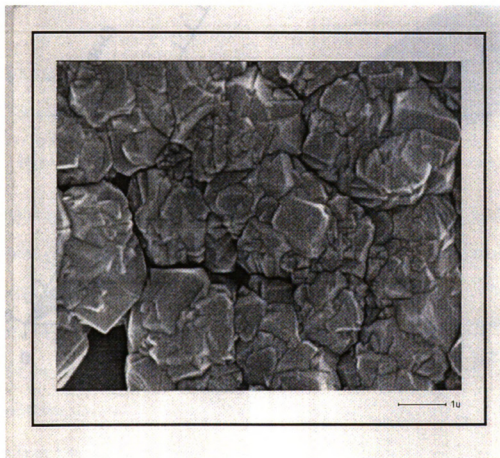
therefore, $\text{CO}/\text{H}_2 = 10\%$ was chosen as the lower limit of the CO concentration. As will be shown in Section 7.2.2.1, although the growth rate increased with CO concentration in hydrogen, the increase was very small. For instance, at $\text{H}_2 = 400$ sccm, $p = 35$ torr, and $\text{CO}/\text{H}_2 \leq 30\%$ the growth rate was $0.220 \mu\text{m/hr}$ while for the same flow rate and pressure but with $\text{CO}/\text{H}_2 \leq 70\%$ the growth rate was $0.231 \mu\text{m/hr}$. That is, with over 130 percent increase in CO concentration, the growth rate increased by only $0.011 \mu\text{m/hr}$ (i.e., 5 percent increase). For this reason, and since only a limited number of experiments were to be carried out with CO, the upper limit of CO concentration in hydrogen was chosen to be 30% for most of the experiments reported in this chapter. As shown in Figure 7.5 the CO concentrations were on the CO line within the well-defined diamond zone of the Bachmann diagram.

This chapter is comprised of three sections. In Section 7.2, for deposition time fixed at 8 hours, an investigation of CO- H_2 diamond CVD film deposition vs. input variables specified in Table 7.1 is carried out. In Section 7.3 a discussion of the results is presented.



SK96

Figure 7.3. SEM picture of the sample deposited at $\text{CO}/\text{H}_2 = 10\%$, $\text{H}_2 = 400$ sccm, and $p = 25$ torr.



SK95

Figure 7.4. SEM picture of the sample deposited at $\text{CO}/\text{H}_2=10\%$, $\text{H}_2 = 100$ sccm, and $p = 35$ torr.

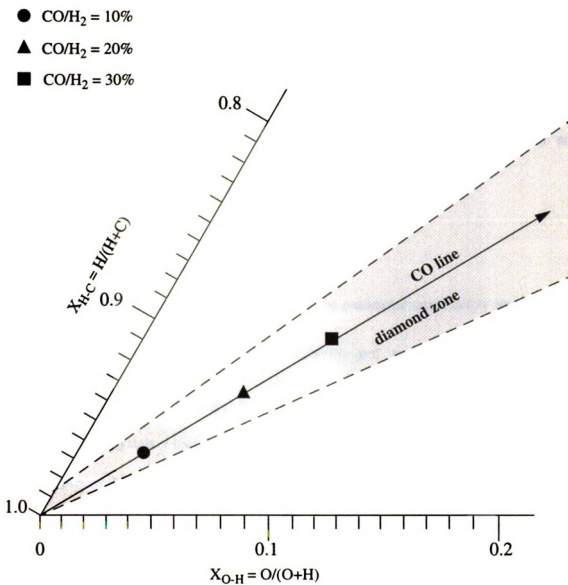


Figure 7.5. Locations of various CO/H_2 gas composition used in this chapter on the C-H-O Bachmann phase diagram.

7.2 CO-H₂ Film deposition vs. input and internal variables for a fixed deposition time of eight hours

7.2.1 Film properties (Y₁) vs. CO/H₂ and pressure

In what follows, morphology, grain size, and structural quality of the CVD diamond films deposited under $H_2 = 400$ sccm, $\frac{CO}{H_2} \in [10, 30] \%$, and $p \in [35, 60]$ torr are investigated.

7.2.1.1 Morphology and grain size

Majority of the diamond films deposited in the parameter space under investigation (i.e., $H_2 = 400$ sccm, $t = 8$ hours, $\frac{CO}{H_2} \in [10, 30] \%$ and $p \in [35, 60]$ torr) displayed {111} morphology. A few films displayed mixed morphologies (i.e., {111} and {100}). Majority of the crystals which had {111} top surface did not look like an octahedron ($\alpha \cong 3$). Figure 7.6 shows the habit that the majority of crystals displayed. Figure 7.7 shows some sample SEM pictures of the CO-H₂ deposited diamond films. Figure 7.8 shows that the film was not continuous at $p = 60$ torr when $CO/H_2 = 10\%$. The same phenomenon was observed for higher concentrations of CO. The substrate temperatures associated with this pressure were 1045°C, 1063°C, and 1082°C for $CO/H_2 = 10\%$, 20%, and 30%, respectively. At lower pressures (i.e., $p = 50$ torr) which corresponded to $T_s = 900 - 990^\circ\text{C}$, the resulting films were continuous. It seemed that the temperature zone of $T_s > 1000^\circ\text{C}$ did not favor the CO-H₂ diamond deposition.

With respect to grain size and twin concentration, it is seen from the SEM pictures of

Figure 7.7 that at $\text{CO}/\text{H}_2 = 30\%$ the average grain size was bigger and twin concentration was smaller than at $\text{CO}/\text{H}_2 = 10\%$, and at $\text{CO}/\text{H}_2 = 20\%$. At $\text{CO}/\text{H}_2 = 20\%$ the grain size was smaller and the twin concentration was larger than those of $\text{CO}/\text{H}_2 = 10\%$.

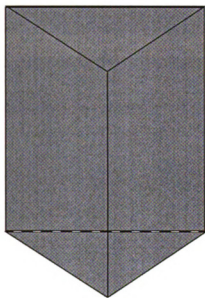


Figure 7.6. The crystal habit common to majority of the crystals deposited under the parameter space investigated in this chapter.

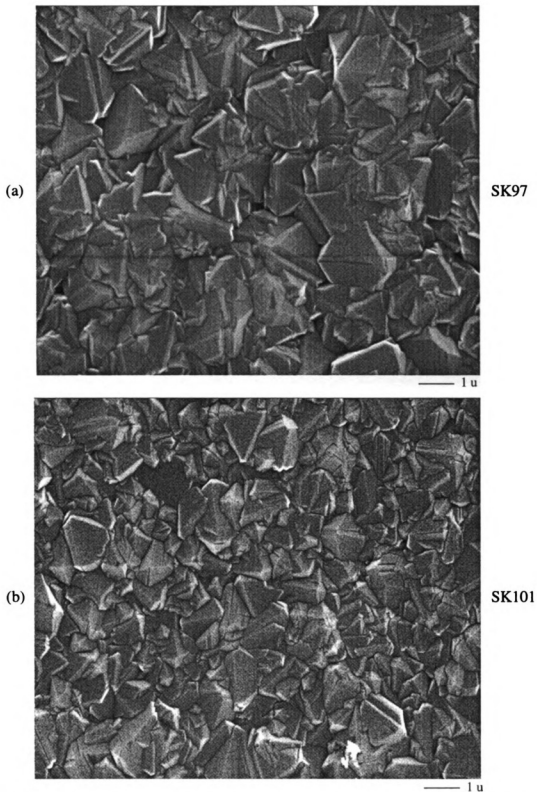


Figure 7.7. SEM pictures of CO-H₂ sample deposited at H₂ = 400 sccm, p = 35 torr, and (a) CO/H₂ = 10%, (b) CO/H₂ = 20%, and (c) CO/H₂ = 30%.

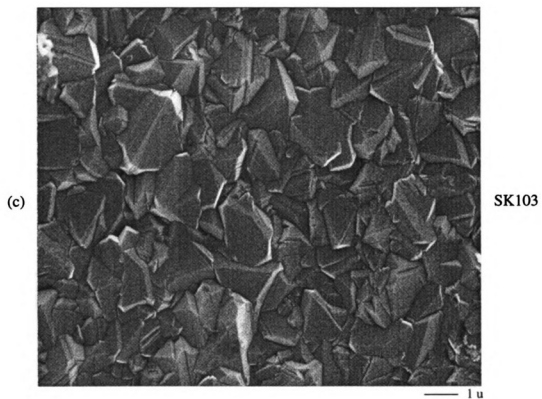
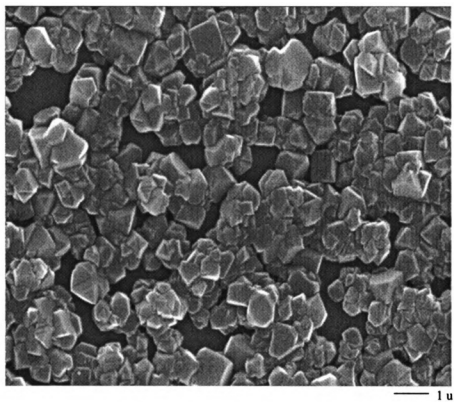


Figure 7.7. Continued.



SK122_2

Figure 7.8. SEM picture of SK122_2 sample deposited at $H_2 = 400$ sccm, $p = 60$ torr, and $CO/H_2 = 10\%$.

7.2.1.2 Structural quality

Figure 7.9 shows the effect of CO concentration on the CO-H₂ diamond film quality determined by Raman spectra. Figure 7.10 shows the plot FWHM vs. CO concentration in hydrogen for H₂ = 400 sccm and p = 35 torr. It shows that FWHM became smaller as the CO concentration in hydrogen increased in its respected range.

The effect of pressure on the film quality is shown in Figure 7.11. This Figure shows the Raman spectra of two samples deposited at H₂ = 400 sccm and CO/H₂ = 20%, with p = 35 torr and 45 torr, respectively. The FWHM associated with the first sample (i.e., p = 35 torr) was measured to be 9.40 cm⁻¹ and that of the second sample (i.e., p = 45 torr) was 8.74 cm⁻¹. Hence diamond film quality was improved with pressure in its respected range.

Finally, it should be mentioned that although pressure and CO concentration in hydrogen affected the CO-H₂ diamond film quality, in the parameter space under investigation (i.e., $\frac{\text{CO}}{\text{H}_2} \in [10, 30] \%$ and $p \in [35, 50] \text{ torr}$), the effect was not very significant and all CO-H₂ diamond films showed FWHM around 9 cm⁻¹. It is seen that one can have high concentrations of CO gas in hydrogen and a large variation in CO concentration in hydrogen and still deposit fine quality diamond films (i.e., sharp diamond and small graphitic peaks). This is contrary to the effect of CH₄ which showed to have a detrimental effect on the diamond film quality when its concentration in hydrogen exceeded a few percent.

