# PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due. MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE
APA 31 2-250	5	
JUN 0 4 2012		

6/01 c:/CIRC/DateDue.p65-p.15

## METAL-CATALYST GROWTH OF SILICON NANOWIRES IN UHV AND FURNACE SYSTEMS

By

Hyun Duk Park

## **A DISSERTATION**

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

## **DOCTOR OF PHILOSOPHY**

## **Department of Computer & Electrical Engineering**

### ABSTRACT

## METAL-CATALYST GROWTH OF SILICON NANOWIRES IN UHV AND FURNACE SYSTEMS

By

### **Hyun Duk Park**

Silicon wires and nanowires were grown on Si(111) substrates at various pressures ranging from ultra high vacuum (~  $10^{-8}$  Torr) to near atmospheric pressure of 500 Torr. Two separate deposition chambers were used in this study, including an ultra high vacuum (UHV) chamber and a high temperature, tube furnace based chamber for operation at the higher pressures of  $10^{-3}$  Torr to atmospheric pressure. In the UHV chamber at a growth temperature of 800 °C, silicon wires were observed growing perpendicular to the silicon substrate by using Pulsed Laser Deposition (PLD) of silicon. The growth scheme was based on vapor-liquid-solid mechanism using gold as the mediating catalyst. Various shaped silicon wires were found, with typical wire diameters of 200-700 nm. The maximum length of the grown wire was approximately 1.6 µm in height. Images of the silicon wires were taken with Scanning Electron Microscope (SEM).

In a separate chamber made for high temperature and higher pressure (near atmospheric) deposition, silicon nanowires were grown simply by annealing gold coated Si(111) substrates. Four different thicknesses of gold films including 5, 10, 18 and 112 nm-were used. The growth temperature was about 1100 °C with pressures ranging from  $1.6 \times 10^{-1}$  Torr to 500 Torr. It was observed that a high

density of silicon nanowires formed only when the thickness of the gold film was greater than about 18 nm. The effect of changing various factors such as further increases in the gold film thickness, annealing time, and the pressure did not significantly affect the density of nanowires or the distribution of diameters among the nanowires. The typical dimensions of the observed silicon nanowires had diameter of 20-160 nm and tens of  $\mu$ m in length. Some nanowires with diameter as small as 10 nm were found. Images of the silicon nanowires were taken with SEM and Transmission Electron Microscope (TEM). The Energy Dispersive X-Ray Spectroscopy (EDS) showed oxygen content in all the nanowires that were grown.

#### ACKNOWLEDGEMENTS

First of all, I would like to thank God for giving me the opportunity to pursue this degree, and for the wisdom and perseverance to complete this research. I am always thankful for his wonderful love He is showing to me as well as to my family.

I would like to thank my thesis adviser Dr Tim Hogan for his guidance, understanding, and patience. I would like to thank Dr Don Reinhard, Dr Tim Grotjohn, and Dr Norman Birge for being in my PhD committee and providing me with sound advice and guidance. I would also like to thank Dr Percy Pierre for his kindness. I would like to thank Roxanne Peacock for lab supplies and also for her kindness.

I would like to thank Chun-I Wu for lab assistance, and Nick Meyer for providing the TEM images. I would also like to thank Fu Guo and Roger Booth for SEM help.

Finally, I would like to reserve my deepest gratitude for my parents, my brother, and my two nephews for their support. Without their love, this research would not have been possible.

iv

# **TABLE OF CONTENTS**

LIST OF TABLES	ix
LIST OF FIGURES	x
INTRODUCTION	.1
CHAPTER I: THEORY	9
A) Pulsed Laser Deposition (PLD)	. 10
1) PLD: Comparison to Other Growth Methods	10
2) Sputtering Mechanisms	14
a) Indirect Collisional	17
b) Thermal	18
c) Electronic	20
d) Exfoliational	20
e) Hydrodynamic	22
3) Metals and Non-metals Laser Ablations	24
4) Plasma Plume	25
5) Velocity	27
6) Deposition Parameters	27
a) Laser Wavelength	28
b) Laser Beam Quality	29
c) Laser Fluence	29
d) Reflectance	30
e) Target Morphology	31
f) Evaporation Rate	33
g) Target-to-Substrate Distance and Chamber Pressure	33
h) Substrate Temperatur	35
i) Off-axis PLD	37
7) Beam-Target Alignment	37
a) Focal Length Calculations	. 37
b) Gaussian Beam Approximation	38
B) Vapor-Liquid-Solid (VLS) Growth Mechanism	. 40
1) General Description	40
2) Metal Catalyst Requirements	44
3) Modes of Crystal Growth	. 45
4) Growth Kinetics	. 46
5) Supersaturation in PLD	49
6) Minimum Radius	49
7) Effect of Ambient Pressure	. 50
C) Au/Si(111) Eutectic Characteristics	. 52
1) Temperature Effect	52

a) Room Temperature Condensation	52
b) Moderate Temperature (T < 400 °C) Condensation	54
c) High Temperature (T > 400 °C) Condensation	54
2) Gold Silicide	55
3) Diffusion-induced Crystallization	56
D) Si Overlayer-Assisted Growth of Nanowires	57
E) Oxide-Assisted (OA) Growth of Nanowires	59
1) Background	59
2) Methods and Nanowires	59
3) Growth Mechanism	60
CUADTED II. EVDEDIMENTAL SETUD	61
A) Experimental Systems	01 61
B) Illtra High Vacuum (IHV) Chamber System	01 62
C) Furnace System	64
D) I aser/Ontics System	+0 66
F) Target and Substrate Prenarations	00 67
F) Growth Procedures	07 68
1) UHV System	68
2) Furnace System	69
CHAPTER III: DEPOSITIONS IN UHV CHAMBER SYSTEM	71
A) Deposition Procedures	71
B) Results	71
1) Gold Only Depositions	
<ol> <li>Gold Only Depositions</li> <li>a) Gold Depositions without Annealing</li> </ol>	71 72
<ol> <li>a) Gold Depositions without Annealing</li> <li>b) Gold Depositions with Annealing (60 shots)</li> </ol>	71 72 73
<ol> <li>1) Gold Only Depositions</li> <li>a) Gold Depositions without Annealing</li> <li>b) Gold Depositions with Annealing (60 shots)</li> <li>c) Gold Depositions with Annealing (900 shots)</li> </ol>	71 72 73 76
<ol> <li>1) Gold Only Depositions</li> <li>a) Gold Depositions without Annealing</li> <li>b) Gold Depositions with Annealing (60 shots)</li> <li>c) Gold Depositions with Annealing (900 shots)</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> </ol>	71 72 73 76 78
<ol> <li>1) Gold Only Depositions</li></ol>	71 72 73 76 78 81
<ol> <li>a) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> </ol>	71 72 73 76 78 81 81
<ol> <li>a) Gold Only Depositions</li></ol>	
<ol> <li>Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> </ol>	71 72 73 76 78 81 81 81 82 84
<ol> <li>Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (6000 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> </ol>	71 72 73 76 78 81 81 82 84 85
<ol> <li>Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (6000 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> </ol>	71 72 73 76 78 81 81 82 84 84 85 88
<ol> <li>a) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> </ol>	71 72 73 76 78 81 81 81 82 84 85 88 89
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> </ul>	71 72 73 76 78 81 81 82 84 85 88 85 88 89 90
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> </ul>	71 72 73 76 78 81 81 81 82 84 84 85 88 89 90 93
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> </ul>	71 72 73 76 78 81 81 82 84 85 85 88 89 90 93 95
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> </ul>	71 72 73 76 78 81 81 81 82 84 85 84 85 89 90 93 95
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) Summary.</li> </ul>	71 72 73 76 78 81 81 82 84 85 85 88 89 90 93 95
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> <li>C) Summary.</li> </ul>	71 72 73 76 78 81 81 82 84 85 84 85 84 90 93 95
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> <li>C) Summary.</li> </ul> CHAPTER IV: GROWTH OF SI WIRES IN UHV SYSTEM BY DEPOSITING ADDITIONAL LAYER OF SI AT ROOM TEMPERATURE.	
<ul> <li>1) Gold Only Depositions</li></ul>	71 72 72 76 78 81 81 82 84 85 84 85 85 90 90 95
<ul> <li>1) Gold Only Depositions.</li> <li>a) Gold Depositions without Annealing.</li> <li>b) Gold Depositions with Annealing (60 shots).</li> <li>c) Gold Depositions with Annealing (900 shots).</li> <li>d) Gold Depositions at Lower Pulse Energy (100-150mJ)</li> <li>2) Gold and Silicon Depositions.</li> <li>a) Gold (5 shots), Silicon (900 shots).</li> <li>b) Gold (900 shots), Silicon (900 shots).</li> <li>c) Gold (900 shots), Silicon (6000 shots).</li> <li>d) Various Deposition Conditions.</li> <li>3) Ge Depositions.</li> <li>a) 500 °C.</li> <li>b) 700 °C.</li> <li>c) 800 °C.</li> <li>c) Summary.</li> </ul> CHAPTER IV: GROWTH OF SI WIRES IN UHV SYSTEM BY DEPOSITING ADDITIONAL LAYER OF SI AT ROOM TEMPERATURE. <ul> <li>A) Procedures.</li> <li>B) Comparisons of Au Only and Au-Si.</li> </ul>	71 72 73 76 78 81 81 82 84 85 84 85 84 90 93 95

1) 900 °C: Silicon (12,000 shots)	
2) 900 °C: Silicon (24,000 shots)	
3) 500 °C	
4) 700 °C	
5) 900 °C: Other Deposition Conditions	
D) Summary	

# **CHAPTER V: GROWTH OF SILICON NANOWIRES IN**

FURNACE SYSTEM	
A) Procedures	
B) Results	
1) Lower Temperature Annealing (8	800 °C) 123
a) 5 nm Thick Gold Film	
b) 10 nm Thick Gold Film	
c) 18 nm Thick Gold Film.	
d) 112 nm Thick Gold Filn	n
2) High Temperature Annealing (11	00 °C) 134
a) 5 nm Gold Thick Film	
b) 10 nm Thick Gold Film.	
c) 18 nm Thick Gold Film.	
d) 112 nm Thick Gold Filn	n
C) Summary	
<b>CHAPTER VI: DISCUSSIONS &amp; CONCLU</b>	U <b>SIONS</b> 164
A) Discussions	164
B) Conclusions	
APPENDIX	
A) Systems/Components Specifications	
1) KrF Excimer Laser	
2) UHV Chamber and Mullite Tube	
a) UHV Chamber	
b) Mullite Tube	
3) Ontics	172
a) Plano-Convex Lens	
a) Plano-Convex Lens b) Laser Mirror	
a) Plano-Convex Lens b) Laser Mirror c) Optics Window	
a) Plano-Convex Lens b) Laser Mirror c) Optics Window d) Plexiglas Beam Box	172 172 173 173 174
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> </ul>	172 172 173 173 174 174
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> </ul>	172 172 173 173 174 174 174 175
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> <li>a) Target Holder/Manipula</li> </ul>	172 172 173 173 174 174 174 175 175 175
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> <li>a) Target Holder/Manipula</li> <li>b) Sample Holder/Heater</li> </ul>	172 172 173 174 174 174 175 175 tor
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> <li>a) Target Holder/Manipula</li> <li>b) Sample Holder/Heater</li> <li>c) SPS Sample Heater Power</li> </ul>	172 172 173 173 174 174 174 175 175 tor
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> <li>a) Target Holder/Manipula</li> <li>b) Sample Holder/Heater</li> <li>c) SPS Sample Heater Power</li> <li>d) Stepping Motor Control</li> </ul>	172 172 173 174 174 174 175 175 175 175 176 176 176 177 177
<ul> <li>a) Plano-Convex Lens</li> <li>b) Laser Mirror</li> <li>c) Optics Window</li> <li>d) Plexiglas Beam Box</li> <li>e) Optics Stand</li> <li>4) Control</li> <li>a) Target Holder/Manipula</li> <li>b) Sample Holder/Heater</li> <li>c) SPS Sample Heater Pow</li> <li>d) Stepping Motor Control</li> <li>e) Chiller</li> </ul>	172 172 173 174 174 174 175 175 175 175 175 176 176 176 177 177 177 178

B) Vacuum Technology	179
1) Pressure Units	179
2) Vacuum Pumps	180
a) Dry Roughing Pump	180
b) Turbo Pump	180
c) Ion Pump	181
3) Vacuum Systems	182
4) Pressure Measurement	185
a) Vacuum Gauge Controller	185
b) Thermocouple Gauge	185
c) Ionization Gauge	186
C) Cleanroom Wet Station	186
D) Operating Manual	187
1) Excimer Laser	187
a) Checking the Beam Path	187
b) Laser Cooling	189
c) Starting the Laser	189
d) Gas Lifetime and Replacement	190
e) Laser Operations	192
f) Shutting Down Laser Device	193
g) Air Filter	193
2) Optical Window Cleaning	194
3) Radiant Quartz Lamp	195
4) SPS Series Power Supply	196
5) Turbo Pump Controller	201
6) PID Controller/Thermocouples	202
7) Scanning Electron Microscope (SEM)	202
a) Operating Manual (JEOL 6400V)	206
8) Wafer Cleaning/Wet Station	210
E) Furnace Aluminum Endcap Designs	212
1) Optics Holder/Components	213
2) Right Pusher	216
3) Middle Stands	218
REFERENCES	219

•

# LIST OF TABLES

Table 1: Qualitative comparison of deposition rates	
of various growth techniques	13
Table 2: Temperatures for melting, boiling, and avaporization Rate of 1 nm/pulse for selected solids	20
Table 3: Thermal stress calculations for Si and Au	21
Table 4: Evaluation of the minimum droplet size by means of Eqn.6	24
Table 5: Numerical calculations showing various factors affecting the substrate temperature in PLD	36
Table 6: Construction of different phases	55
Table:7 Experimental systems	61
Table 8: Size Distributions at Various GoldDeposition Conditions	80
Table 9: Gold thin film sputtering parameters	122
Table 10: Specifications for Lamda Physik 210i KrF Excimer Laser	170
Table 11: Basic specifications for UHV chamber	170
Table 12: Properties of Mullite	171
Table 13: Specification for the plano-convex lens	173
Table 14: Specification for the high power UV laser mirror	173
Table 15: Specifications for the optical window	174
Table 16: Beam box specifications	175
Table 17: Specifications for the aluminum optics stand	175
Table 18: Sample temperature control parameters	200
Table 19: Specifications for the two types of SEMs	203

# **LIST OF FIGURES**

Figure 1: Carbon nanotube transistor	2
Figure 2: Nanowire functional devices: a) silicon nanowire FET b) p-n junction	4
Figure 3: n+ -p-n bipolar transistor	4
Figure 4: Coaxially-gated transistor	4
Figure 5: Nanowires grown in the furnace: a) Zn nanowire b) ZnSe nanowire	5
Figure 6: Nanowires grown by a) MCA and b) OA methods both in the furnace	7
Figure 7: General PLD setup: on-axis target-substrate configuration	11
Figure 8: General PLD setup: off-axis target-substrate configuration	11
Figure 9: Thermal process of laser ablation	15
Figure 10: Droplet formation in the gold target	22
Figure 11: Sketch illustrating the droplet formation in hydrodynamic sputtering	23
Figure 12: VLS growth of silicon nanowire using gold metal catalyst.	41
Figure 13: Binary phase diagram of Au-Si.	42
Figure 14: Top-view general diagram of the UHV system.	63
Figure 15: Side-view photograph of the UHV system.	63
Figure 16: General diagram of the furnace system.	65
Figure 17: Photograph of the furnace system.	65
Figure 18: SEM image of the un-annealed gold deposited	72

Figure 19:	Si(111) substrate. EDS compositional analysis of the deposited gold on Si(111).	73
Figure 20:	60 shots of gold deposited on a Si(111) substrate and annealed to 600 °C.	74
Figure 21:	EDS analysis showing the presence of gold and silicon.	75
Figure 22:	EDS analysis showing only silicon.	75
Figure 23:	Histogram showing the size distribution of the gold agglomerations.	76
Figure 24:	900 shots of gold deposited on Si(111) and subsequently annealed to 600 °C.	77
Figure 25:	Histogram showing the size distribution of the gold agglomerates.	78
Figure 26:	900 shots of gold at 100-150 mJ.	79
Figure 27:	Histogram showing the size distribution of gold dots in Figure 26.	80
Figure 28:	SEM Images of Au-Si growth using an excimer laser source energy of 500mJ and 5 laser shots of the Au target and 900 shots of Si: a) image at 1000X magnification, b) image at 5000X magnification.	82
Figure 29:	SEM Images of Au-Si growth at 500mJ and 900 shots for both Au and Si. a) image at 700X, b) image at 8000X.	83
Figure 30:	EDS analysis showing gold and silicon.	83
Figure 31:	EDS analysis showing only silicon.	84
Figure 32:	SEM images of Au-Si Deposits at 500mJ and 900 shots of gold but at different silicon deposition shots a) image at 6000 shots, b) image at 900 shots.	85
Figure 33:	SEM images at various deposition conditions.	87
Figure 34:	SEM image of the Au-Ge deposits at Au (450), Ge (6000), 500 mJ, 500 °C.	89

Figure 35: Histogram showing the size	distribution of Au-Ge dots.	90
Figure 36: SEM image of the Au-Ge de Ge (6000), 500 mJ and 700 °	posits at Au (450), C.	91
Figure 37: Histogram showing the size	distribution of Au-Ge dots.	92
Figure 38: EDS analysis of the Ge depo	osition.	92
Figure 39: Au (450), Ge (18,000), 500 1	mJ, 800 °C.	94
Figure 40: EDS analysis of the Ge depo	osition.	94
Figure 41: Histogram showing the distr	ibution of Au-Ge dots.	95
Figure 42: SEM image of a Au film on overlayer after annealing to	a Si(111) without silicon 900 °C.	97
Figure 43: EDS analysis at a bright loca	ation of Figure 42.	98
Figure 44: Tilted SEM image of the sili Si (150-room), Si (12,000-9	con wires at Au (300), 00 °C)	101
Figure 45: EDS analysis showing the pr	resence of gold and silicon	102
Figure 46: Histogram showing the diam the silicon wires	neter distribution of	103
Figure 47: Histogram showing the heig the silicon wires	ht distribution of	103
Figure 48: Graph illustrating the width- in the silicon wires: (Series (Series 2: Wire height)	height relationship 1: Wire diameter)	104
Figure 49: Oblique view SEM image of silicon wires on the Si(111)	f the grown	106
Figure 50: Plane view SEM image of the	ne grown silicon wires	106
Figure 51: SEM image showing the var silicon wires shapes	iation in the grown	108
Figure 52: Close side-view of one silico shown in Figure 51	on wire which is also	109

Figure 53:	Close view of the silicon wire in Figure 52 as seen from the top	109
Figure 54:	EDS analysis on the tip of the wire shown in Figures 52 and 53	110
Figure 55:	Histogram showing the diameter distribution of silicon wires	111
Figure 56:	Histogram showing the height distribution of silicon wires	112
Figure 57:	Histogram showing the diameter-height relationship a) samples 1-40 b) samples 41-80. Blue Series= width, Red Series=height of the silicon wires	113
Figure 58:	SEM image of Au (300 pulses)/Si (150 pulses at room temp.)/Si (12,000 pulses at 500 °C), 500 mJ a) Gold-rich dots b) Closer view of gold-rich dots	115
Figure 59:	EDS analysis of the buried gold-rich dots	115
Figure 60:	Histogram of the size distribution of gold-rich dots	116
Figure 61:	SEM image of the deposits at Au (300 pulses)/ Si (150 pulses at room temp.),/Si (12000 pulses at 700 °C). The laser beam energy of 500 mJ was used for all pulses.	117
Figure 62:	EDS analysis on the deposition shown in Figure 61	117
Figure 63:	Angled SEM image of the silicon wires: scale bar 5 μm.	118
Figure 64:	Tilted SEM image of the silicon wires	119
Figure 65:	Close view of the silicon wire in Figure 64.	119
Figure 66:	EDS analysis of the Au/Si tip of the wire shown in Figure 65.	120
Figure 67:	SEM image of the annealed gold film thickness of 5 nm	124
Figure 68:	Histogram showing the diameter distribution	124

<ul> <li>Figure 69: SEM images of the annealed gold film thickness of 10 nm at 800 °C. a) Scale bar 5 μm,</li> <li>b) Scale bar 1 μm.</li> </ul>	126
Figure 70: EDS analysis of the gold dots	127
Figure 71: Histogram showing the diameter distribution of the dots	128
Figure 72: SEM image of the annealed gold film thickness of 18 nm at 800 °C. a) Scale bar 5 μm b) Scale bar 1 μm.	129
Figure 74: Histogram showing the diameter distribution of dots	130
<ul> <li>Figure 75: SEM images of the annealed gold film thickness of 112 nm at 800 °C. a) Scale bar 20 μm</li> <li>b) Scale bar 2 μm.</li> </ul>	131
Figure 76: SEM image of the 112 nm thick gold film for Additional 8 minutes at 800 °C. Scale bars at a) 50 μm, b) 2 μm, and c) 10 μm	133
Figure 77: SEM images of the 5 nm thick gold film at 1100 °C a) Image at the scale bar of 5 mm, b) Image of the empty black pits c) Image of the black pit showing some wire-like growth	135
Figure 78: EDS analysis on the black pits shown in Figure 77c)	136
Figure 79: SEM images of the 5 nm thick gold film with 3 additional hours of annealing at 1100 °C a) Image at the scale bar of 10 mm, b) Image at the scale bar of 5 mm showing wire-like growth inside the region.	138
Figure 80: SEM images of the 10 nm thick gold film annealed at 1100 °C. a) Scale bar 5 µm, b) Scale bar 1 µm.	140
Figure 81: EDS analysis on the regions outside the black pits	141
Figure 82: SEM image of the 10 nm thick gold film annealed for 3 additional hours at 1100 °C.	143
Figure 83: SEM images of the 18 nm thick gold film annealed at 1100 °C a) Scale bar of 50μm, and b) Scale bar of 10 μm.	145

Figure 84: SEM image of the 18 nm thick gold film annealed at 1100 °C.	146
Figure 85: SEM images of the 18 nm thick gold film annealed at 1100 °C at various locations in the substrate.	147
Figure 86: EDS analysis on the bright regions.	148
Figure 87: EDS analysis on the grown silicon nanowires.	149
Figure 88: SEM image of the 18 nm thick gold film annealed for additional 3 hours at 1100 °C. a) Scale bar of 50 μm b) Scale bar of 2 μm	151
<b>Figure 89:</b> SEM images of the silicon nanowires growing randomly on the substrate	152
<b>Figure</b> 90: SEM images of the 112 nm thick gold film at 1100 °C Scale bar of 200 μm b) Scale bar of 50 μm.	154
Figure 91: EDS analysis on the bright rectangular boundary.	155
Figure 92: SEM image of the silicon nanowires growth outside the gold-rich boundary layer for 112 nm thick gold film annealed at 1100 °C.	157
Figure 93: Various types of silicon nanowires found outside the gold-rich boundary layer for the 112 nm thick gold film annealed at 1100 °C.	158
Figure 94: SEM images of the various silicon nanowires with bright dots at the tips.	159
Figure 96: SEM image showing a bright dot within the ring-like nanowire.	160
Figure 97: SEM images of the 112 nm thick gold film at 1100 °C. at the edge of the gold-rich boundary layer.	161
Figure 98: SEM images of the silicon nanowires growing at the gold-rich boundary layer.	162
Figure 99: Photograph of the LPX 200 KrF excimer laser	169
Figure 100: Mullite tube	171

174 175 176
175 176
176
177
177
178
179
180
181
182
182
183
184
185
186
186
187
187 188
187 188 189
187 188 189 189

Figure123: Gas cabinet.	191
Figure124: Pol <sup>TM</sup> metal polisher.	195
Figure 125: Front panel of the SPS power supply.	196
Figure 126: Graph of the time-temperature response.	199
Figure 127: Graph of the knob level-temperature response.	199
Figure 128: Turbo pump controller.	201
Figure 129: Fuzzy logic based PID controller.	202
Figure 130: JEOL 6400V Scanning Electron Microscope.	204
Figure 131: Hitachi S2500 Scanning Electron Microscope.	204
Figure 132: Autosketch drawings of optics side Al endcaps	213
Figure 133: Autosketch drawings of optical window holder.	214
<b>Figure 134: Photographs showing the designed optical-side</b> Al endcaps. a) side view b) front view	215
Figure 135: Autosketch drawing of right-pusher Al endcaps	216
Figure 136: Photograph showing the right pusher Al endcap	217
Figure 137: Middle stands.	218

### **INTRODUCTION:**

Nanotechnology has the potential to impact a wide variety of disciplines from studies of structural materials, to medical applications, and electronics, to cosmetics. A recent definition of nanotechnology is:

Research and technology development at the atomic, molecular or macromolecular levels, in the length scale of approximately 1 - 100 nanometer range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size. The novel and differentiating properties and functions are developed at a critical length scale of matter typically under 100 nm. Nanotechnology research and development includes manipulation under control of the nanoscale structures and their integration into larger material components, systems and architectures. Within these larger scale assemblies, the control and construction of their structures and components remains at the nanometer scale. In some particular cases, the critical length scale for novel properties and phenomena may be under 1 nm (e.g., manipulation of atoms at ~0.1 nm) or be larger than 100 nm (e.g., nanoparticles reinforced polymers have the unique feature at ~ 200-300 nm as a function of the local bridges or bonds between the nanoparticles and the polymer)<sup>1</sup>

Considerable interest has been focused recently by the successful fabrication of

 $\mathbf{v}$  arious nanotubes<sup>2-4</sup> and nanorods materials. The origin of the currently intensive effort

in the area of nanostructures derives from the need for gaining better understanding in

the concepts about how dimensionality and size affect physical properties as well as the

expected benefits to many devices and structures<sup>1</sup>.

To date, most efforts have focused on electrical transport in carbon nanotubes. These

stuction interesting fundamental features, including the existence of coherent

states extending over hundreds of nanometers, ballistic conduction at room temperature,

and Luttinger liquid behavior, and have demonstrated the potential for devices such as

field effect of transistors. However, there are important limitations of nanotubes, such as

the inability to fabricate metallic or semiconductor tubes adhering to specific diameter or

helicity, and the lack of controlled doping of semiconducting nanotubes. Recently there

has been important advancement in the areas of carbon nanotube technology to overcome some of its inherent limitations. Researchers at IBM have successfully fabricated the world's first array of transistors<sup>5</sup> made out of carbon nanotubes using a method called constructive destruction method as shown below in Figure 1. The method consists of applying high voltage to the bundles of metallic and semiconducting carbon nanotubes and selectively destroying the metallic carbon nanotubes, leaving only the semiconducting carbon nanotubes.



Figure 1: Carbon nanotube transistor5

Nanowires in the other hand inherently do not have these limitations. The nanowires can be formed as metallic or semiconductor at the fabrication level. These nanowires will remain metallic or semiconducting independent of diameter. For the semiconductor nanowires especially, it should be possible to take advantage of the vast knowledge from the semiconducting industry to dope the nanowires. Consequently, there is a new interest in the fabrication and properties of the nanowires such as Si, Ge, GaAs, CdS<sup>6</sup>, ZnO<sup>7</sup>, and InP<sup>8</sup> with applications that range from Field Effect Transistors (FETs) to nanolasers. For *silicon* nanowires specifically, some of the recent developments are the demonstration of *silicon* nanowires to function as simple FETs<sup>10-11</sup>, p-n junctions, bipolar transistors, *corrnplementary* inverters<sup>12</sup>, and coaxially-gated transistor<sup>13</sup>. These functional devices are *shown* in Figures 2-4.



Figure 2: Nanowire functional devices: a) silicon nanowire  $\text{FET}^{11}$  b) p-n junction<sup>12</sup>



Figure 3: n+ -p-n bipolar transistor<sup>12</sup>



Figure 4: Coaxially-gated transistor<sup>13</sup>

The recent successes in the actual fabrication of functional nanodevices are due to the significant advancements in the nanowire fabrication over the years, such as the increased number in the growth schemes, as well as the types of materials. Previously, various types of nanowires have been fabricated using differing methods including laser ablation<sup>14-16</sup>, simple evaporation<sup>17-18</sup>, electron beam (EB) lithography<sup>19</sup>, etching<sup>20</sup>, and scanning tunneling microscopy<sup>21</sup> (STM). The types of nanowires that have been grown range from silicon and germanium to GaAs, GaP, InAs, InP, GaAsP, InAsP, ZnSe<sup>22</sup>, CdS<sup>17</sup>, CdSe, SiGe<sup>14</sup>, GaN<sup>23</sup>, GaInAs, SiC, B<sub>4</sub>Si, BP, TiB<sub>2</sub>, TiP, ZrB<sub>2</sub>, ZrP, NbB<sub>2</sub>, NbO, *Si*<sub>3</sub>N<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, NiO, Te, Se and Zn<sup>24</sup>, ZnO<sup>25</sup> to name a few. Following images in Figure 5 **show** the Zn and ZnSe nanowires both grown in the furnace.