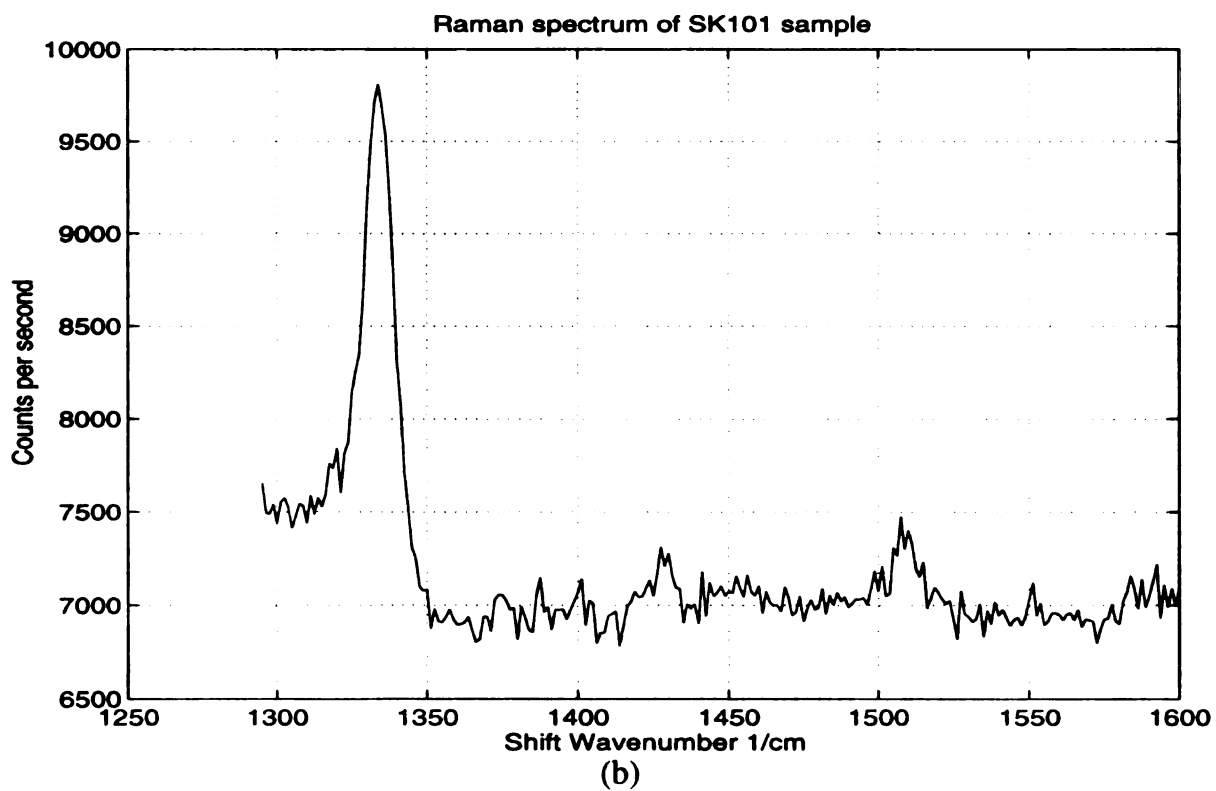
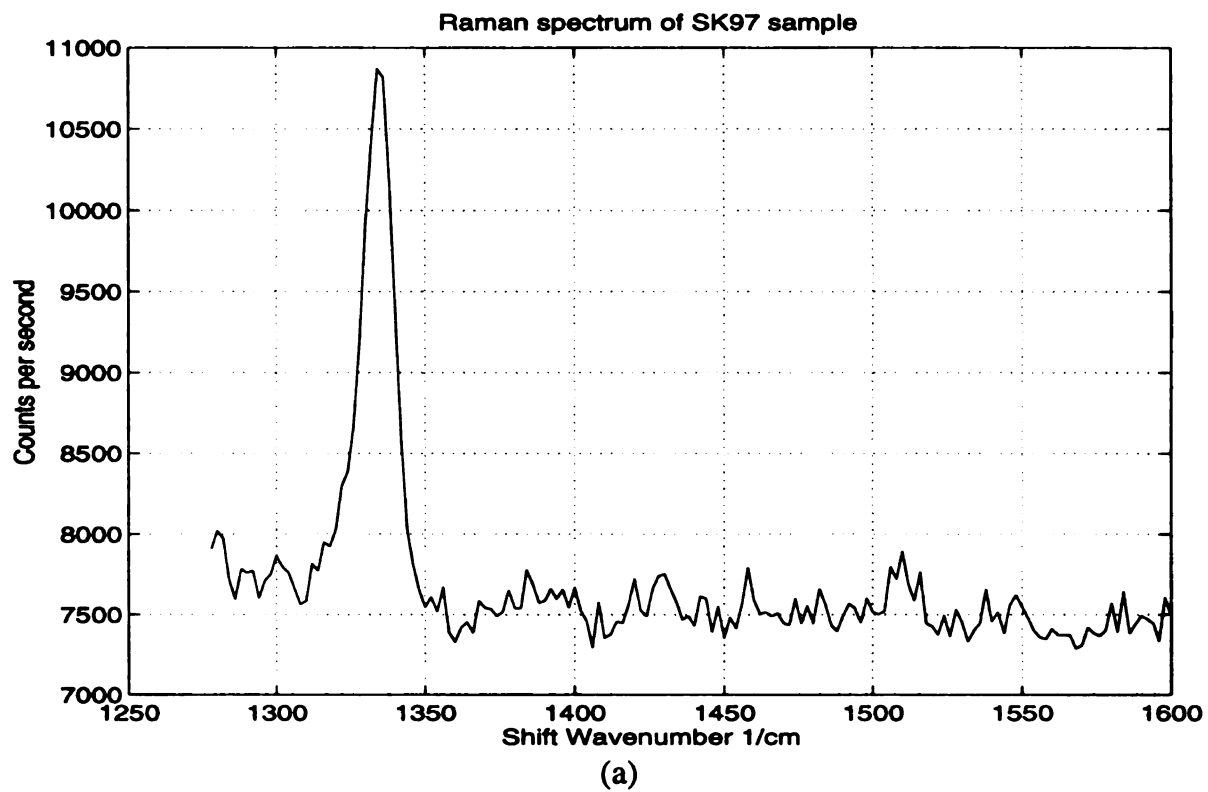


Figure 7.9. Raman spectra of diamond films deposited at $H_2 = 400$, $p = 35$ torr, and $CO/H_2 =$ (a) 10%, (b) 20%, and (c) 30%.

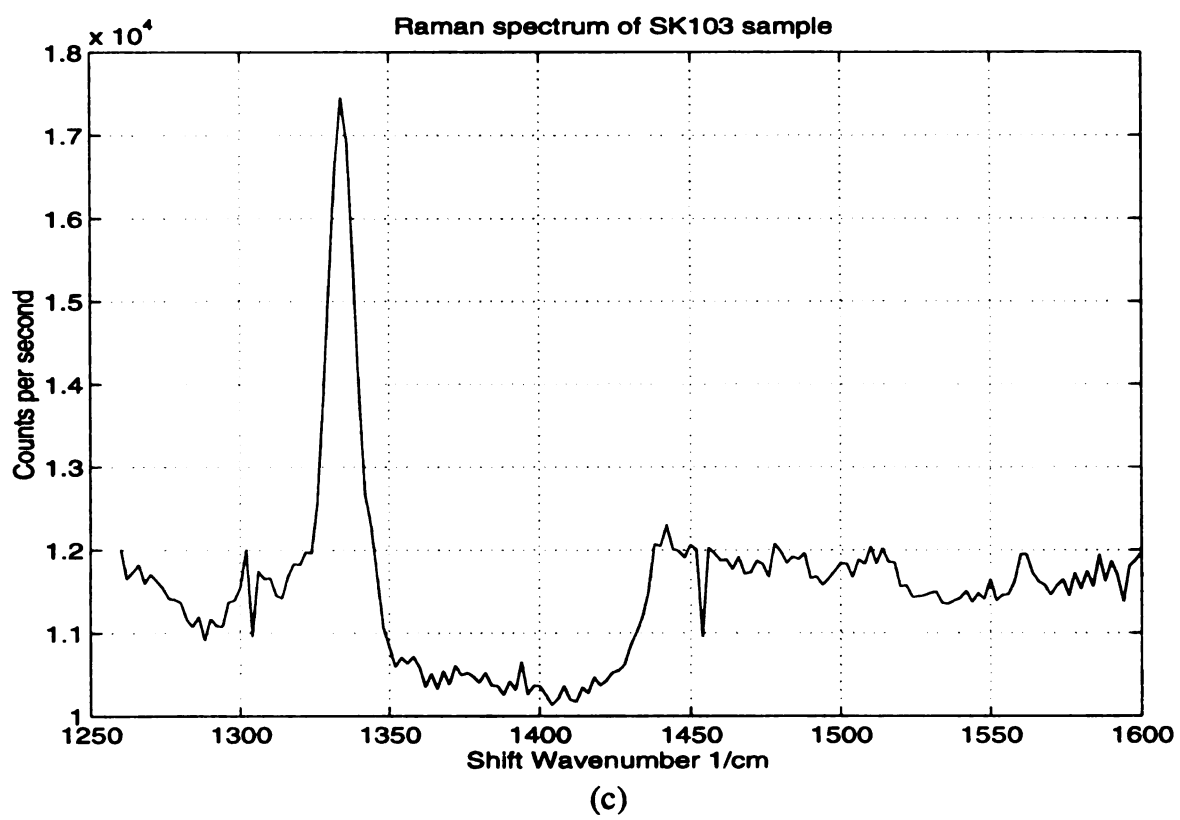
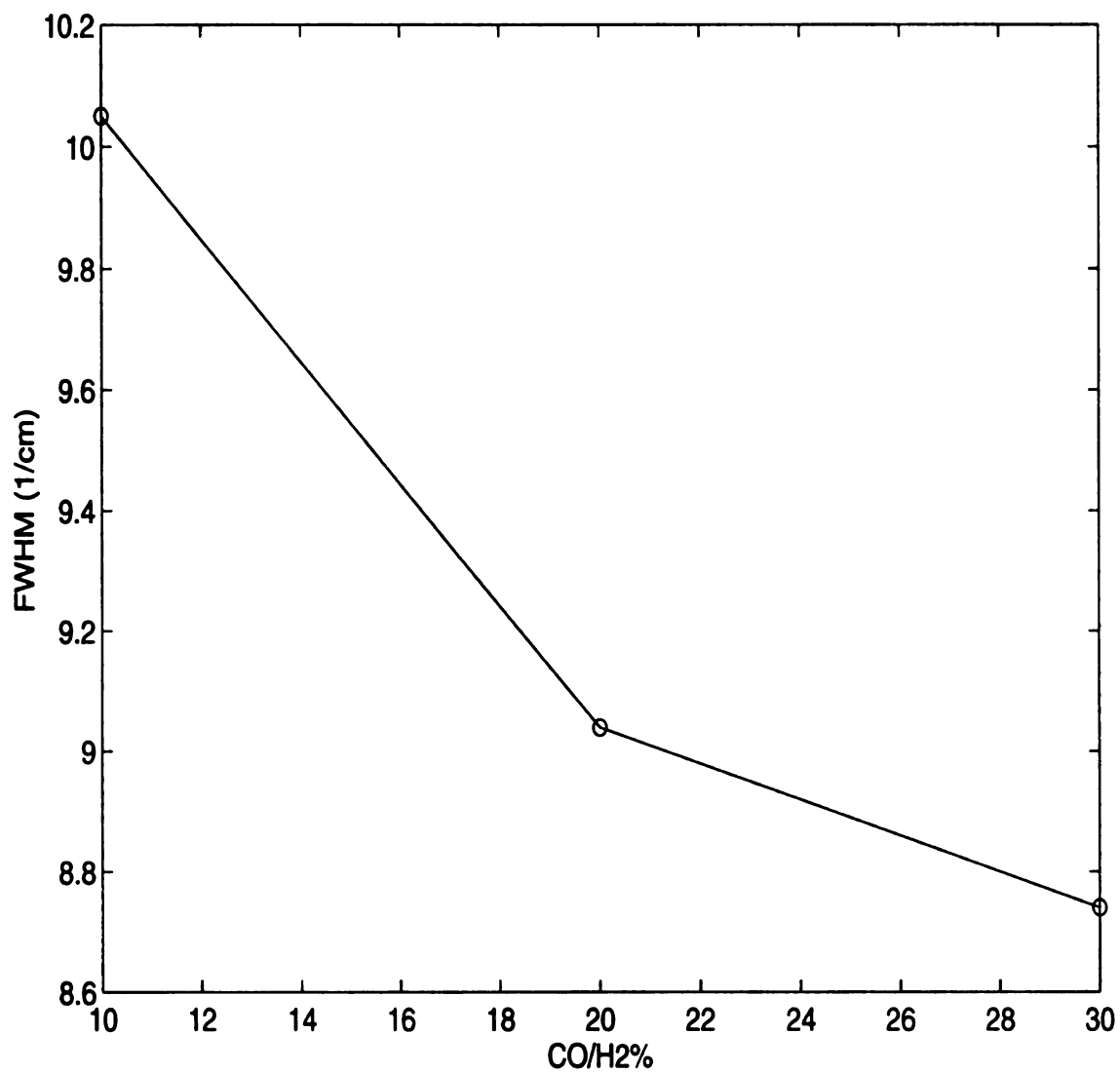


Figure 7.9. Continued.



Sample	%CO/H ₂	FWHM (cm ⁻¹)
SK97	10	10.05
SK101	20	9.04
SK103	30	8.74

Figure 7.10. FWHM vs. CO concentrations for CO-H₂ diamond films deposited at H₂ = 400 sccm and p = 35 torr.

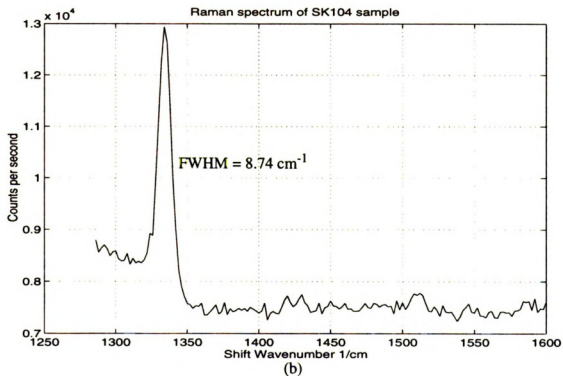
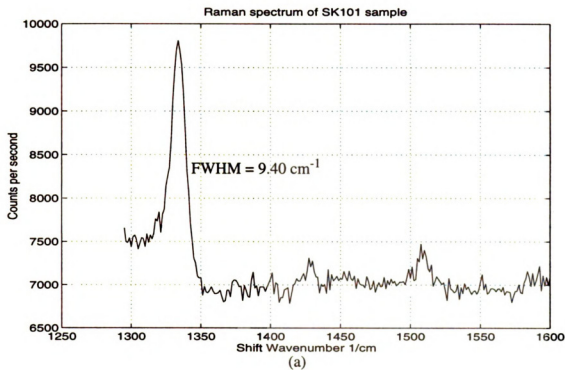


Figure 7.11. Raman spectra of diamond films deposited at $\text{H}_2 = 400$, $\text{CO}/\text{H}_2 = 20\%$, and (a) $p = 35$ torr, and (b) $p = 45$ torr.

7.2.2 Reactor performance (Y_2) vs. CO/H₂ and pressure

7.2.2.1 Linear growth rate

CO-H₂ diamond film linear growth rate were calculated via the method described in Section 4.5.4 (eq. 4.1.). This measurement method determines the average film growth rate over the substrate surface. Figure 7.12 illustrates the dependence of film linear growth rate on the operating pressure and CO/H₂% concentration. The (p, CO/H₂, $\mu\text{m/hr}$) coordinates of some points (specified by O) are included in Figure 7.12. The linear growth rate of these films increased with CO concentration but decreased with operating pressure in their ranges of $\frac{\text{CO}}{\text{H}_2} \in [10, 30] \%$ and $p \in [35, 60]$ torr. As was shown in Figure 7.8 the films deposited at 60 torr were discontinuous so they were expected to have small growth rate. The diamond films in the pressure range of $p \in [35, 50]$ torr were continuous but yet showed a decrease in the linear growth rate as pressure was increased.

7.2.2.2 Carbon conversion efficiency

Carbon conversion efficiency of the CO-H₂ diamond films was calculated from eq. 4.2 - eq. 4.4. Figure 7.13 depicts the plot of carbon conversion efficiency vs. pressure and CO/H₂. Carbon conversion efficiency was very poor due to the large concentrations of CO and small growth rates (i.e., weight gains). Carbon conversion efficiency was shown to be inversely proportional to the operating pressure and CO concentration in hydrogen.

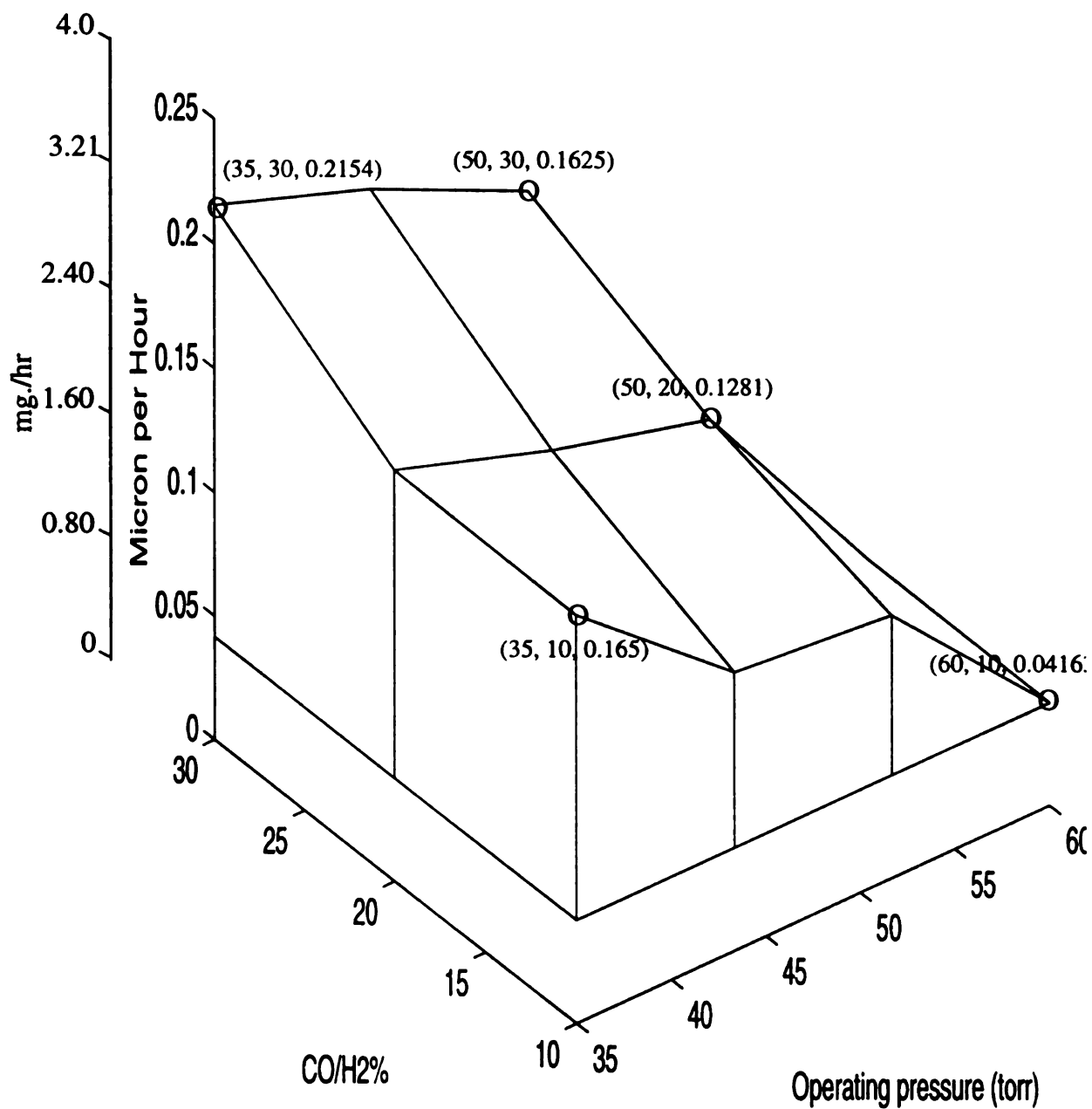


Figure 7.12. CO-H₂ diamond film linear growth rate vs. CO/H₂ and operating pressure. O represents the (p, CO/H₂%, um/hr) coordinates.

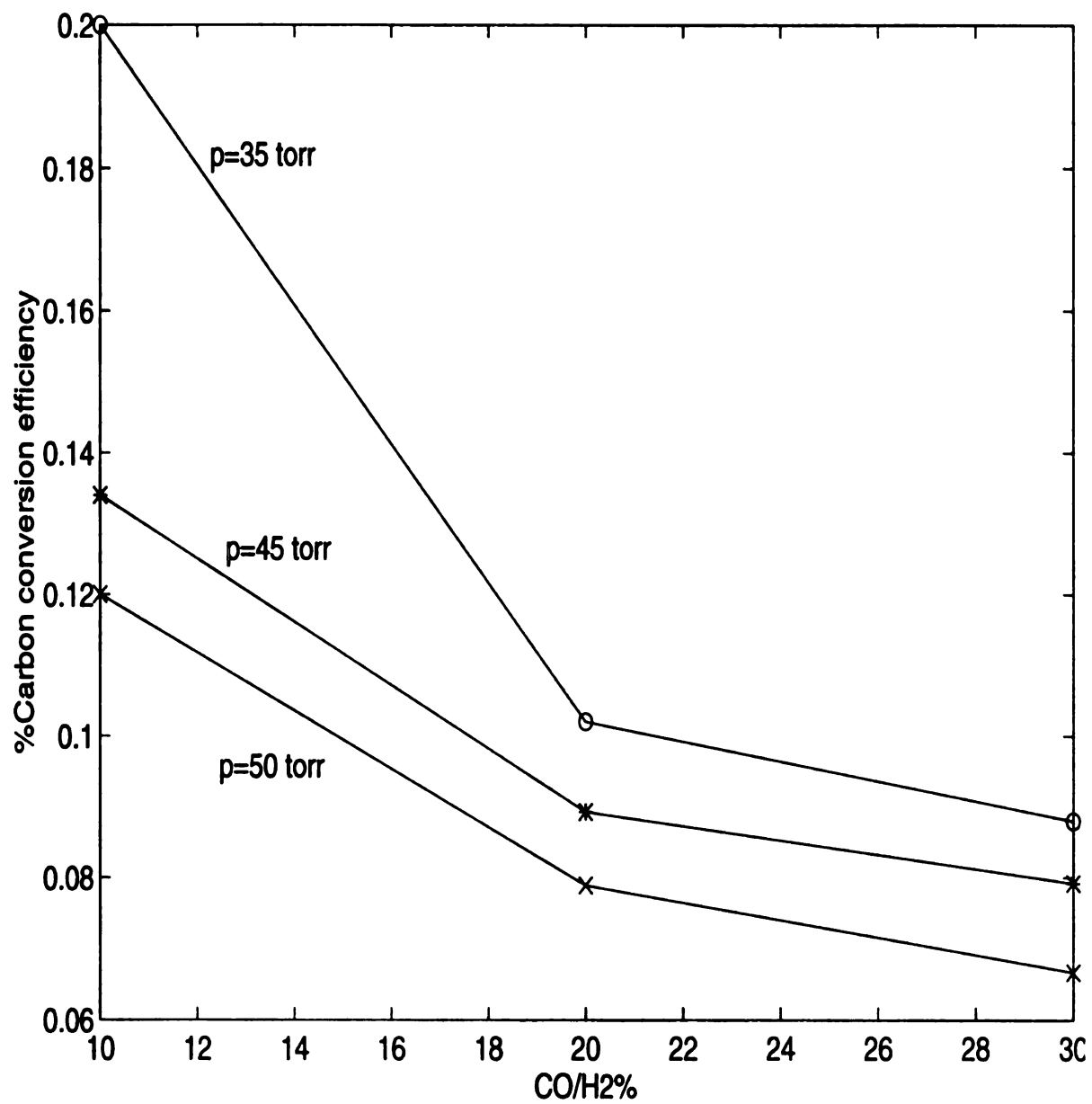


Figure 7.13. % Carbon conversion efficiency vs. pressure and CO/H₂%.

7.3 Discussion

7.3.1 Output variables (Y) vs. CO/H₂ chemistry and pressure

7.3.1.1 Diamond film properties (Y₁) vs. CO/H₂ and pressure

7.3.1.1.1 Morphology vs. CO/H₂ and pressure

It was shown in Figure 5.76 that according to the Walff criterion [36], in CVD processes, only the slowest growing facets survive and other facets go out of existence. With respect to CO-H₂ diamond films deposition, it is seen that only {111} morphology existed. This shows that $V_{100} > V_{111}$ for all the O-H₂ diamond films deposited in their respected range (Table 7.1). As discussed in Chapter 5, high flow rate or small carbon conversion efficiency deposition conditions favor {111} facets formation and as seen in Figure 7.13 the carbon conversion efficiencies associated with the current CO-H₂ diamond films were very small.

7.3.1.1.2 Structural quality vs. CO/H₂ and pressure

From the Raman spectra of Figure 7.9 and Figure 7.11 it is seen that there was almost no graphitic peak (i.e., peak at or around 1550 cm⁻¹) associated with the deposited CO-H₂ diamond films. This can be attributed to the presence of atomic oxygen (a strong graphite etchant) which results from the dissociation of CO molecules into C and O atoms in the plasma. Furthermore, it is seen that one can have a large variation in CO concentration in hydrogen and still deposit fine quality diamond films (i.e., sharp diamond and small graphitic peaks). This was contrary to the effect of CH₄ which showed to have a detrimental effect on diamond film quality when its concentration in hydrogen was

increased by only a few percent. Having been able to deposit fine quality diamond films at high concentrations of CO gas can also be attributed to the presence of atomic oxygen in the plasma which strongly removes graphitic phase in CVD of diamond

7.3.1.2 Reactor performance (Y_2) vs. CO/H₂ and pressure

7.3.1.2.1 Growth rate vs. CO/H₂ and pressure

High pressures result in high temperatures which enhance the $\text{CO} \rightarrow \text{C} + \text{O}$ dissociation. Although atomic oxygen etches graphite, it can compete with carbon containing species in adsorbing to the film surface growth sites. This abundance of atomic oxygen in high pressures may be a reason for having smaller growth rate at higher pressures to the point that at about 60 torr there was so little concentration of carbon containing species on the surface that resulting film did not even become continuous after 8 hours of deposition. Furthermore, atomic oxygen O can combine with atomic hydrogen H and with carbon C to reduce the concentration of H and C. The reduced concentration of H and/or C result in reduced growth rates.

CHAPTER 8

Microwave Plasma Assisted CVD of Diamond Films

on Tungsten Substrates

8.1 Introduction

In this chapter the microwave plasma assisted CVD of diamond films on tungsten substrates (disks) will be examined. The tungsten substrates were 1 inch in diameter and the desired diamond film thickness was at least 15 μm . The diamond films were to be patterned as shown in Figure 8.1. Poor adhesion due to the stresses that result from difference in the thermal expansion coefficient and microstructural mismatch between the diamond and the tungsten substrate is a critical problem associated with CVD of diamond on tungsten. The overall stress is comprised of intrinsic stress due to a mismatch in microstructures, and thermal stress due to the difference between thermal expansion coefficient of the diamond and tungsten ([81], [82]). The thermal stress is compressive since the thermal expansion coefficient of diamond is smaller than that of tungsten (Table 8.1). The adhesion problem becomes more detrimental as film thickness increases. Due to a lesser degree of thermal expansion and microstructures mismatch between the diamond and the silicon, the adhesion problem is generally less severe with respect to CVD of diamond on silicon substrates. Table 8.1 lists some physical, crystallographic and thermal properties of diamond, silicon, and tungsten.

Different approaches have been taken to improve the adhesion of CVD diamond on various substrates. For instance, functionally gradient material interlayer grown between the substrate and the diamond film was shown to enhance the adhesion of diamond to the substrate [84]. In this method a mixture of diamond and the substrate element whose metal content was decreased from the substrate material to the surface continuously, was used to reduce the internal stresses that are caused by a thermal expansion mismatch between the diamond and the substrate. The interlayer grown for this purpose is called a functionally gradient material [84]. Surface roughening of substrates has also been used to improve diamond-substrate adhesion. A possible explanation for surface roughening is that surface roughening offers an increased contact area for bonding and a means of physically anchoring the film onto the substrate surface [81].

With respect to CVD of diamond on tungsten, the following steps were suggested by C. R. Shi and colleagues [81]: (i) mechanical polishing with Al_2O_3 powder, (b) thorough cleaning, (c) treatment in hydrogen plasma, (d) carburization in a mixture of CH_4 and H_2 at $T = 950 - 1000^\circ C$, (e) etching by a hydrogen plasma at $T = 1000 - 1100^\circ C$, (f) surface roughening with diamond grit, and (g) cleaning. Prior to carburization the samples should be treated in a pure hydrogen plasma in order to eliminate contamination of the substrate surface. The purpose of the carburization step was to produce WC layer since the thermal expansion coefficient of WC is lower than that of tungsten. The step (e) was performed to remove graphite which deposits during carburization.

The diamond quality is considered as another factor that affects the adhesion of the diamond film to tungsten substrate. The compressive stress increases with an increase in sp^2 bonding. Therefore, a good quality diamond suffers less from the adhesion problem

[81].