Figure 5: Nanowires grown in the furnace: a) Zn<sup>24</sup> nanowire b) ZnSe<sup>22</sup> nanowire



Of all the nanowires that have been grown thus far, silicon nanowires have occupied the vast research interest over the years for the obvious reason of possessing potential applications in nanodevices such as in electronics and optoelectronics. In addition to the methods mentioned above, silicon nanowires have also been grown using the chemical vapor deposition (CVD) using silane<sup>26</sup>. In the production of bulk quantities of silicon nanowires, the growth schemes are divided into two categories: the metal catalystassisted (MCA) and the oxide-assisted (OA) methods. The first method is the metalcatalyzed growth of nanowires based on the well known Vapor-Liquid-Solid (VLS) **rne**chanism as described in detail by various authors<sup>27-28</sup>, while OA method describes the **rnan**owire growth in the presence of oxygen without using the metal catalyst.

In the MCA method, the nanowires are grown either by CVD using chemical such as silane or physical vapor deposition (PVD) by laser ablating the metal catalyst containing silicon target under the flow of argon gas both inside the furnace. The nanowires grew either perpendicularly on the silicon substrate in the CVD case, or collected on the cold finger downstream in the PVD case. The second method is the oxide-assisted growth of silicon nanowires by either ablating SiO<sup>29</sup> target or silicon powder<sup>30</sup> and thermal evaporation<sup>31</sup> of oxygen containing silicon powder such as SiO under the flow of argon gas also inside the furnace. The nanowires, formed without using the metal catalyst, were collected either directly on the quartz downstream or on a silicon wafer<sup>32</sup>. For the silicon nanowires that have been collected on the silicon wafer, the nanowires have not been grown perpendicularly yet. The following images in Figure 6 show the grown silicon nanowires using these differing methods.



Figure 6: Nanowires grown by a) MCA<sup>33</sup> and b) OA<sup>29</sup> methods both in the furnace

One challenge that remains is the fabrication of nanowires in a manner that is amiable to device fabrication from a manufacturing perspective. The fabricated nanowires shown in Figure 6 are entangled, and must be picked-and-placed onto a suitable substrate to fabricate an individual device. For scale-up into manufacturable devices, it would be preferred to deposit the nanowires in controlled locations, or grow them from desired locations in parallel. Furthermore, a number of devices would be considerably improved if epitaxial interfaces between the nanowire and the electrodes at the ends of the nanowire were realized.

In this work, we are investigating the growth of silicon nanowires directly from the Si(111) substrate. The research will entail exploring various pressure ranges that span from ultra high vacuum (UHV) to higher pressure of about one atmosphere. In order to accommodate the varying pressure ranges, two separate growth systems-UHV chamber and high temperature, high pressure furnace were used. The deposition scheme was accomplished via pulsed laser deposition (PLD) using the KrF excimer laser and the nanowire growth will be based on the well-known vapor-liquid-solid (VLS) mechanism using gold as the mediating metal catalyst. The role of oxygen in the metal-catalyzed nanowire growth method will also be studied in order to gain deeper understanding in the two nanowire growth methods, namely MCA and OA.

### **CHAPTER I: THEORY**

The laser is a powerful tool with attractive properties that has found its applications in many fields such as medicine, materials processing, communications, and nuclear fusion. Due to its narrow frequency bandwidth, coherence and high power density this instrument is used in many scientific research works and experiments. For nanowire growth, lasers provide an effective mean for bulk production of nanowires. This undoubtedly is an attractive factor in commercialization and mass production of nanodevices. There are however, some key points that must be addressed in the usage of the laser as an effective energy source. As will be shown in detail in the following sections, one of the primary advantages in using PLD is in its simplicity of the system set-up. Despite the apparent advantage, the ablation mechanism of the pulsed laser deposition scheme is a very complex phenomenon which requires much review in theories.

The adaptation of PLD for the growth of nanowires with VLS mechanisms can be considered in four general stages: 1) laser-material interaction, 2) plasma, and dynamics of resultant highly energetic and directional plume, 3) the mass transfer of the ablated material onto the substrate surface, and 4) the eventual participation in the growth of nanowires via VLS growth mechanism. To treat all the pertinent processes involved in the nanowire growth, the theories reviewed in this chapter is divided into subsections in the following order: A) Pulsed Laser Deposition (PLD), B) Vapor-Liquid-Solid (VLS) Growth Mechanism, and C) Gold/Si(111) Eutectic.

### A) Pulsed Laser Deposition (PLD)

### 1) PLD: Comparison to Other Growth Methods

Fabrication of the nanostructures can be achieved via several different routes. Some of the well known processing route includes mechanical milling in solid state, electrodeposition, sol-gel, and hydrothermal in the liquid state and chemical vapor deposition (CVD) and physical vapor deposition (PVD) in the vapor state. The selection of the appropriate deposition technique depends on some of the criteria such as the level of purity, sizes, shapes, and cost-effectiveness.

Over the years, vapor deposition techniques have proven to provide highly pure materials with structural control at lower temperature. It can be classified into PVD, CVD, aerosol-based processes, and flame-assisted deposition methods. Pulsed laser deposition, or PLD is a PVD process. Pulsed laser deposition had been known since 1960's, but it recently has become popular due to successful fabrication of thin films of oxide materials, such as high-temperature superconducting<sup>34</sup> and ferroelectric materials. A search by Beech in 1991 lists 128 different materials grown by PLD<sup>35</sup>. The general PLD experimental setup is shown in Figures 7 and 8. Unless otherwise noted, the discussion on PLD in this thesis will be based primarily on the on-axis target-substrate configuration.



Figure 7: General PLD setup: on-axis target-substrate configuration.



Figure 8: General PLD setup: off-axis target-substrate configuration.

The simplified PLD setup as shown in the figures above primarily consists of the high power laser, optical elements such as lens and windows coupling the laser energy and the targets, and substrate and target holders inside either the UHV chamber or a furnace system.

For the growth of nanowires, PLD presents some advantageous features over other deposition methods. These are: 1) growth of high purity nanowires due to UHV condition, 2) the feasibility of depositing under a broad range of ambient pressures of various gases, 3) wide spectrum of materials that can be vaporized, 4) the capability of stoichiometric transfer of material from the target to substrate, i.e. the exact chemical composition of a complex material such as YBCO and GaAs can be reproduced, 5) relatively high deposition rates, typically ~100 Å/min at moderate laser fluences, or power density. (A feature quite unique to PLD is its extremely high instantaneous deposition rate as compared to other methods - millions of times higher than any conventional deposition rates. Rates as high as microns-per-cm<sup>2</sup>-sec are possible with this technique<sup>36</sup>.) 6) since the laser is utilized as an external energy source, the system can be extremely clean process without the filaments needed in other deposition techniques, 7) hazardous chemicals such as silane, which is typically used for CVD fabrication of silicon nanowires, is not used and most importantly, 8) that the system setup is simple.

There are some inherent disadvantages in using PLD. These disadvantages are: 1) the **presence** of the micron-sized globules of molten material, up to ~ 10  $\mu$ m in diameter, 2) **energetic** particulates, as high as 1 keV which causes sputtering of the substrates, 3) and **the narrow** forward angular distribution cos<sup>n</sup> $\theta$  that makes large-area scale-up a very

difficult task. The production of large sized particulates is a major problem in the PLD, and its effect will be pronounced in the nanowire growth endeavor. It not only poses the problem of inefficient and ineffective usage of target materials, but potentially poses undesirable effect on the growth of nanowires by splashing directly onto the large nanowire growth regions. Some of the solutions to alleviate the problems of large-sized particulates are by using mechanical particle filters in the path of the plume, off-axis target-substrate configuration or two-beam ablations to smooth the target surface. The drawback for the first two methods is in the reduction of the deposition rates.

Table1 below lists the qualitative comparisons between the several well knowngrowth methods. Following abbreviations are used: MBE = Molecular Beam Epitaxy,PECVD = Plasma Enhanced Chemical Vapor Deposition, TE = Thermal Evaporation.

Method	Vacuum Requirements	Multi- Element Rate Control	Energy Range (eV)	Typical Deposition Rate (Å/sec)
CVD	HV	Moderate	0.1	20
MBE	UHV	Moderate	0.1	3
PECVD	HV	Moderate	0.1-500	20
PLD	HV	Easy	1-1000	10
TE	HV	Difficult	0.1	20

Table 1: Qualitative comparison of deposition rates of various growth techniques<sup>37</sup>

## 2) Sputtering Mechanisms

Mass removal, either atoms or bulk, from the surface of the laser irradiated material encompasses various complex mechanisms. At sufficiently high flux densities and short pulse duration, all elements in the target are rapidly heated up to their evaporation temperature. Materials are dissociated from the target surface and ablated out with the same stoichiometry as in the target. The instantaneous ablation rate is highly dependent on the fluences of the laser shining on the target. The schematic of the basic thermal process involved in the laser energy absorption at the surface of the target to the subsequent expulsion of particulates is illustrated in Figure 9 in the following page.



Figure 9: Thermal process of laser ablation.

The simplified description of the thermal process involved in the interaction of the excimer laser beam with the given material begins with the absorption of the laser energy at the surface of the material as defined by the penetration depth. The temperature at the surface then rapidly rises to the melting temperature of the target **material** within a first few nanoseconds. Longer pulse length results in lower melting **velocity**. The temperature then continues to rise to the vaporization temperature of the **material**. With the expulsion of atomic and mass evaporation, a plasma front is **subsequently** formed at the surface of the irradiated material. Within the material, a **shock** wave also is formed which causes further expulsion of large sized particulates. **The** actual process involved in the laser ablation of a given material is however, much **imore** complex as stated before, and requires more detailed analysis.

Based on the current understanding, the laser ablation can be divided into several categories: indirect collisional, thermal, electronic, hydrodynamical, and exfoliational SPuttering mechanisms. In general, the first three sputtering mechanisms-indirect collisional, thermal, and electronic- leads to liberation of atomic-sized material from the Surface, while the latter two involves the expulsion of bulk materials. Despite the apparent differences in the size of the emitted materials, the ablation mechanisms are not necessarily distinguishable in a specific laser ablation system if occurring sinultaneously for instance. These processes are dependent on the laser parameters such a pulse energy. The following section treats each sputtering mechanisms in more detail.

### a) Indirect Collisional

Indirect collisional sputtering describes the process where the laser beam interacts with the plasma that is formed during the laser ablation of a given material in air or vacuum condition. The effect of the laser-plasma interaction is apparent in several areas: 1) decrease in the laser transmission energy, 2) the decrease in the volume mass removal rate, and 3) sputtering of the nearby substrate due to the acceleration of the ions in the plasma.

The existence of plasma at the surface of the target material causes attenuation of the **laser** energy, causing the transmission of the laser energy to decrease with the laser **power** density. One study<sup>38</sup> has observed a decrease in the transmission energy to as low **as 20%** of the original pulse as the laser power density increased to about 60 GW/cm<sup>2</sup>. **Anot**her consequence of laser-plasma interaction is the effect on the volume removal **rate** of the materials. The volume V of the material removed by the impinging laser **beam** per pulse, is given as

$$V = \alpha P^n$$
 Eqn. 1

where P is the laser power density,  $\alpha$  is a constant of proportionality, and the exponent *n* is dependent on the type of material. Previous study has observed the phenomenon called roll-off or break point, where there is a change in the value of *n* from a higher value (at lower power density) to a lower value (at higher power density). Using the nm nanosecond lasers, ablation of Cu<sup>39</sup> resulted in the exponent change from 3.9 to while ablation<sup>40</sup> of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> resulted in changes in exponent from 7.4 to 1.5. The served change in the exponent at the break point is hypothesized to be due to the laserplasma interaction. Previously, it has been shown that above the break point, there is a marked increase in the ion fraction, and the drop in the volume removal rate. This means that the part of the laser energy is used to generate additional ions within the plasma, rather than eject more material<sup>41</sup>.

In addition to the above mentioned effects, there also has been report of ions in the **plasma** being accelerated to as much as keV due to the laser-plasma interaction<sup>42</sup>. The **result** is the indirect sputtering of the nearby target materials from the energetic ion **species**<sup>43</sup>. One indication of indirect collisional effect was the substrate erosion, where **the** particles emitted from a laser bombarded Cd target caused significant erosion of a **nearby** surface (0.02 to 0.12 nm/pulse).

### b) Thermal

Thermal sputtering generally denote a process in which the laser energy is converted to lattice vibrational energy prior to the bond breaking, which subsequently releases atomic-sized material from the target surface. In other words, it describes the vaporization process which requires the temperatures well above the melting or boiling Point of the target. The description of the thermal sputtering as described previously in study<sup>44-45</sup> where the classical expression describing the vaporization process from the solid surface is
vaporization flux = condensation flux

$$= \frac{p}{\sqrt{(2\pi mk_BT)}}$$
$$= p_o \left( \exp \frac{-\Delta H_v}{k_BT} \right) \frac{1}{\sqrt{(2\pi mk_BT)}} \text{ atoms/m}^2 \text{-sec} \quad \text{Eqn. 2}$$

where p is the pressure that would exist if the equilibrium vapor were present,  $p_o$  is a **constant**,  $\Delta H_v$  is the heat of vaporization, and the condensation efficiency taken as unity. The total loss from the target is then

Depth/pulse = 
$$\frac{p_o(\sqrt{2\pi m k_B T})}{n_c} \propto \int \exp\left(\frac{-\Delta H_v}{k_B T}\right) T^{-1/2} dt$$
 Eqn. 3

where  $n_c$  is the number of density of the condensed phase. Written in a different form

Depth/pulse ~ 
$$\hat{p}_{am}\hat{T}^{1/2}\tau \mid M^{1/2}\Delta H_{v} \ge 1.53 \ge 10^{6}$$
 nm/pulse Eqn. 4

**where**  $\hat{T}$  is the maximum surface temperature, M is the molecular weight of the

**vaporizing species**,  $\Delta H_{\nu}$  is in electronvolts. Observed sputtering rates are typically

- $1 \mathbf{1} \mathbf{1} \mathbf{0}$  nm/pulse. The Table 2 below lists the condition for thermal sputtering in some
- common materials<sup>46</sup> for the vaporization rate of 1 nm/pulse.