Table 8.1. Some properties of diamond, silicon and tungsten

Element	Crystal structure	Lattice constant (Angstrom)	Thermal conductivity at 298 K (W/m-K)	Coefficient of linear thermal expansion ^a
C (diamond)	f.c.c (Fd3m)	3.5673	990-2320	0.8×10^{-6}
Si	f.c.c (Fd3m)	5.4307	148	3.0×10^{-6}
W	b.c.c (Im3m)	3.1652	174	4.5×10^{-6}

a. The coefficient of linear thermal expansion is the ratio of the change in length per degree K (or C) to the length at 273 K (or 0 °C).

8.2 Experimental

8.2.1 Diamond deposition on tungsten

The substrates used in this work were pure tungsten disks of 1 inch in diameter. The tungsten substrates were spin seeded with a solution of photoresist and diamond powder (see Section 4.3.1) prior to diamond deposition. Due to the surface roughness, the seeding, however, was not necessary for diamond nucleation and continuous film formation. The substrate seeding was carried out to have a better uniformity of diamond film since with the spin seeding procedure diamond seeds were almost uniformly spread on the substrate surface. Appropriate deposition conditions and deposition methodology for adhesion improvement were the steps taken for the CVD of diamond on the tungsten substrates as described below.

(i) Appropriate deposition condition

The deposition conditions at which diamond films were deposited are as follows.

$H_2=400$ sccm

$CH_4/ H_2 = 1.50\%$

Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)

and

$H_2=200$ sccm

$CH_4/ H_2 = 1.50\%$

Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)

The above deposition conditions were chosen to be tested for CVD of diamond on tungsten for the following reasons:

To reduce the compressive stress in the diamond films, deposition conditions that normally lead to diamond films with high graphitic contents (i.e., high CH_4/ H_2 concentrations) were not used in the current work. Since the thermal expansion is directly proportional to the temperature, the deposition pressure (i.e., temperature, T_s) was chosen to be as small as possible and at the same time yield an adequate growth rate and relatively small graphitic content. From the work reported in Chapters 5 - 7, the $T_s \sim 850^\circ\text{C}$ was chosen as the deposition temperature. From the Raman spectra of Figures 5.35 (c) (Raman spectrum of SK179 sample), and 5.37 (c) (Raman spectrum of SK177 sample) and the growth rate Figures 5.47 and 5.48, it is seen that the above deposition conditions seem appropriate to result in diamond films with low graphitic contents and adequate growth rates.

(ii) Deposition methodology for adhesion improvement

(a) **Surface roughening:** The tungsten substrates were examined under a microscope prior to diamond deposition. The substrates looked rough with surface roughness of several microns. This eliminated the need for surface roughening which would have been performed as a necessary step for adhesion improvement other wise.

(b) **Substrate cleaning:** To remove contaminations from the tungsten substrates, the substrates were rinsed with acetone, methanol, and DI water before being seeded.

(c) **Multi-step deposition process:** The preliminary deposition of diamond on the tungsten substrates resulted in diamond films with the growth rate of approximately 0.68 $\mu\text{m/hr}$. Therefore, in order to achieve the required thickness of at least 15 μm , the deposition period of about 24 hours was required. At first, uninterrupted diamond deposition for 24 hours were performed but the adhesion was not good. In the current work the following multi-step deposition process was developed and tested for adhesion improvement.

Step 1.

$\text{H}_2=400 \text{ sccm}$
 $\text{CH}_4/\text{H}_2 = 0.0\%$
 Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)
 $t_1=20 \text{ minutes}$

Step 2.

$\text{H}_2=400 \text{ sccm}$
 $\text{CH}_4/\text{H}_2 = 1.50\%$
 Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)
 $t_2=10 \text{ hours}$

Step 3.

Deposition was halted for a few hours.

Step 4.

$H_2=400$ sccm

$CH_4/H_2 = 0.0\%$

Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)

$t_4=15$ minutes

Step 5.

$H_2=400$ sccm

$CH_4/H_2 = 1.50\%$

Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)

$t_5=14$ hours

The same procedure was followed with respect to a different deposition condition (i.e., $H_2=200$ sccm, $CH_4/H_2 = 1.50\%$, and pressure = 36 Torr). The adhesion of diamond film to the tungsten substrates were tested via forcefully scratching with a sharp object.

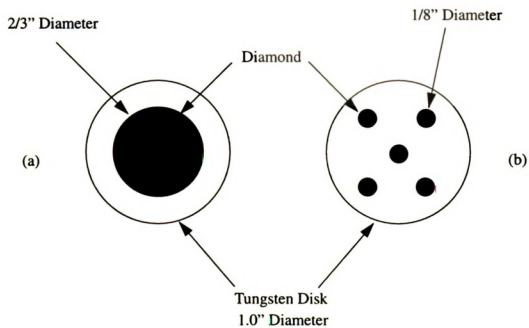


Figure 8.1. Required patterns for CVD diamond films on tungsten disks.

8.2.2 Diamond film patterning using plasma etch

The diamond films were to be patterned according to Figure 8.1. Three different methods were examined to accomplish the diamond patterning on the tungsten substrates.

(i) Patterning via UV photolithography:

The first approach to pattern the diamond films was UV photolithography. In this method the tungsten disks were spin seeded with a solution of photoresist and 0.1 μm diamond particles (see Section 4.3.1 for details). Then the disks were patterned via the standard photolithographic technique to that of Figure 8.2 (d) or Figure 8.3 (d) and then were placed in the CVD chamber for diamond deposition.

(ii) Patterning via stainless steel shadow mask

The second approach to pattern the diamond films was through use of stainless steel shadow masks. In this method stainless steel shadow masks were made and placed on top of the tungsten disks and then the combination of tungsten disks and shadow masks were placed in the CVD deposition chamber. The portions of the disks that were exposed to plasma had diamond deposited on them. The unexposed portions did not have diamond grown on them since the masks were made such that the spacing between the tungsten disks and the masks were too close to let any plasma form underneath the masks. Figure 8.4 illustrate this procedure.

(iii) Patterning via plasma etch

The third and the final approach to pattern the diamond films was the use of atomic oxygen plasma which is known to etch diamond in room temperature [84]. Diamond films were deposited on the entire substrates and then were patterned to those of Figure 8.1 via a plasma etch. The Plasma Quest model 357 W plasma system was utilized for plasma etch. The system was operated by Dr. Grotjohn and B. K. Kim. Figure 8.5 illustrates the schematic diagram of the Plasma Quest etch system [85]. The desired features were masked and the undesired features (areas) were exposed to oxygen plasma to be removed. Aluminum was tested for masking and it was observed that thick aluminum masking could withstand the plasma etch. Shadow masks were used to evaporate aluminum on the diamond films. The task was to remove $\sim 15 \mu\text{m}$ of diamond from selected areas of the diamond films. As the first experiment, a single layer of aluminum was evaporated on the diamond sample and the sample was subjected to plasma etch. The following etch condition [85] was used:

Ar = 6 sccm
 O_2 = 28 sccm
 SF_6 = 2 sccm
 Pressure = 4 mTorr
 Microwave power = 600 W
 RF power = 161 W
 V_{rf} = 145 V
 Etch period = 9800 sec

In the absence of SF_6 , a black film is deposited on the film. SF_6 removes the black film [85]. After completion of the etch period it was observed that a single layer of aluminum mask was not sufficient to withstand the etch. Next, multi-layers (three to four layers) of aluminum were evaporated on a diamond film through a shadow mask and the

sample was subjected to the plasma etch of above condition. Figure 8.6 and Figure 8.7 illustrate the plasma etch procedure.

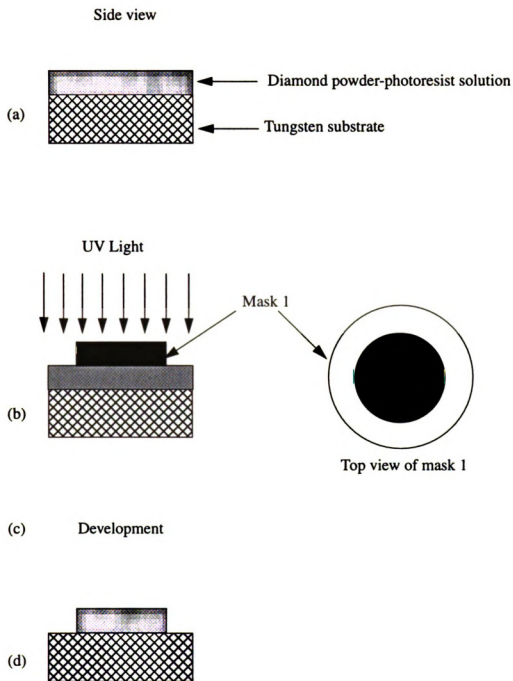


Figure 8.2. Standard UV photolithographic method for patterning the diamond films on tungsten substrates using mask 1.

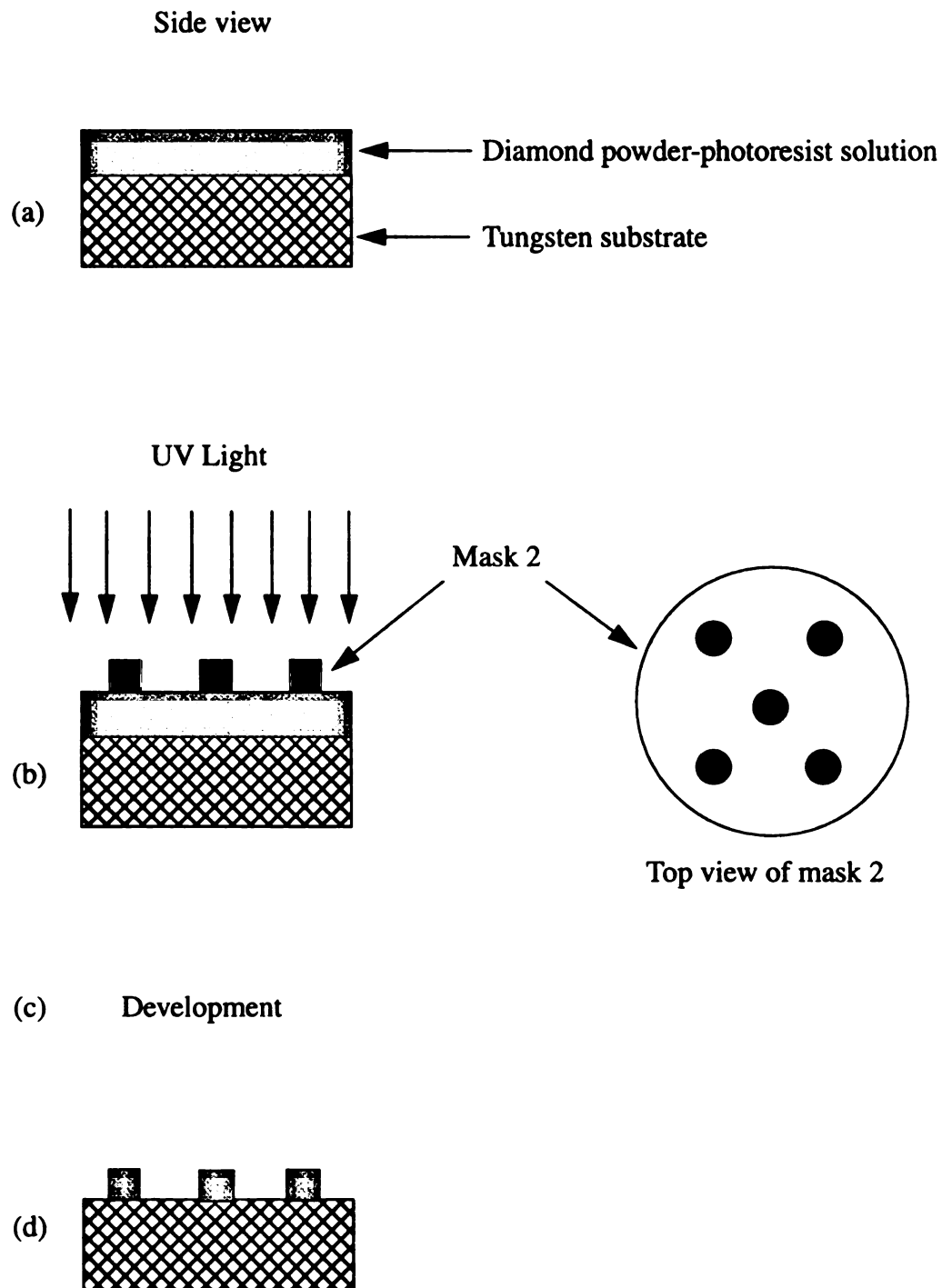


Figure 8.3. Standard UV photolithographic method for patterning the diamond films on tungsten substrates using mask 2.

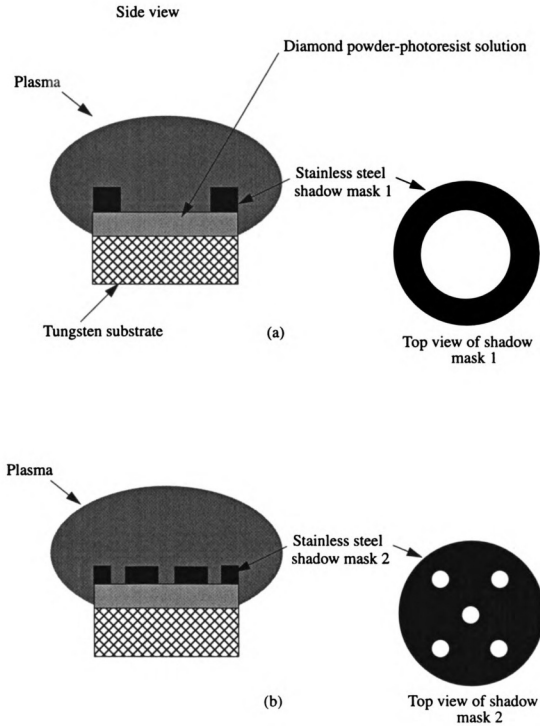


Figure 8.4. Use of stainless steel shadow masks for selectively depositing diamond films on tungsten substrates.

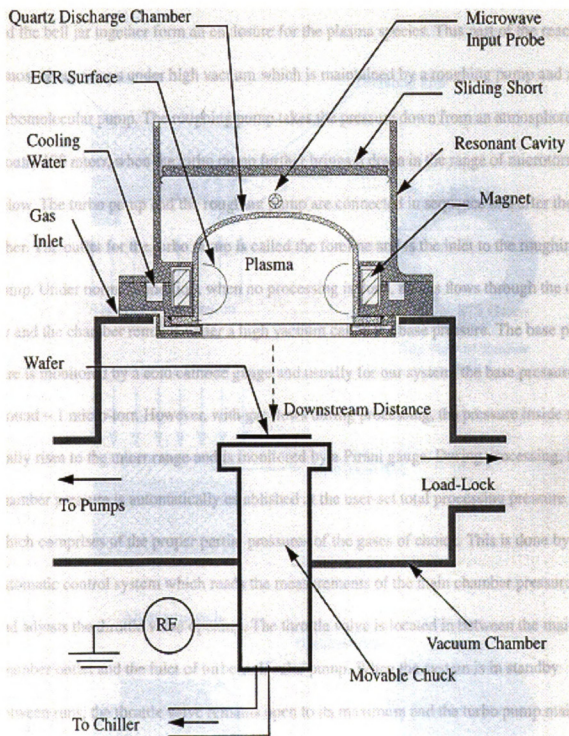


Figure 8.5. Plasma Quest etch system [85].

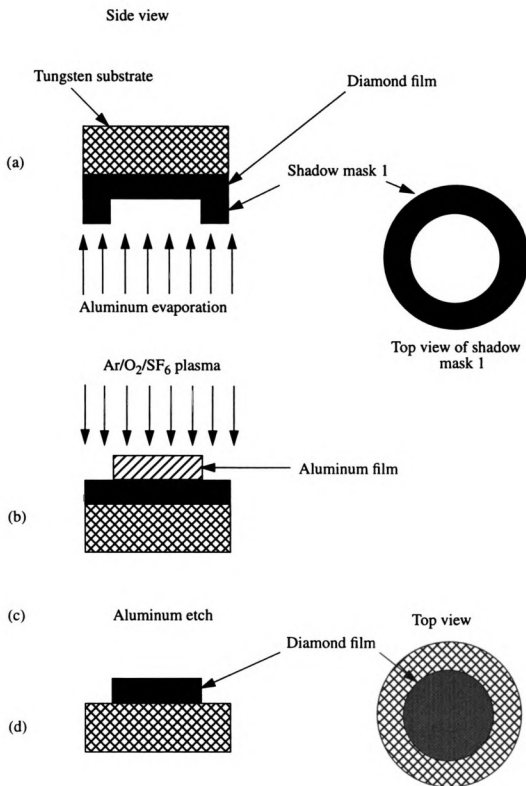


Figure 8.6. Plasma etch procedure using shadow mask 1.

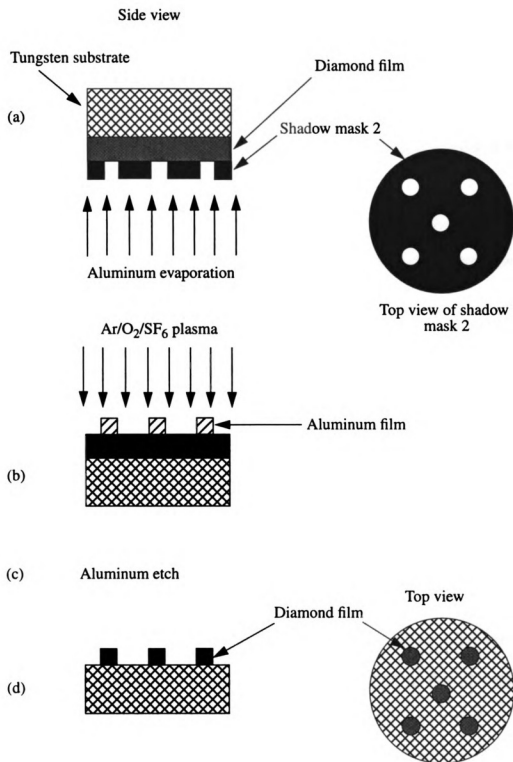


Figure 8.7. Plasma etch procedure using shadow mask 2.

8.3 Results and discussion

8.3.1 Diamond deposition on tungsten

The multi-step deposition procedure outlined above showed to be successful and resulted in CVD diamond on tungsten with good adhesion. In the absence of the multi-step deposition process (i.e., with uninterrupted deposition for 24 hours) the diamond films were prone to spontaneous peel off after the sample was cooled down to the room temperature.

The purpose of step 1 was to further clean the substrate from undesired contaminations. In step 3, the deposition was halted for a few hours. In step 4 the sample was subjected to hydrogen plasma (no CH_4) for 15 minutes. The purpose of these two steps (steps 3 and 4) was to let the film release some of its internal stresses before further deposition was taken place. It is speculated that dislocations in the film move and possibly recombine when the growth is halted for a period of time. This lowers the stress in the film. Furthermore, dislocations in the film could be thermally annealed when the film is subjected to hydrogen plasma only (no growth) at $\sim 850^\circ\text{C}$ after the process was halted. It is also possible that surface recombination takes place (i.e., surface energy decreases) when the process is halted and a second layer is formed through re-nucleation of diamond on top of the first layer so that now the total stress in the film is a combination of the stress between the first diamond layer and the tungsten substrate and the stress between the second and first diamond layers. Step 4 also removes any graphitic layer that might have been deposited during step 2 before a new layer of diamond film is deposited.

In what follows, typical linear growth rate, surface morphology, structural quality, and the carbon conversion efficiency of the diamond films deposited on tungsten

substrates are presented.

The linear growth rate was approximately 0.68 $\mu\text{m/hr}$. The linear growth rate was measured from the weight gain as discussed in Section 4.5.4. Figure 8.8 shows a typical diamond film surface morphology. The structural quality of the diamond films determined by Raman spectroscopy (Figure 8.9) showed a sharp diamond peak around 1332 cm^{-1} . The FWHM of the spectrum of Figure 8.9 was 13.72 cm^{-1} . The carbon conversion efficiency as determined from Section 4.5.5 for the un-patterned films deposited under:

$\text{H}_2=400\text{ sccm}$
 $\text{CH}_4/\text{H}_2 = 1.50\%$
 Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)
 $t_{\text{total}}=24\text{ hours } (t_{\text{total}}=t_2 + t_5)$

was 0.63% and that of

$\text{H}_2=200\text{ sccm}$
 $\text{CH}_4/\text{H}_2 = 1.50\%$
 Pressure = 36 Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$)
 $t_{\text{total}}=24\text{ hours } (t_{\text{total}}=t_2 + t_5)$

was $\sim 1.3\%$.

It might be of interest to compare some properties of a diamond film deposited on tungsten substrate with one deposited on a silicon substrate. Sample SK179 is the counterpart of the sample WSK1. The sample SK179 was deposited on a silicon substrate of 3" in diameter while WSK1 was deposited on a tungsten substrate of 1" in diameter. The deposition time for SK179 was 8 hours and that of WSK1 was 24 hours. Both samples were deposited under $\text{H}_2 = 400\text{ sccm}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, and pressure = 36 torr ($\Rightarrow T_s \sim 850^\circ\text{C}$). In Table 8.2 quantities are normalized to substrate size (cm^{-2}) and to $\mu\text{m/hr}$.

Figure 8.10 and Figure 8.11 illustrate surface morphology and structural quality (Raman spectra) of SK179 and WSK1 samples for a closer comparison.

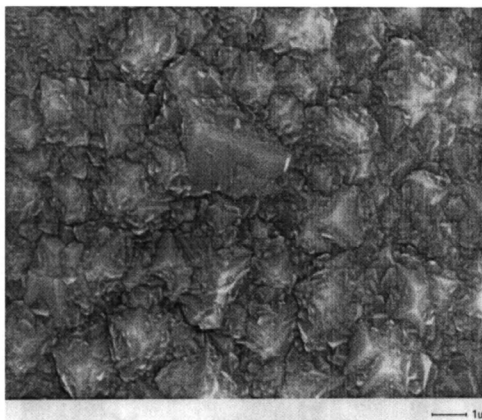
Properties are similar except for growth rate (mg./hr-cm^{-2} and carbon conversion efficiency are related to growth rate). The larger growth rate of diamond film deposited on the tungsten substrate may be attributed to the higher nucleation density on the tungsten substrate which could result from the combined effect of surface roughness and spin seeding of the tungsten substrate. Note that all the silicon substrates used for this dissertation were purchased polished with virtually no surface roughness.

It is seen from Figure 8.11 that the graphitic peak around 1550 cm^{-1} associated with WSK1 sample was larger than that for SK179 sample. The same phenomenon was observed when a different deposition condition was used; graphitic peak was larger for diamond film deposited on a tungsten substrate than on a silicon substrate. It seems that the choice of substrate is a factor that affects film quality. The free energy difference between diamond and graphite is only 0.02 eV. If species reaction with different substrate surfaces are different such that one carbon phase (i.e. sp^2) is more favored with respect to one substrate than another, the origin of depositing more graphite with tungsten than with silicon may be understood.

Table 8.2. A comparison of properties of diamond films deposited on silicon and tungsten substrates. Deposition condition: $f_t = 400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s \sim 850^\circ\text{C}$.

Sample	Substrate	mg./hr-cm ⁻²	Linear growth rate ($\mu\text{m/hr}$)	Morphology	FWHM (cm ⁻¹)	Normalized % carbon conversion efficiency
SK179	Silicon	0.162	0.46	Twinned {111}	12.04	0.0852
WSK1	Tungsten	0.245	0.68	Twinned {111}	13.72 ^a	0.1289

a. In addition to a bigger thermal expansion mismatch between tungsten and diamond than between silicon and diamond, the difference between deposition times of WSK1 and SK179 could have also contributed to the larger FWHM of WSK1 compared to SK179.



WSK1

Figure 8.8. SEM picture of WSK1 sample deposited at $f_l = 400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, $p = 36$ Torr ($\Rightarrow T_s \sim 850^\circ\text{C}$) and $t_{\text{total}} = t_2 + t_5 = 24$ hours.

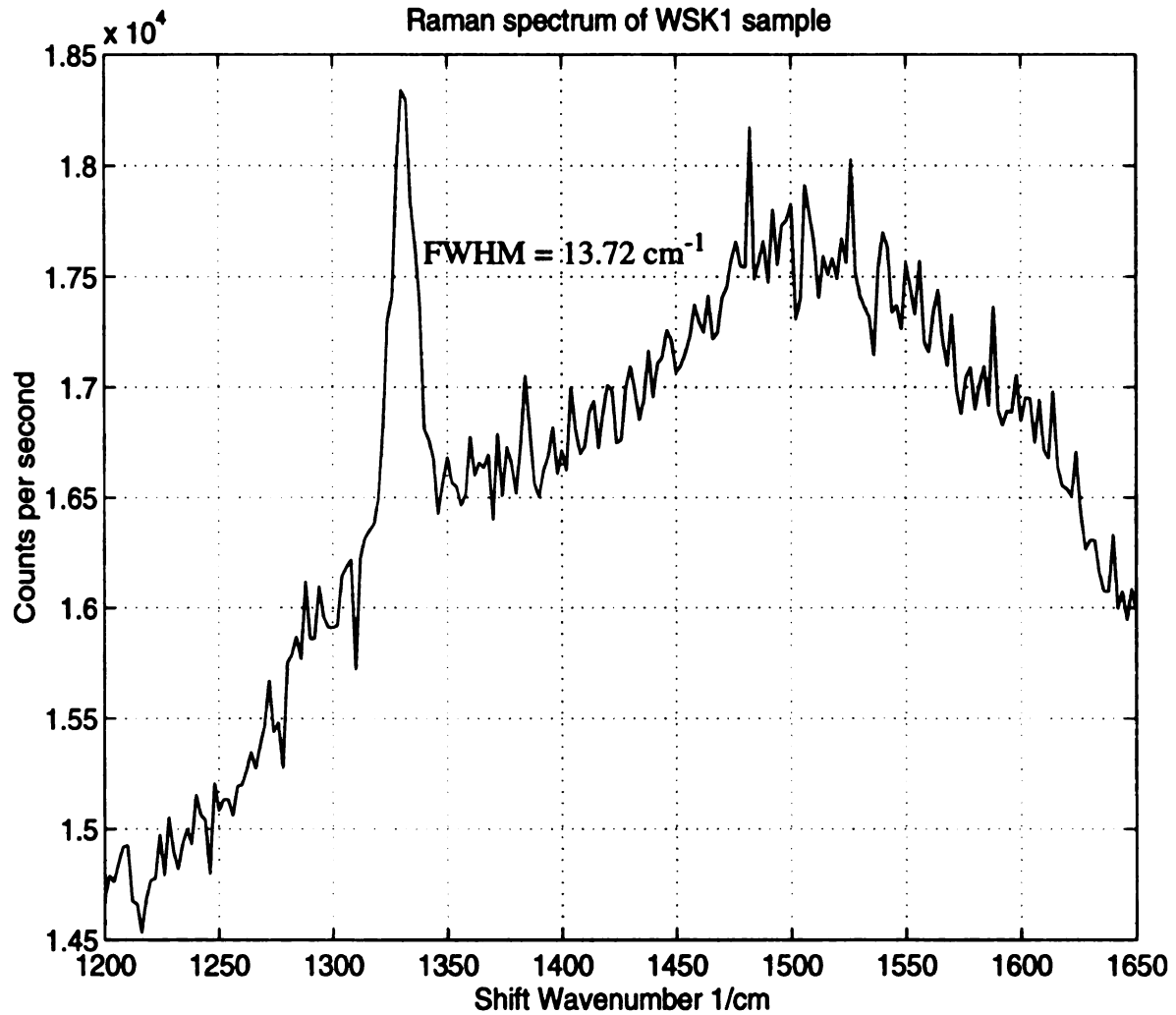


Figure 8.9. Raman spectrum of a diamond film deposited on a tungsten substrate. Deposition condition: $\text{H}_2=400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, pressure = 36 Torr, and $t_{\text{total}} = 24$ hours.