Material	Melting Point (K)	Boiling Point at 1 atm (K)	Temperature for vaporization rate of 1 nm/pulse (K)
Au	1336	3133	4600
Si	1685	3553	4600
W	3683	5828	>6000

# Table 2: Temperatures for melting, boiling, and a vaporization Rate of 1 nm/pulse for selected solids<sup>46</sup>

#### c) <u>Electronic</u>

Electronic sputtering involves the laser-induced electronic excitation which lead directly to bond breaking before an electronic to vibrational energy transfer has occurred. It generally is not known to cause sputtering in metals. The course of electronic excitation begins with the absorption of the laser energy, which causes excitation of the outer atomic electrons. If the excitation energy is greater than the bincling energy, then the bond breaks, and the atoms and ions are liberated.

Electronic sputtering can also describe other excitation and ionization processes. It also arise due to such events as ion explosions<sup>47</sup>, the hole-pair mechanism<sup>48</sup>, defect nation<sup>49</sup> or surface plasmon excitation<sup>50</sup>.

# **D** Exfoliational

Exfoliational sputtering involves the detachment of micron-sized flakes from a target to the repeated thermal shocks. It can be expected to occur whenever the system has

a high linear thermal expansion ( $\Delta L/L_o$ ), where  $L_o$  is the thickness that is heated and  $\Delta L$  is the change in thickness, a high Young's modulus (E), a high melting point ( $T_m$ ), and the laser-induced temperature excursions approach but do not exceed  $T_m$ . The repeated thermal shocks would lead to eventual cracking and detachment of the flakes.

According to arguments of Kelly<sup>45</sup>, the thermal shock can be measure in terms of **thermal stress**:

Stress=
$$E\Delta L/L_o$$
 Eqn. 5

The Table 3 shown below lists some of the material's thermal stress values.

Solid	Linear Thermal Expansion of the Solid ( $\Delta L/L_0$ )	Young's Modulus,E (10 <sup>10</sup> x Pa)	ΕΔL/L <sub>o</sub> (10 <sup>10</sup> x Pa)
Au	0.018	8.0	0.14
Si	0.0054	11.3	0.06
W	0.023	34	0.78

Table 3: Thermal stress calculations for Si and Au<sup>45</sup>

values in the table suggest that exfoliational sputtering will most likely occur with
esten, W, but not for silicon and gold which are the two main materials of interest.
to their low values of thermal stress, the exfoliational sputtering is not expected to
the problem in depositing silicon for the growth of nanowires.

#### e) Hydrodynamic

Hydrodynamic sputtering involves the formation of droplets on the surface of the target material, and the eventual expulsion as a consequence of the transient melting. Figure 10 shows the development of the droplet in the gold target.



Figure 10: Droplet formation in the gold target<sup>45</sup>

The sketch illustrating the hydrodynamic sputtering mechanism is shown in Figure 11 in the following page. According to the thermal expansion model<sup>45</sup>, asperities somehow form on the surface as shown in a). Thermal expansion in the early stage of the laser Pulse drives the melt away to form the asperities as shown in b)





Figure 11: Sketch illustrating the droplet formation in hydrodynamic sputtering.

The laser energy is assumed to be high enough to cause melting. The melt layer is initially thin, and the melt flow is limited. After the laser pulse, thermal contraction drives the melt toward the asperities as shown in c). The thicker melt flows readily. With repeated laser pulses, the asperities grow, eventually reaching the point where it breaks off in the form of large sized droplets. The minimum droplet size r is

$$\mathbf{r} = \left\{ \left( \frac{3\gamma L_o}{\rho_1 L} \right) \left( \Delta t \right)^2 \right\}^{1/3}$$
 Eqn. 6

where  $\gamma$  is the surface energy of the liquid,  $\rho_1$  is the liquid density, L is the total height change of the droplet, and  $\Delta t$  is the difference  $\tau - t_m$ . Here  $\tau$  is the laser pulse length,  $t_m$  is the time when the temperature equals the melting point temperature. Table 4 shows those parameters that are needed to describe the hydrodynamic sputtering for the case of silicon and gold.

Metal	γ Surface Energy of Liquid (J/m <sup>2</sup> )	α∆T Linear Thermal Expansion of Liquid	(ρ <sub>s</sub> -ρ <sub>l</sub> )/3ρ <sub>s</sub> Linear Expansion Due to Melting	R Minimum Droplet Radius (µm)	Observed Droplet Radius (µm)
Au	1.14	0.038	0.019	0.6	0.5
Si	0.730	0.038	-0.032	Probably None	None

Table 4: Evaluation<sup>45</sup> of the minimum droplet size by means of Eqn. 6.

#### 3) Metals and Non-metals Laser Ablations

Laser ablation is a complex process that depends on the laser parameters such as wavelength, pulse width, and fluence. The process is also complicated by the fact that different materials respond differently to the beam irradiation depending on the type of chemical bond. Generally, a chemical bond can be categorized into three types: ionic, covalent, and metallic. Ionic or heteropolar bonding occurs with elements that differ in polarity. One example of ionic bonded solid is NaCl. Covalent or homopolar bonding on the other hand, describes the bonding due to sharing of the outer electrons. Silicon, which is the material of this study, falls into this category. Finally, metallic bonding, which occurs for metals and alloys such as gold, is due to the formation of electron clouds which permeate the entire lattice.

For the laser ablation of ionic and covalent bonded solids, the primary sputtering mechanism seem to be the electronic sputtering, where the interaction of photons causes free-electron acceleration due to an inverse Bremsstrahlung process<sup>51-53</sup>. The accelerated electrons then collide with the lattice and excite the phonon with the time scale of a few picoseconds. For the case of metals, the laser sputtering is clearly not understood. Several proposals have been made to account for the laser sputtering in metals which includes thermal evaporation<sup>54</sup>, exfoliational sputtering and hydrodynamic sputtering<sup>44</sup>. Unlike the semiconductors, the metals generally have a reflection near unity at low frequency, while it drops drastically at higher frequencies. For gold, the reflectance drops to about 40% at the UV region. The absorption coefficient for covalent solid such as silicon is about 10<sup>6</sup> cm<sup>-1</sup>, and increases at higher temperature<sup>55</sup>. The absorption coefficient for metals is lower than the semiconductors, but still high. The difference in the absorption coefficient is manifested in the growth rates of the depositing materials. For gold, the growth rate has been reported to be about 0.23 Å/shot at the targetsubstrate distance of 25 mm<sup>56</sup>. The fluence was 6 J/cm<sup>2</sup> using a laser with a wavelength of 308 nm and pulse width of 20 ns. For silicon, the growth rate is generally about 1-10 Å/shot.

#### 4) Plasma Plume

The degree of ionization and the density of the ionized species depend on the laser fuence. At low laser fluence, small quantities of neutral and ionized species exist. This range of energy density is referred to as below-threshold or near-threshold. For ablation of gold thin film for example, this corresponds to ablation thresholds in the range of about 0.7 J/cm<sup>2</sup> to 0.9 J/cm<sup>2</sup> in the presence of an argon background gas<sup>57</sup>.

Increasing the laser fluence beyond the sub-threshold region causes two effects: Significant removal of target material, and the appearance of a luminous plasma plume. These threshold effects are most often described by evaporation and subsequent partial

absorption of the laser pulse by the vapor as has been discussed<sup>58</sup>. At certain laser fluences, the rapid laser heating rates ( $\sim 10^{11}$  K/sec) overcome the thermal diffusion and radiation losses and evaporation proceeds nonlinearly. Using the Saha equation<sup>37</sup>, the ratio of the singly charged ion to neutrals in the plasma can be estimated.

$$\frac{n_i}{n_n} = 2.4 \times 10^{15} \frac{T^{3/2}}{n_i} e^{-Ui/kT}$$
 Eqn. 7

where  $n_i$  and  $n_n$  are the ion and neutral densities in cm<sup>-3</sup>, *T* is the temperature in K, and  $U_i$  is the first ionization potential in electronvolts<sup>59</sup>. Typical plasma temperatures measured by emission spectroscopy during the initial expansion are ~ 10,000 K (~1 eV), well above the boiling points of most materials<sup>60</sup>. At nanosecond pulse duration, the energy spectrum of the ions is in the region of 1 eV to 2000 eV with a mean energy 100-400 eV. The degree of ionization of the plasma is between 10 % and 70 %, and depends strongly on the energetic and spectral laser parameters<sup>61</sup>. The neutral component of the **plasma** flux has relatively low mean energy (about 10 eV) and comprises 30 % to 90 % of the evaporated material<sup>62</sup>.

During the ablation by the nanosecond laser in a vacuum, a high pressure (-10-500 atm) bubble of hot plasma is formed  $< 50 \ \mu\text{m}$  from the target<sup>63</sup>. The existence of the highly energetic ions impinging onto the substrate surface may cause sputtering of the surface materials, as well as induce various type of damage to the substrate. The temperature of the substrate can also seen to increase in some cases. These facts will be especially evident in the case of deposition in the ultra high vacuum condition.

#### 5) Velocity

The laser sputtering involves the expulsion of materials encompassing all three physical state-vapor, liquid, and solid. The type of materials emitted varies in shape and size ranging from nanometer-sized monatomic and diatomic neutral and ionized species to micron-sized clusters and macroscopic materials. Typically, the liquid particulates emitted from the hydrodynamic mechanism are spherical while the solid particulates formed from the clustering and exfoliational mechanism are irregular in shape. With the variation in the shape and physical state, the velocity of the emitted species also differs. During the expansion of the plume, the larger sized particulates generally occupy the middle of the expansion front with lower velocity while the smaller sized particulates are at the edges with high velocity. Previously, the velocity of the particulates has been investigated by a number of groups. Measuring techniques involved the use of a highspeed camera<sup>64-65</sup>, a rotating velocity filter or shutter<sup>66</sup>, a rotating substrate device<sup>67</sup> or laser beam deflection measurements<sup>68</sup>. The reported velocity all fall within a narrow range of  $10^3$  cm/s –  $10^4$  cm/s. For the atoms and ionized species, the velocity is about 10-100 times higher in magnitude.

### **6) Deposition Parameters**

The effectiveness of utilizing the laser as an efficient energy source depends on **Perating** it under an optimal condition. This requires finding the right laser parameters **that** would yield optimal deposition condition for the growth of nanowires. Some of the **Parameters** that need to be taken into consideration are such factors as laser fluence,

ablation rate, deposition rate and target-to-substrate distance, etc. This section reviews some of the important laser parameters affecting the growth condition of the nanowires.

#### a) Laser Wavelength

The materials that are primarily used in this study are silicon and gold. As has been discussed in the previous section on semiconductor and metal laser ablation, the range of wavelength most appropriate for the ablation of these materials falls in the range 200-400 nm. The absorption coefficient is generally very high for these materials in this spectral region. The increase in the absorption coefficient means decrease in the beam penetration depth into the target materials, which consequently means potential decrease in the material size of the emitted particulates. This favorable condition of ablating thinner layers of the target not only translates into better cost-effectiveness of the target materials, but to better deposited films of the source material also. Theoretically, ablating the thinnest layer of the target would means expulsion of only atoms, instead of large size particulates. Another consequence of operating the laser at the short wavelength regions is the decrease in ablation fluence thresholds. This means the laser can be delivered at lower pulse energies while still retaining favorable results. But operating the laser below the wavelength of 200 nm, however, is not effective, since the strong absorption by the Schumann-Runge bands of molecular oxygen can make working in this part of the spectrum difficult. There are currently several lasers that **Operate** within the 200 nm to 400 nm ranges that have previously been used not only as a thin film deposition work, but also in the growth of nanowires. These include excimers lasers such as KrF<sup>29, 69</sup> and frequency multiplied pulsed Nd:YAG<sup>70</sup> solid lasers. These

lasers are capable of easily delivering the high-energy densities (>1 J/cm<sup>2</sup>), in relatively large areas (10 mm or larger).

#### b) Laser Beam Quality

A homogenous uniform laser output is required for good quality deposition work. Hot spots and deviations from uniformity should be avoided as much as possible. This is especially important when working with multi-component deposition targets. Poor beam quality can result in undesirable droplet formation<sup>71</sup>. The beam quality control is generally inherent to the laser device itself, so there isn't any parameter adjustment by the laser operator. The beam profile of the typical Lamda Physik KrF excimer laser is rectangular shape with the dimensions of 36x10mm. For estimating the focal length of the laser beam, a Gaussian beam profile is used. The focal length calculations will be shown in section 7.

### c) Laser Fluence

As has been discussed previously, one of the disadvantages of the PLD is in the **production** of micron-sized particulates and droplets from the exfoliational and **hydrodynamic** sputtering mechanisms. There are some existing methods available to **resolve** this problem such as mechanical particle filter usage or dual laser ablation **scheme**. Alternatively, some control can be exercise to resolve this problem by adjusting **the** laser output. To reduce the production of large-sized droplets for instance, the laser **Power** density or fluence on the target should be operating at the minimal achievable **energy** level given the beam spot size on the target. For the Lamda Physik LPX210i KrF



excimer laser, the 'minimal achievable' energy level is about 300 mJ, where below, the laser beam output is unstable, consequently resulting in the laser system shutting down altogether. Large fluence tends to generate many particulates of various sizes. It has been found from the ablation of silicon that high fluence also causes deeper penetration into the target material, forming deep crater depths and subsequently emitting large sized droplets from the target surface<sup>72</sup>. In another study, irradiance threshold of silicon was determined using the nanosecond laser ablation. For the laser ablation below the irradiance threshold, normal evaporation was seen, while above the irradiance threshold, both normal evaporation and explosive boiling was observed leading to appearance of large-sized droplets<sup>73</sup>. In the other hand, the reduction of the fluence results in a smaller amount of plume. The reduction of deposition rate means longer deposition time. To remedy this case, the substrate can be placed closer to the target. There has to be some compromise in these parameters to find the optimal condition.