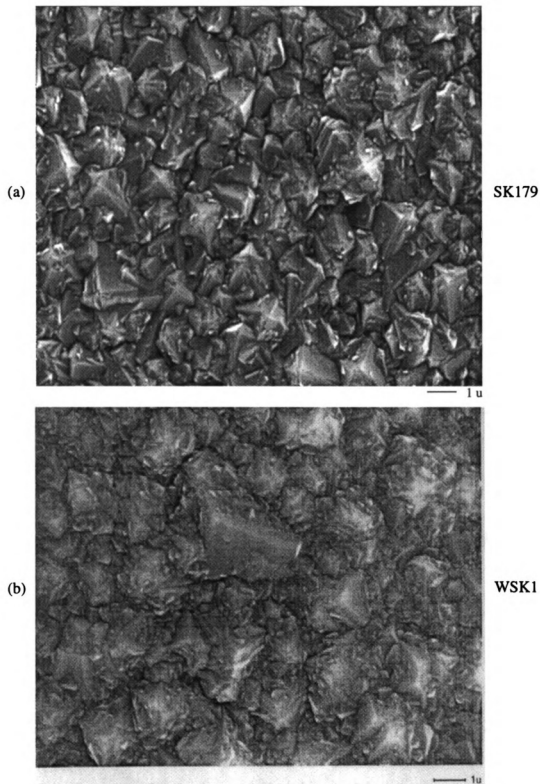


Figure 8.10. SEM pictures of SK179 and WSK1 samples deposited at $f_t = 400$ sccm, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s \sim 850^\circ$ with $t_{\text{SK179}} = 8$ hours and $t_{\text{WSK1}} = 24$ hours.

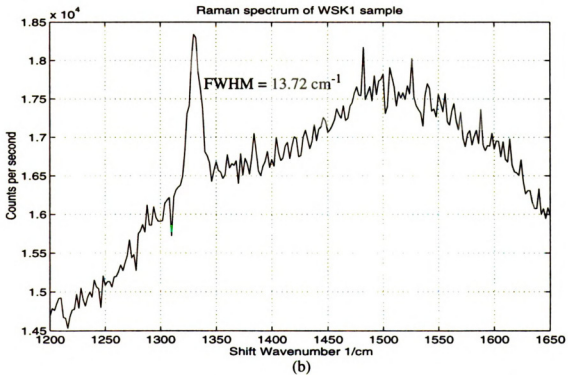
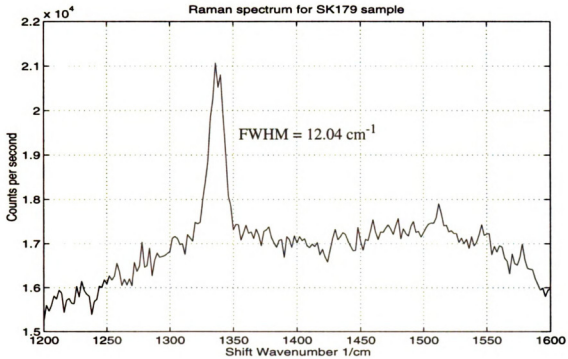


Figure 8.11. Raman spectra for diamond films deposited on (a) a silicon substrate, and (b) a tungsten substrate. Deposition condition: $f_t = 400 \text{ sccm}$, $\text{CH}_4/\text{H}_2 = 1.50\%$, and $T_s \sim 850^\circ\text{C}$ with $t_{\text{SK179}} = 8 \text{ hours}$ and $t_{\text{WSK1}} = 24 \text{ hours}$.

8.3.2 Film patterning using plasma etch

Method 1 (patterning via UV photolithography) for diamond film patterning was unsuccessful because the tungsten substrates had rough surfaces which helped diamond nucleate every where on the surface without a need for diamond seeds. Diamond film grew on seeded and on un-seeded areas.

Method 2 (patterning via stainless steel shadow mask) resulted in selective diamond growth. Diamond film grew on the areas that were exposed to the plasma and there was no diamond growth on the areas covered by the stainless steel shadow masks. The problem with this approach was that the transition from diamond to non-diamond zones was not abrupt (Figure 8.12 (b)) and use of thinner masks did not fully solve the problem. This problem was even more severe with respect to small diamond features (i.e., shadow mask2). Figure 8.12 (a) describes the cause of this phenomenon. Plasma species approach the sample from every direction. In mask-substrate boundaries some of the species that approach the substrate are absorbed by the mask rather than by the substrate. Furthermore, some of the species that approach the substrate obliquely are blocked by the mask (i.e., shadowing effect) and do not reach the substrate. Hence, species concentration in the mask-substrate boundaries is smaller than elsewhere on the substrate. This resulted in the diamond thickness profile of Figure 8.12 (b).

Method 3 (patterning via plasma etch) yielded very successful results. The transition from non-diamond to diamond regions was abrupt (Figure 8.13). This method was selected for the diamond film patterning in this chapter.

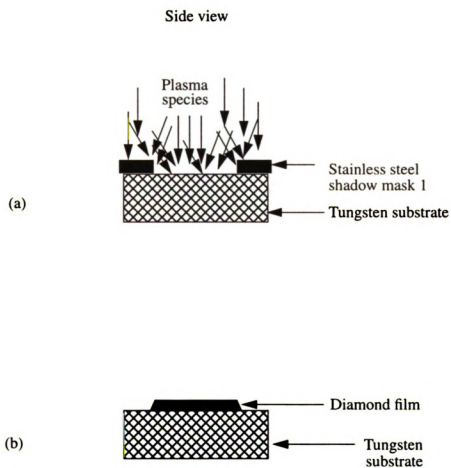


Figure 8.12. (a) Plasma species in-flux on to the sample. (b) Thickness profile resulted when a shadow mask (i.e., shadow mask 1) is used for selective film growth.

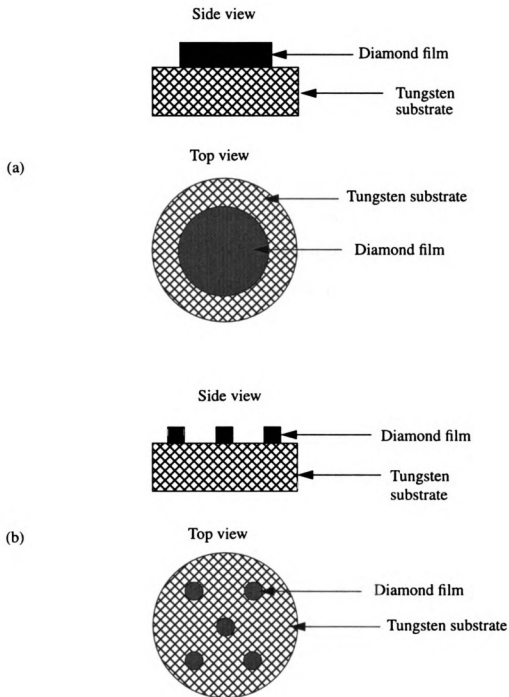


Figure 8.13. (a) and (b) Diamond film patterns formed via plasma etch.

CHAPTER 9

Summary

9.1 Summary of the experimental measurements

The experimental performance of the Microwave Cavity Plasma Reactor (MCPR) has been investigated. The MCPR is currently used in the commercial production of diamond thin film products and is also used by a number of research groups in scientific investigations concerned with thin film deposition. This microwave plasma reactor has also demonstrated an experimental versatility that few, if any, other plasma reactors have exhibited. It can deposit diamond films under a very wide range of experimental conditions. That is, it can deposit diamond at low temperatures and low pressures [86], moderate pressures (as described in this thesis), and using a more “thermal plasma like discharge” at high pressures [27], it has also demonstrated high diamond film deposition rates [27]. Thus it is a very useful diamond film deposition machine. Thus a detailed definition of the MCPR operation performance would be very useful for current and future reactor users. This thesis research is devoted to a careful experimental characterization of the MCPR in the moderate pressure (20 - 80 Torr) regime.

Microwave plasma assisted diamond deposition is a process that involves an understanding of complex relationships between many experimental variables. At this time these relationships can not be described by simple or complex theories. Therefore,

these relationships can only be determined from extensive experimental data as described in this thesis. The experiments described and analyzed in this thesis represent the most extensive experimental investigation reported in the open literature for a specific plasma assisted diamond thin film deposition reactor. Of course, similar detailed experimental knowledge of other reactors may exist in industrial laboratories where they are held in secrecy for proprietary reasons. It is expected that the experimental knowledge developed in this thesis will be useful in developing theoretical models of reactor performance and the deposition process itself. Additionally, researchers who are interested in depositing diamond films with specific properties such as morphology, i.e., {111}, {100}, cauliflower, and small aggregates, will now be able to use the deposition field maps developed in this thesis to deposit their films.

This thesis has relied on the extensive experimental knowledge of microwave plasma reactors developed at M.S.U for many plasma applications. It has specifically drawn upon the past microwave plasma reactor knowledge gleaned from the many experiments performed by J. Asmussen over the past 20 to 30 years and the more recent experimental diamond thin film reactor developments of Asmussen, J. Zhang and K. Kuo ([14], [27]). The data reported in this thesis consists of about 350 experiments involving approximately 3000 hours of experimental run time. The unique feature of this investigation is that it explores the relationships between output variables and input variables more thoroughly than other investigations that have been reported in open literature. The resulting experimental data was used to develop reactor deposition maps that describe the relationships between the reactor input variables and specific output variables of interest such as film morphology, structural quality, growth rate, etc.

Therefore, an important result of this thesis is the understanding of the relationships between input and output variables of the MCPR reactor. In particular, by using the results of this thesis reactor users can now routinely and precisely deposit films with pre-determined properties by just specifying the experimental input variables and using the experimental methodologies described in this thesis.

The experimental performance of the MCPR was determined by measuring specific output variables vs. the many experimental input variables. The output variables are divided into two variable groups. The first group, Y_1 , is concerned with the output diamond thin film characteristics such as film morphology, grain size, and structural quality. The second group, Y_2 , is concerned with the reactor performance variables such as linear growth rate, carbon conversion efficiency, and specific yield. Y_1 and Y_2 outputs are experimentally measured vs. a multi-dimensional input variable space U , consisting of pressure (p), microwave power (P_t), total gas flow rate (f_t), methane concentration (CH_4/H_2), and deposition time (t). In addition, changes in the reactor geometry input variable (U_2) are also studied.

Some important results of this thesis are summarized below.

Experimental film morphology field maps were developed which describe the complex relationships between film morphology and the multi-dimensional input variable space. It was found that film morphology not only depends on the usual input variables of CH_4/H_2 , and substrate temperature (T_s), but also is dependent on total gas flow rate (f_t), deposition time (t), and reactor geometry (U_2). The fact that the film morphology is dependent upon f_t , t , and U_2 is demonstrated extensively in this thesis and is studied and described in great detail. Since other investigations have not carefully studied these

variables, establishing this dependence represents an important contribution of this research. Most of the investigators have identified CH_4/H_2 , pressure, and substrate (p) temperature (T_s) as the important deposition variables. As reported in the literature, the experimental output performance, such as film morphology, deposition rate, etc. of plasma reactors vs. the experimental input variables varies considerably from one reactor to another (see Chapter 3). However, even when the performance of similar reactors, i.e., tubular microwave CVD [10], are compared important differences in output performance such as film morphology vs. the input variables are observed. This suggests that all the important experimental variables have not been identified and controlled in these investigations. Indeed, the research in this thesis identifies the important input variable space as CH_4/H_2 , substrate temperature (T_s), total gas flow rate (f_t), deposition time (t), and reactor geometry (U_2). It is shown that Y_1 and Y_2 output variables are complex

functions of a multi-dimensional input variable space, i.e., $Y_1 = f\left(\frac{\text{CH}_4}{\text{H}_2}, T_s, f_t, t, U_2\right)$

and $Y_2 = f\left(\frac{\text{CH}_4}{\text{H}_2}, T_s, f_t, t, U_2\right)$.

Film structural quality vs. the multi-dimensional input variable space was also extensively studied. FWHM of Raman spectra were used as a measure of the structural quality of the films. It was found that well-faceted films had good structural quality with $\text{FWHM} = 6 - 11 \text{ cm}^{-1}$ while films with cauliflower and small aggregate morphologies had FWHM larger than 15 cm^{-1} . While the result is similar to that reported in the literature by others ([34], [38], [40]), the experimental data described in this thesis defines the

deposition regime for the MCPR where films with good structural properties can be synthesized.

Film growth rates vs. the multi-dimensional input variable space were also extensively investigated and are presented in a greater detail than presented by other investigators [14]. The reactor performance variables Y_2 such as film growth rates are related to film properties Y_1 such as film morphology and film quality. It is interesting to highlight two important results, one concerning highly faceted films with {111} morphology and the other concerning highly faceted films with {100} morphology. It was found that for the total flow rates of $f_t = 60 - 400$ sccm maximum growth rates ($\sim 0.7 \mu\text{m/hr}$ or $\sim 11 \text{ mg./hr}$) occurred at $T_s = 1000^\circ\text{C}$ and $\text{CH}_4/\text{H}_2 = 1\text{-}2\%$ and produced films with {111} morphology ($\alpha \cong 3$) and excellent FWHM of Raman spectra of $8 - 11 \text{ cm}^{-1}$. These results are summarized in Table 9.1. {100} films were produced primarily at low total gas flow rates ($f_t \leq 200$ sccm), at a low substrate temperature regime of $T_s \leq 850^\circ\text{C}$, and with $\text{CH}_4/\text{H}_2 = 0.6 - 2.0\%$. Under these experimental conditions the film growth rate varied between $0.15 \mu\text{m/hr}$ (2.40 mg./hr) and $0.47 \mu\text{m/hr}$ (7.53 mg./hr) and the film Raman FWHM were $7 - 10.5 \text{ cm}^{-1}$.

Reactor carbon conversion efficiencies were found to be directly proportional to substrate temperature and inversely proportional to CH_4/H_2 concentrations and total gas flow rates. Carbon conversion efficiencies in the range of $2\% - 50\%$ were achieved. Well-faceted {100} and {111} films were deposited with higher carbon conversion efficiencies than the films with cauliflower and small aggregate morphologies.

It was found that as deposition time varied, both Y_1 and Y_2 variables also varied. It

Table 9.1. Maximum growth rate and the corresponding deposition conditions, film characteristics Y_1 , and reactor performance Y_2 for the 5" quartz dome/3" substrate reactor configuration.

Total gas flow rate (sccm)	CH ₄ /H ₂ %	Substrate temperature (°C)	α	FWHM (cm ⁻¹)	$\mu\text{m/hr}$	% Carbon conversion efficiency
400	1.50	1000	3	11.2	0.663	5.42
200	1.50	1000	3	7.05	0.660	10.78
100	2.0	1000	3	9.09	0.590	14.56
60	2.0	1000	3	7.53	0.591	24.26

was already well-known from the literature [87] that film growth rates often increase with deposition time and film thickness. Film morphology vs. deposition time was specifically investigated and was observed that for constant experimental input variables, film morphology varied vs. deposition time, i.e., $\alpha \cong 1$ for $t = 8$ hours and $\alpha \cong 3$ for $t = 41$ hours. It was demonstrated by the results in this thesis that film morphology could be controlled and held constant by varying CH₄/H₂ vs. time.

A unique feature of this thesis was the investigation of the change in the reactor performance, i.e., Y_1 , and Y_2 variables, when only the discharge size (i.e., U_2 reactor geometry variable) was varied. In particular, both 5" and 4" discharges were investigated. The quartz dome size and substrate holder and substrate sizes were varied from 5" quartz dome/3" substrates to 4" quartz dome/2" substrates. This geometry variation changes the relationship between pressure (p), absorbed microwave power (P_t), and substrate

temperature (T_s). The smaller reactor requires a lower absorbed microwave power (P_i) and a slightly higher pressure (p) to achieve a given substrate temperature (T_s). The reactor operating road map, therefore, changes with the variation in reactor geometry. At a given T_s , the absorbed microwave volume power densities are 3 to 4 times higher in the small reactor than in the large reactor. That is, with an increase in the substrate temperature from 750°C to 1000°C, the microwave volume power density increased from 10 W/cm³ to 16 W/cm³ in the larger discharge to 32 W/cm³ to 57 W/cm³ in the smaller discharge. Similarly, at a given T_s , the absorbed microwave area power densities are 2 to 3 times higher in the small reactor geometry configuration than in the large reactor geometry configuration, i.e., with an increase in the substrate temperature from 750°C to 1000°C, the microwave area power density increased from 26 W/cm² to 40 W/cm² in the larger discharge to 53 W/cm² to 96 W/cm² in the smaller discharge. Thus, these changes in the steady state power densities are expected to change the relationships between multi-dimensional input variables and output variables (Y_1 , Y_2) for the two reactor geometries.

The changes in the reactor output performance, i.e., Y_1 and Y_2 variables for the two reactor configurations are summarized below.

Y_1 : Output film properties

(i) Film morphology: film morphology trends for the two reactors were similar. High flow rates, i.e., $f_t = 400$ sccm, produced {111} films at substrate temperatures in the range of $T_s \geq 800^\circ\text{C}$ and methane concentrations in the range of $0.6 < \text{CH}_4/\text{H}_2 \leq 1.50\%$. Lower flow rates (i.e., $f_t \leq 200$ sccm) produced {111} films at high substrate

temperatures (i.e., $T_s \geq 850^\circ\text{C}$) and $0.60 \leq \text{CH}_4/\text{H}_2 \leq 2.0\%$ and produced {100} films at lower substrate temperatures (i.e., $T_s \leq 850^\circ\text{C}$) and $0.60 < \text{CH}_4/\text{H}_2 \leq 2.0\%$. Well-faceted {100} and {111} films were produced at $\frac{\text{CH}_4}{\text{H}_2} \leq 2$. Films with cauliflower and small aggregate morphologies were produced at higher methane concentrations. However, the CH_4/H_2 , T_s , f_t variable “volume” to achieve well-faceted films is smaller for the small reactor than for the large reactor. Thus the morphology variations in the small reactor are more sensitive to changes in the input variables than for the large reactor.

(ii) Film structural quality: the FWHM did not vary significantly with the variation in the reactor geometry configuration. Similar to the large reactor, well-faceted {100} and {111} films displayed good Raman FWHM in the range of $7 - 11 \text{ cm}^{-1}$ while films with cauliflower and small aggregate morphologies displayed larger FWHM values ($\text{FWHM} > 15 \text{ cm}^{-1}$).

Y_2 : Reactor performance

Reactor performance variables (Y_2) are divided into two sets of “overall performance” variables (Y_2') and “normalized performance” variables (Y_2'') as follows:

Y_2' : Overall performance

Table 9.2 displays the mg./hr, carbon conversion efficiency (CCE), and specific yield (KW-hr/g) associated with the two reactor geometries under similar operating conditions. It also includes the ratio of the mg./hr, CCE, and specific yields of the two reactors. It is

seen from this table that changing the reactor geometry from the 5" quartz dome/3" substrate configuration to the 4" quartz dome/2" substrate configuration significantly reduced the reactor performance variables as expressed by mg./hr, carbon conversion efficiency, and specific yield. The reduction in the mg./hr and carbon conversion efficiency almost equaled the ratio of the substrate areas (i.e., $S = A_{LD}/A_{SD} = 2.25$ where LD stands for large dome, and SD stands for small dome). This suggests that the larger reactor had a better overall performance than the smaller reactor and that the reactor overall performance will improve as the size increases.

Table 9.2. Ranges and ratios of the overall performance variables associated with the two reactor geometries.

Y_2'	Large reactor 5" dome/3" substrate	Small reactor 4" dome/2" substrate	Ratio
mg./hr	4.2 - 11.5	2 - 5	~ 2.2
CCE ^a	1.2% - 50%	0.5% - 22%	~ 2.2
Specific Yield (KW-hr/g)	180 - 300	307 - 850	1.7 - 2.8

a. CCE = Carbon conversion efficiency

Y_2'' : Normalized performance

When the growth rates and the carbon conversion efficiencies were normalized by dividing by the substrate areas, the values for both reactors were similar under similar input conditions. Table 9.3 shows the mg./hr-cm², normalized carbon conversion efficiency (i.e., CCE/cm²), and normalized specific yield (KW-hr/g-cm²) associated with

the two reactor geometries. It is seen from this table that changing the reactor geometry from the 5" quartz dome/3" substrate configuration to the 4" quartz dome/2" substrate configuration did not significantly influence the normalized growth rate and normalized carbon conversion efficiency but the normalized specific yields were significantly larger for the small reactor than the large reactor.

Table 9.3. Ranges and ratios of the normalized performance variables associated with the two reactor geometries.

Y_2''	Large reactor 5" dome/3" substrate	Small reactor 4" dome/2" substrate	Ratio
mg./hr-cm ²	0.09 - 0.25	0.098 - 0.247	~ 1
CCE/cm ²	0.026% - 1.1%	0.025% - 1.1%	~ 1
Specific Yield (KW-hr/g-cm ²)	3.95 - 6.6	15 - 42	~ 3.8 - 6.4

9.2 Recommendations for future research

(1) The experimental relationships between output and input variables of the MCPR are now determined. It is now possible to deposit diamond films with pre-determined characteristics. It is useful to perform some insitu plasma and substrate diagnostics to relate output variables to internal variables.

(2) Introduce dopant/impurity and investigate the changes in output variables.

(3) Combine the extensive knowledge acquired in this thesis with the carburization/bias enhanced nucleation steps to synthesize highly oriented films.

(4) Increase the discharge size for better overall reactor performance.

LIST OF REFERENCES

LIST OF REFERENCES

- [1] Robert F. Davis, Diamond films and coatings, North Carolina State University, Department of Material Science and Engineering, Raleigh, North Carolina, Noyes publications, New Jersey, 1993.
- [2] J. C. Angus, F.A. Buck, M. Sunkara, T.F. Groth, C.C. Hayman, and R. Gat, "Diamond growth at low pressures", MRS Bulletin, October 1989, pp 38-47.
- [3] Timothy Grotjohn, "A review of CVD diamond research", 1994.
- [4] D. R. Kania, M. I. Landstrass and M. A. Plano, "Diamond radiation detectors", Diamond and Related Materials, 2 (1993), pp 1012-1019.
- [5] V. S. Vavilov, "Diamond as a material in solid state electronics", Mat. Res. Soc. Symp. proc., Vol. 242, 1992, pp 87-95.
- [6] L. S. Pan, S. Han, D. R. Kania, M. A. Plano, and M. I. Landstrass, "Electrical properties of high quality diamond films", Diamond and related materials, Vol. 2, 1993, pp 820-824.
- [7] Y. Mori, H. Yagi, M. Deguchi, M. Kitabatake, K. Nishimura, A. Hatta, T. Ito, T. Hirao, T. Sasaki, and A. Hiraki, "Crystallinities and electrical properties of homoepitaxial diamond films grown from carbon monoxide", 2nd Int. Conf. on the appli. of Diamond Films and Related Materials. Yoshikawa, Vol. 2, Tokio, Japan, 1993, pp 393-398.
- [8] B. V. Spitsyn, L. L. Bouilov and B. V. Derjaguin, "Vapor growth of diamond on diamond and other surfaces", Journal of Crystal Growth, 52 (1981), pp 219-226.
- [9] Hiromu Shiomi, Keiichirou Tanabe, Yoshiki Nishibayashi and Naoji Fujimori, "Epitaxial growth of High Quality Diamond Film by the Microwavw Plasma-Assisted Chemical-Vapor-Deposition Method", Japanese Journal of Applied Physics, Vol. 29, No. 1, January, 1990, pp 34-40.
- [10] Huimin Liu and David S. Dandy, Diamond Chemical Vapor Deposition, Noyes Publications, 1995.

- [11] F. P. Bundy, H. M. Strong, and R. H. Wentorf, Jr., *Chem. Pys. Carbon* 10, 213 (1973).
- [12] James E. Butler and Richard L. Woodin, "Thin film diamond growth mechanism", *Thin Film Diamond*, Edited by Lettington and J. W. Steeds, Published by Chapman & Hall for the Royal Society, 1994, pp 15-30.
- [13] John c. Angus, Alberto Argoitia, Roy Gat, Zhidan Li, Mahendra Sunkara, Long Wang, and Yaxin Wang, "Chemical vapor deposition of diamond", *Thin Film Diamond*, Edited by Lettington and J. W. Steeds, Published by Chapman & Hall for the Royal Society, 1994, pp 1-14.
- [14] Jie Zhang, "Experimental Development of Microwave Cavity Plasma Reactors for Large Area and High Rate Diamond Film Deposition," Ph.D. dissertation, Department of Electrical Engineering, Michigan State University, 1993.
- [15] Ken Takeuchi and Toyonobu Yoshida, *J. Appl. Phys.* 71, 2636 (1992).
- [16] A. B. Bronwell and R. E. Beam, *Theory and Applications of Microwaves*, McGraw-Hill Book Company Inc., New York and London, 1947.
- [17] J. Asmussen and J. Zhang, "Apparatus for the Coating of material on a Substrate Using a Microwave or UHF Plasmas," U.S. Patent No. 5,311,103, May 10, 1994.
- [18] A. Masood, "Technology of electronic properties of CVD diamond film microsensors for thermal signals," Ph.D. dissertation, Department of Electrical Engineering, Michigan State University, 1992.
- [19] K. Suzuki, A. Sawabe, H. Yasuda, and T. Inuzuka, *Appli. Phys. Lett.* 50, 728 (1987).
- [20] K. Suzuki, A. Sawabe, H. Yasuda, and T. Inuzuka, *Jpn. J. Appli. Phys.* 29, 153 (1990).
- [21] S. Matsumoto, I. Hosoya and T. Chounan, *Jpn. J. Appl. Phys.* 29, 2082 (1990).
- [22] L. M. Hanseen, W. A. Carrington, J. E. Butler, and K. A. Snail, *Mater. Lett.* 7, 289 (1988).
- [23] S. Matsumoto, M. Hino, and T. Kobayashi, *Appl. Phys. Lett.*, 51, 737 (1987).
- [24] M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, *J. Cryst. Growth* 62, 642 (1983).
- [25] Peter K. Bachmann, Dieter Leers and Hans Lydtin, *Towards a general concept of diamond chemical vapour deposition, Diamond and Related Materials*, 1 (1991) 1-12.