### d) Reflectance

One of the factors that determine the effectiveness of material ablation is the reflectance and consequently the absorption coefficient of the given target material. The approximate reflectance calculation from the coupling of excimer laser energy with gold and silicon are shown below. For the gold target, the excimer laser-target is especially favorable since the reflectivity of metallic material in the UV range is generally lower than in longer wavelengths. The surface reflectivity, *R*, at the wavelength of the excimer laser is given by the expression for normal light incidence:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
 Eqn 8



where *n* and *k* are the real and imaginary parts of the refractive index. For gold for instance, n = 1.22 and k = 1.49, which gives R = 0.3. The absorption coefficient  $\alpha$ , is given by

$$\alpha = \frac{4\pi k}{\lambda}$$
 Eqn. 9

and the laser penetration depth  $\delta$  is defined as

$$\delta = \alpha^{-1}$$
 Eqn. 10

where  $\lambda$  is the wavelength. As an example, KrF laser with  $\lambda = 248$  nm,  $\alpha = 7 \times 10^7 \text{m}^{-1}$ , and  $\delta = 14$  nm for gold.

#### e) Target Morphology

The target surface has a great influence in the quality of the deposition, especially for the optical window-target-substrate configuration that has limited spatial movements. The surface of the target must be smooth as possible to reduce not only splashing, but also redirection of the ablated materials toward the laser window. The large sized microstructures have been shown to point toward the direction of the incoming laser beam due to shadowing effect<sup>74</sup>. The loss of ablated materials away from the substrate not only shortens the effective lifetime of the target materials, but more importantly, **causes** undesirable deposition in the optical window which seriously degrades the **transmission** of the laser beam. Suitable polishing compound can be used to clean the **Optical** window after deposition, but the transmission quality will degrade from the **ori**ginal condition with each polishing.

Some options are available to resolve the poor target surface problem. The first **Option** would be to polish the target prior to each run. This task is tedious, and can also

- ati **p**0! U. 12. 00 Pi T)( an 21 DC p ] hi N T d 2

- - Ī

adversely contaminate the target by imbedding undesirable impurities during the polishing process. Another option might be in using multiple target systems where targets are rotated. For experiments that require long deposition times, the "spent" targets can be rotated to a new one during the continuous run. The ultimate target surface conditioning however might be in the utilization of the molten state of the target. Previously, molten target of germanium was created by raising the temperature above its melting point, with a result in complete elimination of the particulates due to exfoliation and hydrodynamic mechanisms<sup>75</sup>. The only drawback to this method is the very limited availability of materials which satisfies the thermodynamic requirements, namely negligible evaporation rate at a given melting point temperature. Silicon however, is a potential candidate for implementation of this method. Given the melting temperature of 1410 °C, the vapor pressure is only  $5x10^{-4}$  Torr, which is too low to yield a sufficiently high evaporation rate.

Another consequence of the poor target surface is the entrapment of the vapor plume within the crater created by repeated laser pulse impingement in the same focal spot<sup>76</sup>. The crater depth will increase in depth *d* with each pulse, causing a local increase in the density of the vapor plume. The result is the decrease in the ablation rate due to the **absorption** of the laser beam in the vapor. The problem can be minimized in part by **rotating** the target during the ablation, but cannot be completely eliminated.

#### f) Evaporation Rate:

The evaporation rate for lasers at different pulse durations and repetition rates  $R_{dep}$  can be estimated by using the equations given below<sup>76</sup>. For low laser intensity used in this experiment, the evaporation rate  $R_{eva}$  is

$$R_{evp} \approx \frac{I}{\Omega x M}$$
 Eqn. 11

where I is the intensity of the laser pulse,  $\Omega$  is the heat of vaporization, and M is the molecular weight. For silicon, with pulse width of 25 ns,  $\Omega = 384$  KJ/mole, we have  $R_{evp} = 0.8 \times 10^{27}$  atoms/cm<sup>2</sup>-sec. The number of atoms evaporated per single pulse can be expressed as

$$N_{pulse} = R_{evap} S_{foc} \tau_{las}$$
 Eqn. 12

The deposition rate is proportional to the number of atoms evaporated per second

$$N\left[\frac{atoms}{s}\right] = N_{pulse}R_{dep} = R_{dep}R_{evap}S_{foc}\tau_{las}$$
 Eqn. 13

where  $\tau_{las}$  is the laser pulse duration,  $S_{foc}$  is the beam spot size. For example, using the values of low intensity,  $I \sim 1 \times 10^8$  W/cm<sup>2</sup>,  $R_{evap} \sim 10^{27}$  atoms/cm<sup>2</sup>-sec,  $S_{foc} = 0.03$  cm<sup>2</sup>, and  $\tau_{las} = 25$  ns for KrF excimer laser, we have,  $N_{pulse} \sim 1 \times 10^{17}$ /pulse. If the repetition rate of 10 Hz is used, then deposition rate is N ~  $1 \times 10^{18}$  atoms/sec.

#### g) Target-to-Substrate Distance and Chamber Pressure

Another factor that affects the deposition rate is the target-to-substrate distance  $R_0$ . By allowing the target-to-substrate distance  $R_0$  to be adjustable, optimized depositions can be obtained. For most applications,  $R_0$  falls in the range 3 to 15 cm, although longer distances (~20 cm) could be desirable to increase the surface area which is uniformly deposited. The minimal  $R_0$  is determined by the angle of incidence of the laser beam.

When the deposition takes place in the vacuum condition, the effect of target-tosubstrate distance is mainly reflected in the angular spread of the ejected flux. In general, the particulate trajectories are more divergent when a defocused laser beam is used, as opposed to emerging as a collimated jet for a tightly focused beam. However, when a PLD experiment is done at higher pressures, with an ambient gas, or at a substantially large target-to-substrate distance in which coalesce of particulate can take place, markedly different particulate appearance may occur, depending on the position of the substrate.

The specific effects of the target-to-substrate distance and ambient pressure are interrelated. Due to the increased collisions between the laser-produced plume and the background gas, the plume dimension decreases as the background gas pressure increases. When the target-to-substrate distance is much smaller than L, the length of the plume, there is no marked difference in particulate size or density. As the target-tosubstrate distance increases, the proportion of the smaller particulates decreases, and a few larger particulates appear, indicating a merge during flight. Once the substrate is located far beyond L, the adhesion to the substrate of ejected matter, including the particulates and atomic species is poor.

The estimation of the deposition rate with the target-to-substrate distance can be found by the following equation. The deposition rate  $N_{dep}$  is defined as:

$$N_{dep} = \frac{N}{2\pi R_0^2}$$
 atoms/cm<sup>2</sup>-sec Eqn. 14

where  $R_0$  is the distance between the target and the substrate. The deposited thickness  $d_{dep}$  per second by definition is

$$d_{dep} = \frac{N_{dep}}{n_{dep}}$$
 cm/sec Eqn. 15

where  $n_{dep}$  is the number density of the deposited film. Taking the distance between the substrate and the target to be about 8 cm, and assuming that the density of the deposited film is the same as the target of a given material, we have  $N_{dep} \sim 10^{16}$  atoms/cm<sup>2</sup>-sec, and  $d_{dep} \sim 10$  Å/sec.

#### h) Substrate Temperature

To produce good adhesion and/or epitaxy of the nanowires, the substrate must be heated to high temperature. This is due to the fact that in the process of nanowire growth, the diffusion distance of the vapor atoms on the substrate surface, and the desorption time of the vapor atoms from the substrate surface are strong functions of temperature. This is especially true for the nanowire growth dominated by the atoms diffusing on the substrate surface to the metal-semiconductor molten alloy droplet.

In general, the substrate temperature is primarily controlled by the sample heating units. For the ultra high vacuum system, this would be the radiant heater assembly, while electric resistive heating is provided to the furnace system. The temperature for both systems is monitored using the pyrometer and the embedded thermocouple near the substrate. For the system using the pulsed laser deposition scheme however, the temperature profile of the substrate is altered due to the impingement of the highly energetic atoms and ions. Furthermore, it has been shown that other experimental conditions can influence the substrate temperature such as diffusivity of the substrate material, molecular weight of the incident particles, latent heat of vapor-solid formation, deposition rate, and target-to-substrate spacing. The Table 5 summarizes the effect of various factors on the substrate temperature<sup>77</sup>.

Parameter	Temperature Rise		
Kinetic energy of the incident particles	Linear (Major factor)		
Diffusivity of the substrate material	Indirectly proportional		
Molecular weight of the incident particles	Indirectly proportional		
Pulse deposition rate	Linear		
Vapor-solid latent heat	Linear (Minor factor)		
Target-substrate spacing d	Approximately proportional to $1/d^2$		

 Table 5: Numerical calculations showing various factors affecting the substrate temperature in PLD

For instance, it has been shown by calculations that the carbon particles with kinetic energy of 100 eV impinging on the quartz substrate, the surface temperature can rise as high as 100 K<sup>77</sup>. For silicon which is used in this study, the effect of the impingement of the highly energetic particles on the substrate temperature is not as pronounced as in the case of quartz due to lower substrate diffusivity: the rise in temperature can be one order of magnitude smaller in silicon compared to the quartz. Nonetheless, the effect imposed by the slight alteration of temperature profile due to the particle impingement in the growth of nanowires is not known.

#### i) Off-axis PLD

Experiments with PLD systems are primarily done in an on-axis position, where the target and substrate are placed parallel to each other, however, the off-axis configuration can also be utilized where the target and substrate are configured perpendicular to each other. The UHV system used in this work can accommodate both on-axis and off-axis target-to-substrate configurations, while the furnace system in our lab is limited to the off-axis configuration. Previously, the off-axis configuration was used to grow very smooth thin films<sup>78</sup>. This configuration can be used to reduce the problem of droplets being deposited on the substrate. There are several disadvantages of off-axis PLD however: the deposition rate is reduced, and if the ambient gas is used, then the mobility of the adatoms on the substrate surface is lowered since the depositing species are thermalized from the collision with the ambient gas.

#### 7) Beam-Target Alignment

#### a) Focal Length Calculations

The focal length of a lens purchased from a given optics company is typically tabulated under a given wavelength. In order to compute the focal length at the desire wavelength, a thin lens formula needs to be used to make the conversion. For example, purchasing the lens with the tabulated wavelength of 589 nm, the thin lens formula for the plano-convex lens that was used in this study was

$$f_{\lambda} = f_{589} \frac{(n_{589} - 1)}{(n_{\lambda} - 1)}$$
 Eqn.16

where  $n_{589}$  is the index of refraction and  $f_{589}$  is the manufacturer's listed focal length both at the wavelength of 589 nm, while  $f_{\lambda}$  and  $n_{\lambda}$  are, respectively, the focal length and index of refraction at the desired wavelength. The index of refraction at 248 nm is 1.51, and the corresponding focal length is 36 inches.

#### b) Gaussian Beam Approximation

The shape of the laser beam in the KrF excimer laser used in this study is rectangular. To gain an approximation of the focus point of the beam at the desired target point, in conjunction with the type of optical lens being used, the beam profile is assumed to be circular. This assumption allows the usage of the Gaussian Beam Approximation equations to calculate the focus point, and compare to the focus point found by simple ray tracing method. For the Gaussian beam, the focus point can be found by using:

$$\frac{\lambda_0}{\pi w^2(z)} = \frac{1/z_{01}}{(1-z/f)^2 + (z/z_{01})^2}$$
Eqn. 17  
$$z_{01} = \frac{\pi w_{01}^2}{\lambda_0}$$
Eqn. 18

where

where z is the beam propagation distance, f is the focal length,  $w_{01}$  is the original beam width and  $\lambda_0$  is the wavelength. The "focal" spot size  $w_{02}$  can be found by

$$\frac{\lambda_0}{\pi w_{02}^2(z)} = \frac{1/z_{01}}{(1-z/f)^2 + (z/z_{01})^2}$$
 Eqn. 19

or

- Ŵ pr h ]] Ç ľ 0 ľ 0

$$w_{02} \cong \frac{2\lambda_0}{\pi} \frac{f}{2w_{01}}$$
 Eqn. 20

solving for z, we get the approximate distance of the focal point of the laser beam propagating through the optical lens.

The desired approximate impinging beam dimension on the target will be assumed to be about 0.35 inches. This means  $2w_{02} = 0.35$  inches = 8.89 x10<sup>-3</sup> m, or  $w_{02} = 0.175$ inches or  $4.45 \times 10^{-3}$  m. For KrF laser,  $\lambda_0 = 248$  nm. The focal length for the planar convex lens used in this study is f = 36 inches or f = 0.9144 m. Substituting these values into the equation, the distance z of the focal point is 31 and 71 inches. Two values are obtained since the equation is quadratic. The first value 31 inches corresponds to the value when the beam is converging to the focal point, while the second value corresponds to the value when the beam is diverging away from the focal point.

#### B) Vapor-Liquid-Solid (VLS) Growth Mechanism

#### 1) General Description

The vapor-liquid-solid or (VLS) growth mechanism is a process that utilizes a mediating metal catalyst to foster the growth of crystalline structures (typically in the shape of wires). The formation of a molten metal-semiconductor alloy serves as a preferential site for the wire growth on a substrate due to the high sticking coefficient of the molten alloy. This mechanism enables control over the diameter and the growth rate of the wires. The growth of silicon wires by the VLS growth mechanism was first described by Wagner, et al<sup>27</sup> and subsequently detailed by Givargizov<sup>28</sup>. Based on this growth mechanism, numerous whiskers and nanowires of various materials have been grown over the years.

Whiskers are filamentary crystals with a length and diameter typically around 1mm and 1  $\mu$ m, respectively, while nanowires consist of structures with diameters below 100 nm. Recently, the direct confirmation of the time evolving VLS growth mechanism has been made *in-situ* during the growth of germanium nanowires in a TEM system while using gold as the metal catalyst<sup>79</sup>. The different stages of metal-semiconductor alloying, nucleation and axial crystal growth of the nanowires have been positively identified. However, it must be pointed out that the presence of the molten alloy at the tip of the grown nanowire is not an absolute condition for validating the VLS growth mechanism. It has been observed that nanowires sometimes grew without the presence of any molten alloy at the tip despite the fact that a mediating metal catalyst was used in the growth process. One possibility of the absence of a molten alloy tip might be

instabilities developed from sudden stopping of the experiment, or at a sudden drop in temperature. Another possibility is the progressive evaporation of the molten alloy tip at high temperature during the growth<sup>80</sup>.

The basic VLS growth mechanism consists of three main steps: 1) mass transport of the nanowire growth species in the vapor phase, 2) dissolution of the nanowire growth species and subsequent diffusion through the liquid alloy phase and 3) the incorporation of the growth species into a crystal lattice at the liquid-solid interface. To illustrate the basic VLS growth mechanism, the growth of silicon nanowires using this method is shown below. Figure 12 depicts the axial growth of silicon nanowire on a given substrate, while Figure 13 shows the Au-Si binary phase diagram that is used to predict the silicon nanowire growth temperature and atomic percent weight of silicon concentration.







Figure 13: Binary phase diagram of Au-Si.

In Figure 12, the vapor feed is silicon, and the metal catalyst is gold. Initially, gold is deposited on the silicon substrate either as a thin film at room temperature or as gold deposits at the processing temperature. For the room temperature deposition of gold, the rise in temperature of the substrate causes the thin film to break apart into various agglomerates of gold-silicon molten alloy. Depending on the thickness of the gold thin film, the size of these molten alloys can be controlled to some degree. If the gold is deposited at the processing temperature, the molten alloys are immediately formed upon condensation of the gold particles on the silicon substrate. The dimension of the nanowires will be determined primarily by the initial dimensions of these droplets.

The next phase involves the mass transport of the vapor feed that will be needed for the axial growth of nanowires. The arriving silicon vapor impinges on the surface of the substrate and participates in diffusion and nucleation. At high substrate temperatures, the

arriving atoms can diffuse to the molten alloy locations where the sticking coefficient is large. Then further incorporation of the vapor feed, causes supersaturation of the alloy subsequently followed by axial nanowire growth. Using the binary phase diagram of Figure 13, five stages typifying the VLS mechanism can be identified in detail. This description is general, and the closer look at the interaction of gold and silicon at the molecular level will be discussed in the Au/Si(111) Eutectic Characteristic section below.

**Region (I):** The solid line at 373 °C denotes the Au-Si eutectic temperature. Below the eutectic temperature, gold and silicon coexist as solids.

**Region (II) Alloying**: With an increase in the weight percent concentration of silicon above the eutectic temperature, gold and silicon form an alloy and liquefy. The volume of the alloy droplet increases, while the alloy concentration crosses sequentially from left to right, a biphasic (solid gold and Au-Si liquid alloy) and a single phase region (liquid) Here, the newly formed liquid alloy serves as the energetically favored reaction site for the highly anisotropic growth of nanowire. Due to its higher sticking coefficient as compared to the solid surface, the liquid alloy is the preferential site for the absorption of adatoms.

**Region (III) Nucleation**: With further absorption of atoms from the vapor feed, the liquid alloy reaches supersaturation and silicon crystals begin to precipitate out of the molten alloy. This occurs in the binary phase diagram when the composition of the liquid alloy passes through the second liquidus line and enters the region where the

nanowire nucleation starts (Au-Si alloy liquid and silicon crystal). Experiments have verified that the nucleation indeed begins not the equilibrium liquidus line, but at the supersaturated alloy liquid state.<sup>79</sup>.

**Region (IV) Axial Growth**: The Au-Si binary phase diagram of Figure 13 indicates that at 800 °C, as the silicon concentration rises above 35 atomic %, the silicon will drop out as a solid while the gold alloy will remain a liquid. As the crystal grows, it lifts the liquid catalyst up and a nanowire crystal is formed. Longer vapor exposure time produces longer nanowires, while higher substrate temperature yields large diameter sized nanowires due to increased agglomeration of metal catalyst. Under optimal conditions, silicon has been found to preferentially grow in the [111] crystallographic direction.

Other possible metal catalysts can be used for silicon, such as: Si-Fe, Si-Ni and Si-Ga<sup>81</sup>. Examination of the binary Si-metal diagrams<sup>82</sup> show that like Si-Au, Si-Fe and Si-Ni exhibit eutectic Si-rich regions with silicon as the primary solid phase. But these binary pairs require transition temperatures in the high temperature region ~1000 °C. Unlike the previous ones, Si-Ga binary pair offers the fabrication of silicon nanowires at a much lower temperature below 400 °C. The resulting nanowires however, tend to be polycrystalline in structure.

#### 2) Metal Catalyst Requirements

Typical metal catalysts for the application of VLS growth mechanism are metals such as gold, silver, iron and nickel. In order to implement effective control over the growth of nanowires via VLS growth mechanism, following requirements must be observed in choosing the appropriate metal catalyst.

- 1. The metal catalyst must form a liquid solution with the crystalline material to be grown. The eutectic condition is predicted using the appropriate phase diagram.
- The solubility of the catalyst must be far less than one at the deposition temperature.
   Too high a solubility tends to lower the supersaturation, thus impeding the growth process.
- 3. Optimal growth temperature must be chosen, since the increase in the temperature, increases the solubility, which in turn affects the growth kinetics as noted in 2 above.
- 4. The catalyst must be chemically inert with the crystalline material to be grown. It should not form intermediate reaction products that would either contaminate the crystalline structure or hinder the growth process itself.
- 5. The liquid-solid interface must be well defined crystallographically, especially if the oriented nanowires are desired.

For this study silicon (111) substrates were used and gold was chosen as the mediating metal catalyst. The element is very commonly used for VLS mechanism since it forms low eutectics with silicon at the temperature of 373 °C, is chemically inert, and does not oxidizes.

#### 3) Modes of Crystal Growth

There are two modes of crystal growth from the vapor phase: physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD denotes the case where

the depositing species are derived from the transfer of vapor from the source after being physically dislodged by some means such as simple heating to high temperature. The process is typically characterized by such factors such as low vapor pressures, relatively high condensation coefficients, small adsorption coverages, large diffusion path, etc.

CVD in the other hand is based on the chemical reaction to produce the necessary species that condenses on the given surface. It is characterized by high vapor pressures, small condensation coefficients of species, high coverages, small diffusion path, etc. For the case of laser assisted growth of nanowires in this study, the crystal growth mode is PVD. However, due to such factors as high vapor pressure and small diffusion path, the crystal growth mode using PLD should resemble the CVD more so than other physical vapor deposition techniques.

#### 4) Growth Kinetics

In this section, the thermodynamics of the nanowire growth is considered. The growth kinetics of the nanowires grown by VLS growth mechanism and its dependence on the supersaturation is reviewed in detail. The relationship between the supersaturation and the growth behavior is determined by the Gibbs-Thompson effect. For the wires with the diameter greater than 1  $\mu$ m, this effect is no longer applicable. According to the Gibbs-Thompson effect, the decrease of supersaturation as a function of whisker diameter, *d*, can be given as

$$\Delta \mu = \Delta \mu_{\rm o} - 4\Omega \alpha_{\rm VS}/d \qquad \qquad \text{Eqn. 21}$$

where  $\Delta \mu$  is the effective difference between the chemical potentials of silicon in the nutrient (vapor or liquid) phase and in the whisker,  $\Delta \mu_0$  is the same difference at a plane

interface  $(d \to \infty)$ ,  $\alpha_{VS}$  is the specific free energy of the whisker surface and  $\Omega$  is the atomic volume of silicon.

The dependence of the growth rate V on supersaturation  $\Delta \mu/kT$  is unknown a priori and must be determined from experimental data. For the singular faces the dependence is not linear and in many cases is of *n*th power:

$$V \sim (\Delta \mu/kT)^n$$
 Eqn. 22

This proportionality can be written as an exact equation.

$$V = b(\Delta \mu/kT)^n$$
 Eqn. 23

where b is a coefficient independent of supersaturation. It is this independence that can be a criterion for the determination of n from experiments. Substituting we obtain

$$V^{1/n} = (\Delta \mu_o / kT) b^{1/n} - (4\Omega \alpha_{VS} / kT)^{1/n} (1/d)$$
 Eqn. 24

corresponding to a linear dependence of  $V^{1/n}$  versus 1/d.

There is evidence that the whiskers in the VLS process grow by a two-dimensional nucleation. One possible explanation is that the VLS whisker growth occurs by a two-dimensional nucleation with very low activation energy. It is known that the two-dimensional nucleation rate is

$$J \sim \exp(-\pi \Omega \kappa^2 / k Th \Delta \mu)$$
 Eqn. 25

where  $\kappa$  is the specific free edge energy of the nucleus and h its thickness. As will be shown below, a polycentric nucleation takes place here, therefore the whisker growth rate must be

$$V = h(v^2 J)^{1/3}$$
 Eqn. 26

where v is the linear rate of the growth steps. Hence

$$V = V_o \exp(-\pi \Omega \kappa^2 / 3k Th \Delta \mu)$$
 Eqn. 27

where  $V_o$  is a constant or slowly varying quantity. The intercept on the 1/d axis, from the extrapolation of the straight lines, determine the critical diameters  $d_o$ .

The information on the relationship of growth rate to the diameter of the nanowires has been obtained practically all from the CVD results, where the nanowires have been able to grow straight up from the given substrate. From these results, it has been shown that the growth rate grew in proportion to the diameter of the nanowire, i.e. thicker wires grew faster than the thinner wires<sup>28</sup>. Only one case in the literature reviewed for CVD deposition differed in this respect. Using much lower vapor pressure in a Molecular Beam Epitaxy (MBE) system, it has been found that growth rate did not depend on the diameter at all<sup>83</sup>. Based on this, one might hypothesize that the growth behavior of the nanowires depends on the vapor pressure. This seems to imply that PVD process which generally is characterized by very low vapor pressure should not show any relationship between the growth rate and the diameter. Furthermore then, despite the fact that PLD is a PVD process, it should show the growth dependence on the diameter due to its very high vapor pressure. The prerequisite to validating any claims regarding PLD-assisted nanowire growth however, would be to grow nanowires straight up from the substrate in order to accurately determine the growth rate. It is not surprising then that there seem to be lack of information on the growth behavior based not only on PVD but also on PLDassisted growth since the nanowires that have been produced thus far are basically grown entangled.

#### 5) Supersaturation in PLD

PLD has a high degree of supersaturation, depending on the laser fluence. High laser fluence results in a high degree of supersaturation and as a consequence, a small critical nucleus (practically one atom)<sup>84</sup>. At the extremely high deposition rates in PLD, the plasma flux supersaturation reaches the value of 10<sup>5</sup> J/mol<sup>85</sup> which is many orders of magnitude higher than in the conventional stationary deposition techniques. In PLD, the supersaturation m is given by the following equation

$$m = kT \ln \frac{R}{R_e}$$
 Eqn. 28

where k is the Boltzman constant, R is the actual deposition rate, and  $R_e$  is its equilibrium value at temperature T.

#### 6) Minimum Radius

The diameter of the nanowire is generally determined by the dimension of the molten alloy. This has been shown for the case of silicon nanowires<sup>86</sup>. Using the classical nucleation theory, the minimum diameter of the nanowire crystallization from the given molten alloy can be found. According to the classical nucleation theory, the critical nucleus radius for the solute precipitation from the dissolved solution under equilibrium condition is

$$r_{\min} = \frac{4\Omega\alpha}{RT\ln(\frac{C}{C_{\infty}})}$$
 Eqn. 29

where  $\Omega$  is the molar volume of the liquid,  $\alpha$  is the liquid-vapor interface free energy, *R* is the gas constant, *T* is the temperature *C* and  $C_{\infty}$  are the concentration of the solute in the alloy, and the equilibrium respectively. For the metal-Si binary system, the expected minimum radius of the silicon crystallization is expected to be greater than about  $0.2 \ \mu m^{28}$ . Thus for the formation of metal-Si droplet using the PLD on the silicon substrate, there is already a minimum dimension defined by the nucleation theory. For the growth of nm-sized silicon wires, this limitation would not be favorable. But this can be overcome in the PLD-assisted nanowire growth scheme if the molten alloy and consequently the nanowires are grown within the vapor and not on the substrate. Due to the inherently high supersaturation, the laser ablation of the metal catalyst produces radius defining nanocrystals with sizes that are much smaller than the minimum radius imposed by the theory. The consequence is the production of nanowires within the vapor as small as 3 nm<sup>14</sup>.

#### 7) Effect of Ambient Pressure

The effect of the ambient gas on the dimension of the nanowires is discussed in this section. In the presence of ambient gas, the size of the nanowires has been shown to be a function of the ambient pressure. For the growth of silicon nanowires, it has been found that the higher the ambient pressure, the larger the diameter of the silicon nanowires<sup>28, 87-</sup><sup>89</sup>. Previously, the relation between the diameter,  $d_m$ , of ultrafine particles and the ambient gas pressure p by the inertia fluid model was derived<sup>87</sup>.

$$d_m \propto p^n$$
  $n = 1/3$  Eqn. 30

which was obtained for silicon nanoparticles produced by laser ablation in constant pressure inert gas. A similar result was obtained by for the growth of Al and Cu ultrafine particles<sup>28</sup>.

#### C) Au/Si(111) Eutectic Characteristics

Gold forms a eutectic with silicon at the temperature of 373 °C. This means that gold and silicon dissolve to form a molten alloy. The previous section (section B) provided the basic description of the VLS growth mechanism, however to fully comprehend the nanowire growth via VLS growth mechanism, the interaction of gold and silicon atoms at the molecular level is needed. The existence of the mutual diffusion of gold and silicon within the eutectic region and the subsequent formation of the gold silicide deserves detailed analysis. This section reviews the gold and silicon eutectic behavior at various temperatures. Previously, extensive study on the eutectic behavior of gold particularly with Si(111) has been done by various authors over the years, and has been reviewed in detail<sup>90</sup>. The Au-Si eutectic has received considerable interest due to its applications in the semiconductor industry.

#### 1) Temperature Effect

#### a) Room Temperature Condensation

At room temperature, the structure of the deposited gold film on Si(111) is amorphous, growing in a quasi-continuous mode. It usually has an orientation parallel to the substrate<sup>91</sup>. Beyond the monolayer (one gold atom per silicon atom), intermixing occurs. The gold silicide forms, where the silicon atoms form metallic bonds with gold atoms as evident from the silicon LVV Auger peak at 92 eV broadening and splitting into a doublet at 90-95  $eV^{92-93}$ .
There is also a fraction of Au diffusion into silicon in the submonolayer range even at room temperature<sup>94</sup>. On top of the substrate one finds a sandwich structure: i) a diffuse and alloyed zone about 15 Å thickness, ii) an almost pure gold film, and iii) a silicon rich surface overlayer (composition close to that of the bulk Au-Si eutectic of ~20 % atomic silicon)<sup>90</sup>. An interesting observation is that this overlayer on top of the gold film has the same eutectic-like composition as the first layer formed on silicon upon room temperature condensation<sup>95</sup>. It is the accumulation of the silicon atoms on the overlayer that causes oxidation at its surface. The thickness of the oxidation layer resulting from the gold-eutectic is lower than the bare silicon substrate oxidation. This is interesting in how the silicon atoms are able to dislodge from the rigid crystal structure even at the room temperature and proceed with the low temperature diffusion.