- [26] Y. Mitsuda, T. Yoshida, and K. Akashi, *Rev. Sci. Instrum.* 60, 249 (1989).
- [27] Kuo Ping Kuo, "High Pressure Synthesis of Diamond Films Using Microwave Cavity Plasma Reactor, Ph.D thesis, Department of Electrical Engineering, Michigan State University, 1997.
- [28] A. van der Drift, "Evolutionary selection", Philips research report, 22 (1967), pp 267-288.
- [29] R. E. Clausing, L. Heatherly, and E.D. Specht, "Control of texture and defect structure for hot-filament CVD diamond films", *Diamond and diamond-like film and coatings*, 1991, pp 611-618.
- [30] R. E. Clausing, L. Heatherly, and E.D. Specht, G. M. Begun, and Z. L. Wang, "Textures and morphologies of CVD diamond", *Diamond and related materials*, 1 (1992), pp 411-415.
- [31] C. Wild, P. Koidl, W. Muller-Sebert, H. Walcher, R. Kohl, N. Herres, and R. Locher, "Chemical vapour deposition and characterization of smooth {100}-faceted diamond films", *Diamond and related materials*, 2 (1993), pp 158-168.
- [32] C. Wild, R. Kohl, N. Herres, W. Muller-Sebert, and Koidl, "Oriented CVD diamond films: twin formation, structure and morphology", *Diamond and Related Materials*, 3 (1994) 373-381.
- [33] A V. Hetherington, C. J. H. Wort, and P. Southworth, *J. Mater. Res.*, 5 (1990) 1591.
- [34] Wei Zhu, Brian R. Stoner, Brad E. Williams, and Jeffrey T. Glass, "Growth and characterization of diamond films on nondiamond substrates for electronic applications (invited paper)", *Proceeding of IEEE*, Vol. 79, No 5, May 1991, pp 621-646.
- [35] Wei Zhu, "Microwave plasma-enhanced chemical vapor deposition and structural characterization of diamond films", Ph.D thesis, The pennsylvania State University, 1990, pp 206-211.
- [36] M. Moore, *Ind. Dia. Rev.* 2, 67 (1985).
- [37] P. Hartman and W. G. Perdok, "On the relations between structure and morphology of crystals. II", *Acta Crystallographica* 8 (1955) 49, pp 521-524.
- [38] Koji Kobashi, Kozo Nishimura, Yoshio Kawate, and Takefumi Horiuchi, "Synthesis of diamond by use of microwave plasma chemical-vapor deposition: Morphology and growth of diamond films", *Physical Review B*, Vol. 38, No. 6, 15 August 1988, pp 4067-4084.

- [39] Hiromu Shiomi, Keiichirou Tanabe, Yoshiki Nishibayashi and Naoji Fujimori, "Epitaxial growth of High Quality Diamond Film by the Microwave Plasma-Assisted Chemical-Vapor-Deposition Method", Japanese Journal of Applied Physics, Vol. 29, No. 1, January, 1990, pp 34-40.
- [40] B. E. Williams and J. T. Glass, "Characterization of diamond thin films: Diamond phase identification, surface morphology, and defect structures", J. Mater. Res., Vol. 4, No. 2, Mar/Apr 1989, pp 373-384.
- [41] Lee Chow, Alan Horner, and Hooman Sakouri, "Growth of (100) oriented diamond thin films on ball structure diamond-like particles", J. Mater. Res., Vol. 7, No. 7, Jul 1992, pp 1606-1609.
- [42] Koji Kobashi, Kozo Nishimura, Koichi Miyata, Kazuo Kumagai, and Akimitsu Nakae, "(110)-oriented diamond films synthesized by microwave chemical-vapor deposition", J. Mater. Res., Vol. 5, No. 11, Nov 1990, pp 2469-2482.
- [43] S. Haq, J. A. Savage and D. L. Tunnicliffe, "Nucleation of diamond onto silicon by low pressure plasma-CVD", Applications of Diamond Films and Related Materials, Y. Tzeng, M. Yoshikawa, M. Murakawa, A. Feldman (Editors), Elsevier Science Publishers B. V., 1991, pp 405-410.
- [44] Yoon-Kee Kim, Ki-Young Lee, Jai-Young Lee, "Texture-controlled diamond films synthesized by microwave plasma-enhanced chemical vapour deposition", Thin Solid Films 272 (1996), pp 64-70.
- [45] S. Matsumoto, Y. Sato, M. Tsutsumi, and N. Setaka, "Growth of diamond particles from methane-hydrogen gas", Journal of Material Science, 17 (1982), pp 3106-3112.
- [46] Y. Liou, A. Inspektor, R. Weimer, D. Knight, and R. Messier, "The effect of oxygen in diamond deposition by microwave plasma enhanced chemical vapor deposition", journal of Materials Research, Vol. 5, No. 11, Nov 1990, pp 2305-2312.
- [47] R. G. Buckley, T. D. Moustakas, Ling Ye, and J. Varon, "Characterization of filament-assisted chemical vapor deposition films using Raman spectroscopy", J. Appl. Phys. 66 (8), 15 October 1989, pp 3595-3599.
- [48] Walter A. Yarbrough and Russell Messier, "Current Issues and Problems in the Chemical Vapor Deposition of Diamond", Science, Vol. 247, February 1990, pp 688-696.
- [49] Guangtian Zou, Chunxiao Gao, Zengsun Jin, Tiechen Zhang, Xianyi Lu, "Characteristic of Epitaxial Growth of Diamond Films on Cubic Boron Nitride Surface By DC Glow Discharge Chemical Vapor Deposition", Advances in New

Diamond Science and Technology, S. Saito, N. Fujimori, O. Fukunga, M. Kamo, K. Kobashi and M. Yoshikawa (Editors), MYU, Tokyo, pp 291-294.

- [50] L. J. Giling and W. J. P. Van Enckevort, "On the influence of surface reconstruction on crystal growth processes", *Surface Science* 161 (1958), pp 567-583.
- [51] Katsuyuki Okada, Shojiro Komatsu, Takamasa Ishigaki, Seiichiro Matsumoto, and Yusuke Moriyoshi, "Surface and step reconstructions on {100} and {111} planes of diamonds prepared by combustion flame deposition", *J. Appl. Phys.* 71 (10), May 15 1992, pp 4920-4924.
- [52] Eiichi Kondoh, Tomohiro Ohta, Tohru Mitomo, and Kenichi Ohtsuka, "Effect of gas phase composition on the surface morphology of polycrystalline diamond film", *Diamond and related materials*, 3 (1994), pp 270-276.
- [53] M. P. Everson and M. A. Tamor, "Investigation of growth rates and morphology for diamond growth by chemical vapor deposition", *J. Mater. Res.*, Vol. 7, No. 6, Jun 1992, pp 1438-1444.
- [54] John C. Angus, Alberto Argoitia, Roy Gat, Zhidan Li, Mahendra Sunkara, Long Wang, and Yaxin Wang, "Chemical vapor deposition of diamond", *Thin Film Diamond*, Edited by Lettington and J. W. Steeds, Published by Chapman & Hall for the Royal Society, 1994, pp 1-14.
- [55] Weertman Johannes and Weertman Julia R., *Elementary Dislocation Theory*, 1964.
- [56] Hull D. and Bacon D. J., *Introduction to Dislocations*, 3rd Edition, 1984.
- [57] Hirth John Price, *Theory of dislocations*, 1968.
- [58] Smith William F., *Principles of Material Science and Engineering*, 1986, McGraw-Hill, Inc.
- [59] R. E. Reed-Hill, *Physical Metallurgy Principles*, International Student Editions, 1964, D. Van Nostrand Company (Canada), LTD.
- [60] J. P. Hirth, "On Dislocation Interactions in the fcc Lattice", *J. Appl. Phys.* Vol. 32, No. 4, April 1961, pp 700-706.
- [61] E. Schmid and Ing. W. Boas, *Plasticity of Crystals with special reference to metals*, 1968, Published by Chapman and Hall limited, distributed in USA by Barnes and Noble Inc.
- [62] J. Narayan, "Dislocations, twins, and grain boundaries in CVD diamond thin films: Atomic structure and properties", *J. Mater. Res.*, Vol. 5, No. 11, Nov 1990, pp 2414-2423.

- [63] Z. L. Wang, J. Bentley, R. E. Clausing, L. Heatherly and L. L. Horton, "Growth mechanisms of CVD diamond films determined by a novel TEM technique", *Applications of Diamond Films and Related Materials*, Y. Tzeng, M. Yoshikawa, M. Murakawa, A. Feldman (Editors), Elsevier Science Publishers B. V., 1991, pp 489-494.
- [64] C. P. Sung and H. C. Shih, "The interfacial structure and composition of diamond films grown on various substrates", *J. Mater. Res.*, Vol. 7, No. 1, Jan 1992, pp 105-116.
- [65] James E. Butler and Richard L. Woodin, "Thin film diamond growth mechanism", *Thin Film Diamond*, Edited by Lettington and J. W. Steeds, Published by Chapman & Hall for the Royal Society, 1994, pp 15-30.
- [66] B. G. Yacobi, J. Lebens, K. J. Vahala, A. R. Badzian and T. Badzian, "Preferential incorporation of defects in microcrystalline diamond films", *Diamond and Related Materials*, 2 (1993), pp 92-99.
- [67] Andrzej Badzian and Teresa Badzian, "Diamond homoepitaxy by chemical vapor deposition", *Diamond and Related Materials*, 2 (1993), pp 147-157.
- [68] C. Wild, N. Herres, and P. Koidl, "texture formation in polycrystalline diamond films", *J. Appl. Phys.* 68 (3), 1 August 1990, pp 973-978.
- [69] J. Narayan and A. R. Srivatsa, "On epitaxial growth of diamond films on (100) silicon substrates", *Appl. Phys. Lett.* 53 (19), 7 Nov. 1988, pp 1823-1825.
- [70] P. Hartman and W. G. Perdok, "On the relations between structure and morphology of crystals. I", *Acta Crystallographica* 8 (1955) 49, pp 49-52.
- [71] P. Hartman, in: *Crystal growth: An introduction*, Ed. P. Hartman (North-Holland, Amsterdam, 1973) pp 358-402.
- [72] Somorjai Gabor A., *Introduction to Surface Chemistry and Catalysis*, 1994, John Wiley and Sons, Inc.
- [73] Sunagawa, "Growth and morphology of diamond crystals under stable and metastable conditions", *J. Crystal growth* 99 (1990), pp1156-1161.
- [74] S. L. Flegler, J. W. Heckman, K. L. Klomparen, *Scanning and transmission electron microscopy an introduction*, Oxford University Press, Newyork and Oxford England, 1993.
- [75] Bohr-ran Hang, D. K. Reinhard, and J. Asmussen, "Electrical properties of undoped large-grain and small-grain diamond", *Diamond and Related materials*, 2

(1993) 812-815.

- [76] Richard L. C. Wu, Alan Garscadden, Patrick Kee, Hemant D. Desai, and Kazuhisa Miyoshi, "Synthesis and characterization of fine grain diamond films", *J. Appl. Phys.* 72 (1), 1 July 1992, pp 110-116.
- [77] E. S. Etz, "Requirements of a standard for the chemical characterization of CVD diamond by Raman spectroscopy", *Applications of Diamond Films and Related Materials*, Y. Tzeng, M. Yoshikawa, M. Murakawa, A. Feldman (Editors), Elsevier Science Publishers B. V., 1991, pp 603-609.
- [78] Diane S. Knight and William B. White, "Characterization of diamond films by Raman spectroscopy", *J. Mater. Res.*, Vol. 4, No. 2, Mar/Apr 1989, pp 385-393.
- [79] Joerg Mossbrucker, "Measurement and characterization of the Raman spectrum of diamond films", Ms. thesis, Department of Electrical Engineering, Michigan State University, 1994.
- [80] Growth of well-adhering diamond coating on sintered tungsten, *Diamond and Related Materials* 4 (1995) 1079-1087.
- [81] X. Jiang and C. L. Jia, "Diamond epitaxy on (001) silicon: An interface investigation", *Appl. Phys. Lett.* 67 (9), 28 August 1995, pp 1197-1199.
- [82] S.-A. Stuart, S. Praver, P.S. Weiser, *Diamond and Related Materials* 2 (1993), p. 753-757.
- [83] M. Kowarada, K. Kurihara, and K. Sasaki, "Synthesis of a diamond and metal mixture by the chemical deposition process", *J. Appl. Phys.* 71 (3), 1 February 1992, pp 1442-1445.
- [84] Rabindra Nath Chakraborty, "Post-Depositional Processing of Diamond Film Using Electron Cyclotron Resonance Plasmas", Ph.D. Dissertation, Department of Electrical Engineering, Michigan State University, 1995.
- [85] M. Ulczynski, D. K. Reinhard, M. Prystajko and J. Asmussen, "Thin film diamond coating on glass", *Applications of Diamond Films and Related Materials. Third International Conference*, pp. 573-575, Eds. A. Feldman, W. A. Yarbrough, M. Murakawa, Y. Tzeng, and M. Yoshikawa, NIST Special Publication 885, (1995).
- [86] K. P. Kuo and J. Asmussen, "An Experimental Study of High Pressure Synthesis of Diamond Films Using a Microwave Cavity Plasma Reactor", submitted to the *Diamond and Related Materials*.

MICHIGAN STATE UNIV. LIBRARIES



31293015706868