The room temperature migration of silicon however, did not occur under all conditions. It was shown that the strength of the film adherence of the evaporated thin film to the substrate strongly affects the low temperature migration. For example, silicon wafers slightly oxidized in hot nitric acid show a weak adherence to the evaporated gold films and an anneal of such species at temperature as high as 300 °C induce little, if any, SiO<sub>2</sub> layer on top of the gold layers<sup>96</sup>. It was also shown in the same study that the crystallographic orientation of the silicon substrate has a marked influence on the rate of silicon accumulation. Oxide growth on gold films was shown to be more rapid with a {110} interface than with a {111}.

## b) Moderate Temperature (T < 400 °C) Condensation

It is this temperature range where the gold forms a eutectic with silicon. Either from the deposition of gold at moderate temperatures or annealing of room temperature deposited gold films, the gold deposits agglomerates into ball-like islands at a temperature range of room temperature and T < 400 °C. This was observed upon annealing of thick gold films (100-1000 Å)<sup>91</sup>. The underlying texture on the terrace is identified as the Si(111)6x6-Au surface reconstruction<sup>97-98</sup> as observed at temperature of T=225 °C. Under these conditions, the external amorphous gold silicide layer formed on the continuous gold film at room temperature can be crystallized producing several kinds of (Low Energy Electron Diffraction) LEED patterns. With an increase in the gold coverage, Stranski-Krastanov growth mode is observed with the initial 6x6 layer followed by three-dimensional gold islands on top.

## c) <u>High Temperature (T > 400 °C) Condensation</u>

At high temperature, a behavior quite different from the room temperature condensation occurs<sup>90</sup>. In analogy to the eutectic behavior at moderate temperature, the growth mechanism is Stranski-Krastanov mode. The AES condensation curves are markedly different from those obtained at room temperature; three sharp LEED patterns are successively observed along the two linear segments of the curves namely the Si(111) 5x1 –Au structure completed at  $\theta = 2/5$ , the Si(111)  $\sqrt{3} \times \sqrt{3} - R(30^\circ)$ -Au structure completed at the first break ( $\theta = 1$ ); this first monolayer further incorporates more gold atoms until  $\theta=1.5$  to form the Si(111)  $6 \times 6$ -Au structure which corresponds to a mixed reconstructed Au-Si layer, eutectic-like in composition. Table shows the corresponding parameters in the observed structure.

System	Phase	Half crystal energy(kcal/mol)	Vibration frequency of an atom in the phase
Au/Si(111)	Si(111) 5×1 Si(111) $\sqrt{3} \times \sqrt{3}$ Si(111) 6×6	85 82 76	$   \begin{array}{r}     1.7 \times 10^{13} \\     1.5 \times 10^{13} \\     9.0 \times 10^{12}   \end{array} $

Table 6: Construction of different phases<sup>90</sup>

In summary, several key points can be pointed out from the review.

- i) Interfaces evolve from a metastable room temperature state to a stable interface structure beyond T = 400 °C.
- ii) In this metastable state, a tendency to intermixing is present.
- iii) The growth of the stable interface structure at high temperatures follows a Stranski-

Krastanov mode.

## 2) Gold Silicide

Several different structures of gold silicide seem to exist depending on various factors such as preparation methods, temperature, etc. For instance, quenching alone produces an amorphous phase<sup>98</sup> while annealing produces a variety of crystalline phases. A few types of crystalline phase of gold silicide previously been reported include  $\lambda$ -brass type structure with approximate composition of Au<sub>31</sub>Si<sub>8</sub><sup>99</sup>, two fcc structures with differing lattice constants<sup>100</sup>, and an orthorhombic unit cell having a composition of Au<sub>3</sub>Si<sup>101</sup>.

The rate of formation of gold silicide depends on several factors such as deposition temperature, film thickness, annealing temperature, substrate purity, etc. For instance, it was observed that the purity of the substrate had a strong influence on the gold silicide formation rate. Except for the unetched silicon surface covered with heavy layer of oxide, the diffusion of silicon was determined to be possible at other conditions of surface purity<sup>91</sup>. The silicide surface layer thus begins to grow at room temperature, but it does not seem to grow indefinitely. Based on the result of depositing 100 to 1000 Å of thin gold film on silicon substrate, the maximum thickness of the gold silicide of 30 Å is reached at high temperature.

## 3) Diffusion-induced Crystallization

There is an interesting phenomenon that occurs during the process of gold silicide formation, namely the formation of enhanced silicon crystal quality due to diffusion of silicon in the gold layer. Previously, the growth of enhanced silicon crystals has been observed from the diffusion of polysilicon through the gold layer at various low temperatures in the range of 300-450  $^{\circ}C^{102-103}$ . It has been shown via SEM and TEM images that the large grain size silicon crystal grew at the expense of the smaller grain sized silicon layer with the gold layer providing the fast diffusion path. The diffusioninduced crystallization of silicon did not exhibit any gold trapped within the crystal structure.

#### D) Si Overlayer-Assisted Growth of Nanowires

This section describes the hypothesis that was applied in the growth of silicon wires in the UHV system. It is based on the VLS growth mechanism, but modified by depositing additional layer of silicon on top of the gold thin film at the room temperature.

The diffusion-induced crystallization of silicon in a gold layer was reviewed in previous sections, with the observation of enhanced crystal quality of silicon. It was stated that the large grained sized crystals grew at the expense of the smaller sized grains. One key observation in this growth process is the preference of the gold layer in dissolving smaller-sized grains over the large-sized grains of silicon since smaller sized grains are more disordered. Additionally, depending on the layer configuration of gold and silicon, the diffusion-induced crystallization suggests the existence of direction of gold diffusion and consequently silicon crystallization.

With the termination of the diffusion process, the usual silicon substrate-gold layer configuration results in the silicon being at the top of the gold layer. From the nanowire growth standpoint using the VLS growth mechanism with the gold on top of the silicon, diffusion-induced crystallization is actually the opposite process and it is expected that the gold will dissolve some of the silicon substrate instead of growing up from the substrate. Thus if some method is implemented to mimic the VLS growth mechanism in the diffusion-induced crystallization then the conditions for the nanowire growth could potentially be improved. One possible method to accomplish this might be in the deposition of additional overlayer of silicon on top of the gold thin film at low temperatures (such as room temperature). The advantageous features of having a silicon

overlayer then stems from the possibility of not only providing a better eutectic geometry in sandwiching gold with Si(111) substrate, but also in altering the diffusion behavior of gold into the silicon crystal structure to the state beneficial to the wire growth at a later stage. It is speculated that the silicon layer deposited at the room temperature would be in an amorphous state, and the diffusion of gold would be preferred through this amorphous silicon instead of diffusion into the single Si(111) crystal substrate as temperature is increased. In other words, the gold would rapidly diffuse through the silicon overlayer, thus moving silicon atoms from the overlayer toward the Si(111) substrate. This would preserve the substrate crystallinity, and place the gold-silicon alloy, already involved in the VLS growth mechanism, on the top of silicon source for the subsequent axial growth of nanowire would then be provided by the silicon target ablating by the laser at high processing temperature.

#### E) Oxide-Assisted (OA) Growth of Nanowires

## 1) Background

Oxide-Assisted, or OA growth mechanism is a different crystal growth method that has emerged rather recently in the growth endeavor of nanowires. Compared to the VLS growth mechanism, the level of understanding of its growth mechanism still has not yet reached its mature stage. Based on the successful fabrication of various types of nanowires recently, better insight has been gained in its growth mechanism. The following section will briefly describe the growth mechanism. The review in this growth mechanism is pertinent to understanding the role of oxygen in the growth of nanowires.

## 2) Methods and Nanowires

Nanowires utilizing this method have been grown primarily either by thermal evaporation or laser ablation. The first case is done by evaporating an oxygen containing powder under an ambient gas inside a high temperature furnace. The type of nanowires in this category that have been grown includes Si nanowires using SiO  $^{31-32,104-105}$ , GaAs nanowires using Ga<sub>2</sub>O<sub>3</sub>  $^{106}$ , Ge nanowires using GeO<sup>107</sup>, and carbon nanowires using CO<sup>108</sup>. For the latter case of using the laser ablation, silicon nanowires have been grown primarily by ablating SiO<sup>30</sup> or silicon powder target<sup>29</sup>.

#### 3) Growth Mechanism

The key feature to OA growth mechanism seems to be the production and reduction of volatile oxide in the intermediate chemical step. In this section, the growth mechanism as applied in the growth of silicon nanowires by laser ablation of Si and SiO<sub>2</sub> powder target is described<sup>30</sup>. According to this model, the nucleation step of silicon nanowires is assumed to occur via the chemical reaction between Si and SiO<sub>2</sub> induced by the high power laser consequently producing the intermediate product SiO as shown below:

$$Si + SiO_2 = 2SiO$$

This "volatile" SiO vapor would then be transported to the substrate by the flowing ambient gas such as argon inside the furnace. On the substrate, SiO would decompose into nanoparticles with Si as the core and  $SiO_2$  as the outer layer according to the following chemical reaction:

$$2SiO = Si + SiO_2$$

These nanoparticles nucleate the Si nanowires. The growth step is assumed to involve the following factors. The  $Si_xO_y$  layer at the tip of the nanowires forms a semi-liquid, which acts as a sink to absorb more SiO. The  $SiO_2$  formed on the outer wall, functions to restrict the sideway growth of nanowires. One notable mention is that this growth mechanism has yet to produce nanowires that grow straight up from the substrate.

### **CHAPTER II: EXPERIMENTAL SETUP**

# A) Experimental Systems

Two types of growth systems have been assembled and utilized in this study of silicon nanowire growth: an ultra high vacuum (UHV) chamber and a high temperature tube furnace based chamber capable of higher pressure depositions (up to atmospheric pressure). The usage of the two different growth systems has allow significant flexibility in exploring wide range of pressure regimes from  $1 \times 10^{-9}$  to about 500 Torr. The differences in these systems are summarized below in Table 7.

Table:	7 E	xperimental	systems

	UHV System	Furnace System
Heating Method	Radiant Heating	Resistive Heating
Maximum Achievable Temperature (°C)	~930	~1100 (pyrometer)
Chamber Structure	Stainless Steel	Ceramic
Lowest Vacuum (Torr)	10 <sup>-9</sup>	10 <sup>-1</sup>
Target/Substrate	Rotatable	Fixed
Target-Substrate Orientation	On/Off- Axis	Off-Axis

### B) Ultra High Vacuum (UHV) Chamber System

This section describes the UHV system and its components. The specifications for each component and the procedures for operating each component are discussed in Appendix A, B, and D. The general diagram and photograph of the UHV system are shown in Figures 15 and 16, respectively. The custom designed 18" diameter stainlesssteel vacuum chamber fabricated by Thermionics houses the substrate and target assembly. A fused silica optical window provides entry of the laser beam energy into the UHV condition. The vacuum level inside the vacuum chamber is provided by the combination of Tri-Scroll 330 roughing and V551 turbo pumps, both from Varian. The vacuum levels are measured using a Convectorr thermocouple detector and a nude Bayard-Alpert ionization gauge. An RNN Rotary Seal manipulator from Thermionics provides azimuthal rotation of the substrate assembly while maintaining the vacuum condition. In order to provide UHV through the RNN Rotary Seal, a small ion pump is utilized for differential pumping. The substrate holder is designed to hold 2" wafer, and is capable of axially rotating the wafer by a motorized control. The substrate is heated using two quartz halogen lamps as radiant heaters which are supplied power by a SPS Series Power Supply from Thermionics. The target holder is capable of holding up to six different targets with dimensions of 1" in diameter which have motorized rotation for use during the ablation process. The target manipulator allows the loading/unloading of the targets inside the chamber while maintaining the UHV main chamber vacuum condition through a load-lock entry chamber. A chiller is used to provide the necessary cooling of the substrate and target assemblies. The circulating pressure is about 55 psi at the temperature below 20 °C.



Figure 14: Top-view general diagram of the UHV system.



Figure 15: Side-view photograph of the UHV system.

## C) Furnace System

The general diagram and the photograph of the furnace system are shown in Figures 16 and 17, respectively. The outer diameter of the ceramic furnace is 10 inches while the inner diameter is 4 inches. The slightly oblong Mullite tube housing the substrate and the target has an average diameter of about 3.75 inches, and extends about 3 inches on both sides of the ceramic housing. The ends of the Mullite tube are enclosed by the watercooled aluminum end caps. The vacuum is provided by the Tri-Scroll roughing pump. ConvecTorr vacuum gauge from Varian is used to measure the pressure inside the tube. To measure the temperature, a K-type thermocouple is inserted inside the tube, and is connected to a PID fuzzy logic based controller. The target and substrates are placed inside the tube near the center of the furnace, supported by the target-substrate ceramic assembly. Both are glued onto the assembly using the alumina cement. The dimension of the target-substrate assembly is about 8 inches long and 3 inches high. The laser beam passes into the furnace through the fused silica optical window of 1.4 inches in diameter. Ar gas inlet is provided near the optical window. The pressure inside the furnace is controlled by the valve located near the rear of the furnace.



Figure 16: Side-view general diagram of the furnace system.



Figure 17: Photograph of the furnace system.

## **D)** Laser/Optics System

The laser employed for the deposition scheme for both growth systems is the Lambda Physik LPX 210i KrF excimer laser. Detailed description of its specification is discussed in Appendix A, and the operating procedure is discussed in Appendix D. The laser operates at the wavelength of 248 nm. The energy of the pulse can be varied from 0~1000mJ, with pulse duration of 25 ns, and an average power of 65 W. The repeated testing of the laser showed that the laser energy tend to show instability below about 300 mJ. A water line (tap water) has been connected to the laser to provide the necessary coolant at the rate of 1 liter/min. Coupling of the energy from the laser to the target is achieved by placing the appropriate UV-graded fused silica optical elements between the output port of the laser and the deposition systems. Focusing of the laser beam is achieved via a plano-convex optical lens of 2 inches in diameter. For the furnace system, a UV-graded mirror was additionally placed in front of the lens to redirect the laser beam into the furnace system.

## **E) Target and Substrate Preparations**

Circular 2.54 cm x 0.3176 cm 99.999-99.9999% pure gold and silicon targets were used. For the substrates, the ultra high vacuum chamber experiments used 2 inch diameter <111> intrinsic and doped silicon wafers while the furnace system used smaller sized substrates with same parameters. Due to the crystal orientation, the resulting nanowire is expected to grow perpendicular to the substrate surface. Two types of scanning electron microscopes (SEMs) were used to observe the surface of the substrate after the growth process. For growth with high aspect ration of nanowires, namely very long nanowires, Transmission Electron Microscope (TEM) was used to verify the crystal orientation of the grown nanowires.

Prior to loading the substrate into the vacuum chamber and furnace system, the silicon substrates were cleaned by treating with acetone, then methanol, and followed by rinsing with deionized water. To remove the native oxides, the substrates were soaked in the buffered hydrofluoric (HF) solution for about 5 minutes. The removal rate of the oxides was approximately 1000 Å/min based on known rates for the HF:H<sub>2</sub>O mixture used.

### F) Growth Procedures

## 1) UHV System

The steps to growing the Si wires via the VLS growth mechanism in the vacuum chamber system included the following. Prior to the deposition, a circular 5.04 cm diameter by 250  $\mu$ m thick p-type Si(111) substrate (1-20  $\Omega$ -cm) was cleaned in acetone and methanol, followed by a deionized water rinse. The native oxide was removed with a chemical etching using a buffered hydrofluoric acid (HF) solution. Using the load lock and sample transfer arm, the Si substrate was subsequently placed into the chamber having a base pressure of  $< 10^{-9}$  Torr. A Lambda Physik LPX 210i KrF excimer laser beam operating at wavelength of 248 nm and 25 ns was used to ablate all the targets at 500 mJ and 5Hz. During the ablation, the targets were rotated at 10 degrees/sec. The distance from the substrate to the target was 8~9 cm. The size of the rectangular laser beam spot on the targets was 1 mm x 3 mm. The Au was first deposited onto the rotating Si substrate by ablating the Au target for 1 minute followed immediately by 30 seconds of Si deposition both at room temperature. The temperature of the Si substrate was then slowly raised in the 3-4 hours ramp time to 900 °C as indicated by the PID controller using the radiant heater. The long ramp time would provide good eutectic and control over the substrate cracking. Using the pyrometer, the temperature at the center of the substrate was found to be 850 °C, while further drop in the temperature as much as 50 °C was found at the edges. The emissivity of Si used for pyrometer measurement was 0.6. The Si was then ablated for 1 hr and 20 minutes. JEOL scanning electron microscope (SEM) operating at 20 KV was used to obtain the images of the Si wires. Energy

Dispersive X-ray Spectroscopy (EDS) was used to analyze and confirm the Au-mediated VLS growth mechanism.

# 2) Furnace System

The steps to growing the silicon nanowires via VLS growth mechanism in the furnace system are described next. The same type of silicon wafers and cleaning procedure that was used for the UHV chamber system were utilized here to prepare the silicon wafers. The cleaned wafer was then coated with gold film with thickness of about 5 nm-112 nm using the EMSCOPE SC 500 gold sputter coater. For the growth of silicon nanowires by annealing at high temperature, the following procedure was used. The pieces of Si(111) substrate were then adhesively bonded to an alumina substrate holder and placed near the center of the furnace. The initial vacuum was about  $1.5 \times 10^{-1}$  Torr. The furnace was then purged with 200 sccm of high purity (99.999%) argon gas for about 30 minutes at room temperature. The temperature was then subsequently raised to  $1100 \,^{\circ}$ C. By adjusting the value between the vacuum pump and the chamber, a pressure range of  $1.5 \ge 10^{-1}$  to 400 Torr was investigated. The argon gas passed through the mullite tube at the flow rate of 200 sccm. The substrate was allowed to cool before removing it from the furnace. To measure the temperature, silicon target was glued onto the substrate-target assembly. Using the pyrometer, the temperature at the center of the furnace was found to be about 1070 °C. The emissivity of silicon used for pyrometer measurement was 0.6. The temperature measured by the thermocouple type K also gave similar results. JEOL scanning electron microscope (SEM) operating at 20 KV was used to obtain the images of the silicon nanowires. Energy Dispersive X-ray Spectroscopy

(EDS) was used to analyze and confirm the Au-mediated VLS growth mechanism.

Images in this dissertation are presented in color.

### **CHAPTER III: DEPOSITIONS IN UHV CHAMBER SYSTEM**

#### **A) Deposition Procedures**

This chapter discusses the results from depositing gold and silicon using the excimer laser. It describes the series of research endeavors to grow the silicon nanowires using the gold as the metal catalyst in the VLS growth mechanism.

### **B)** Results

## 1) Gold Only Depositions

To correlate the amount of gold deposits with the number of laser shots, a series of gold depositions were carried out by varying the pulse energy and the number of shots. Since the diameter of the nanowires approximately corresponds to the diameter of the gold droplets, the results would give some information on the control aspect of the nanowire growth. The energy of the laser was varied between 100 mJ to about 500 mJ, while the number of pulses was varied between a single shot to as many as 900 shots. The distance from the target to substrate was about 8~9 cm. The gold was deposited onto the Si(111) substrate at room temperature, and the samples were annealed at an elevated temperature by briefly raising the substrate temperature to 600 °C, followed immediately with the lowering to room temperature. One of the samples was examined without subjecting to annealing. All the samples were examined and photographed using the JEOL Scanning Electron Microscope (SEM) and EDS (Energy Dispersive X-Ray

Spectroscopy) was concurrently carried out to determine the elements present in the sample.

#### a) Gold Depositions without Annealing

In Figure 18 shows the SEM image of a gold deposited silicon substrate with the deposition done at room temperature. A total of 60 laser pulses at energy of 500 mJ against the gold target were used, and this sample was not subjected to annealing. The scale bar is 7.5 µm. The image shows two bright balls against the smooth grayish background. The line joining the two round balls is an artifact from the SEM measurement system. The EDS analysis in Figure 19 shows the presence of primarily gold throughout the entire region including the bright round balls. The presence of some silicon on the substrate is also observed. The bright balls of gold-rich regions could have been caused by. The SEM image and the EDS indicate the presence of thin film deposit of gold on the entire surface area of the silicon substrate.



Figure 18: SEM image of the un-annealed gold deposited Si(111) substrate.

The traces of iron in the sample were also detected indicating either the presence of impurity content inside the chamber or the introduction of this impurity during sample handling. Typical impurities found in stainless chambers and sample tweezers include Fe, Ni, and Cr. The peak at the left side of the EDS at zero energy is due to the artifact from the usage of the SEM.



Figure 19: EDS compositional analysis of the deposited gold on Si(111).

#### b) Gold Depositions with Annealing (60 shots)

The SEM image in the Figure 20 shows the gold deposits with 60 shots at the pulse energy of 500 mJ and annealed at the temperature of 600 °C. The SEM image show the formation of islands of gold agglomerate from the room temperature thin film deposit due to the differences in free surface energy at higher temperature. The free surface energy of silicon and gold is  $1.2 \text{ J/m}^2$  and  $1.6 \text{ J/m}^2$ , respectively. The scale bar is  $13.7 \mu$ m. The EDS analysis as shown in Figure 21 shows the presence of gold and silicon in the bright regions, while the EDS analysis as shown in Figure 22 indicates the presence

of primarily silicon in the dark background. The histogram in Figure 23 shows the size distribution of the gold agglomerates. The average size of the gold agglomerate seems to fall in the range 250-500 nm with a density of about  $0.25/\mu m^2$ . Some small as 100 nm were also found in the image.



Figure 20: 60 shots of gold deposited on a Si(111) substrate and annealed to 600 °C.



Figure 21: EDS analysis showing the presence of gold and silicon.



Figure 22: EDS analysis showing only silicon.

#### Total Sample Size: 78



Figure 23: Histogram showing the size distribution of the gold agglomerations.

## c) Gold Depositions with Annealing (900 shots)

The number of pulses for gold ablation was increased from 60 shots to 900 shots. The pulse energy was the same as before at 500 mJ. The gold deposited substrate was then annealed at 600 °C as before, and the results were observed under the SEM as shown in Figure 24 with a scale bar of 50  $\mu$ m. The image clearly shows the differences in the gold deposit coverage on the silicon substrate with the number of pulses. The increase in the number of pulses corresponded to larger gold agglomerate sizes as expected since more ablated materials would be deposited on the substrate. The gold

agglomerates seem irregularly shaped, but upon closer examination, they triangular and trapezoidal shapes, indicative of the Si(111) substrate underneath the gold deposit. The histogram showing the size distribution of the gold agglomerates is shown in Figure 25. The average size of the gold agglomerate for the case of 900 shots is much larger than the 60 shots case with the value of about 3  $\mu$ m and a lower density of about 0.1/ $\mu$ m<sup>2</sup>. Some small gold agglomerates on the order of 500 nm were also found in the image. In deriving the average size distribution, the gold agglomerates were assumed as round during the measurement. The EDS analysis was done, and showed similar results as before.



Figure 24: 900 shots of gold deposited on Si(111) and subsequently annealed to 600 °C.



Figure 25: Histogram showing the size distribution of the gold agglomerates.

## d) Gold Depositions at Lower Pulse Energy (100-150mJ)

Gold and silicon depositions at varying pulse energy levels were explored. The excimer laser is not able to sustain stable operation at low pulse energies below about 300 mJ. At the lowest repetition rate of 1 Hz, the laser device shuts down completely. Operating at higher repetition rate greater than 5 Hz seem to prevent the laser from shutting down, however the integrity of the laser beam is questionable. Despite the beam stability issue, the comparisons between the differences in the gold deposits at different pulse energy were done. The following SEM image in Figure 26 shows the result of the annealed gold deposit at different pulse energy of 100-150 mJ. The number of pulses was 900.

With the lowering of the pulse energy, the differences in the size of the gold agglomerate as well as the density are quite evident. The shape of the gold "dots" is round, while varying in dimension. The non-uniformity in the gold deposit is also apparent where the gold dots on the left side are much larger. This feature might be attributed to the unstable laser beam at low pulse energy as discussed above. The Figure 27 shows the size distribution of the gold dots. The average gold dot size of the bigger gold dots on the left side of the image are approximately 2.5  $\mu$ m, while the smaller gold dots had an average size of about 300-500 nm. Some were as large as 4  $\mu$ m in diameter, while some as small as 400 nm were found throughout the image. The EDS showed the similar results as above, with the presence of gold in the sample.



Figure 26: 900 shots of gold at 100-150 mJ.



Figure 27: Histogram showing the size distribution of gold dots in Figure 26.

The Table 8 summarizes the results of gold deposits with number of pulses and pulse

energy.

Pulse Energy (mJ)	A(B,C) <sup>*</sup> 60 shots (µm)	A(B,C) 900 shots (μm)
100-150		1.59 (0.4-3.8)
500	0.457 (0.1,0.8)	2.27 (0.5-3.9)

Table 8: Size Distributions at various gold deposition conditions

\* A(B,C): A: average diameter, B: smallest diameter, C: largest diameter

## 2) Gold and Silicon Depositions

The following section describes the results from variation of gold and silicon deposits. It is a compilation of a series of research endeavors in growing silicon nanowires via the VLS growth mechanism. The gold deposits were varied from 5 to 900 shots, while the silicon deposits were varied from 900 to 54,000 shots. The range of pulse energy used was 300-500 mJ. The distance from substrate to target was about 8~9 cm. The deposition of silicon took place at temperatures of 850-910 °C. During the SEM analysis, the substrate was observed from top as well as from tilted view at an angle of about 15~20 degrees to look for any evidence of nanowire growth. Size distribution analysis on the obtained results was not performed since it would not offer any additional information.

# a) Gold (5 shots), Silicon (900 shots)

The number of pulses for the gold deposits was 5 shots, while 900 shots were used for the silicon ablations. The SEM images in Figure 28 below shows the result. The image in (a) shows the result at the magnification of 1000X, and the image in (b) shows the result at the magnification of 5000X. The SEM image in a) show numerous dots, and what appeared to be round "smeared" regions. At higher magnification as shown in image (b), the "smeared" regions seem to be occupied by dots themselves, while being enclosed by brighter dots. The EDS analysis only revealed the presence of silicon in the deposits. It is not clear why there were differences in the brightness of these dots. Due to the absence of gold in the EDS, the "smeared" regions might indicate the initial stages of silicon thin film growth.



(a)

(b)

Figure 28: SEM Images of Au-Si growth using an excimer laser source energy of 500mJ and 5 laser shots of the Au target and 900 shots of Si: a) image at 1000X magnification, b) image at 5000X magnification.

#### b) Gold (900 shots), Silicon (900 shots)

The number of pulses for the gold depositions was increased from 5 to 900 shots with an equal number of pulses for the silicon deposits, and a pulse energy of 500 mJ for both cases. The resulting SEM images are shown in Figure 29. In Figure 29(a), various round, bright agglomerates are shown. The EDS analysis shown in Figure 30 indicates the presence of gold and silicon in the large-sized agglomerates. The shadowing of the large sized agglomerates seems to show the collection of nearby gold on the silicon substrate. In Figure 29(b), the result from magnifying the grayish regions between the large-sized agglomerates is shown. The EDS analysis as shown in Figure 31 on the smaller sized "dots" with reduced brightness indicates the presence of only silicon.



(a)

(b)

Figure 29: SEM Images of Au-Si growth at 500mJ and 900 shots for both Au and Si. a) image at 700X, b) image at 8000X.



Figure 30: EDS analysis showing gold and silicon.



Figure 31: EDS analysis showing only silicon.

#### c) Gold (900 shots), Silicon (6000 shots)

The number of pulses for the silicon was increased from 900 to 6000 shots, while maintaining the number of pulses for gold at 900 shots. The pulse energy was also the same as before at 500 mJ. The SEM image in Figure 32(a) below shows the results from the increase in the number of pulses for the silicon deposits. The result from the previous silicon deposits with 900 shots is also shown in Figure 32(b) for comparison. The obvious effect of the increase in the number of pulses is evident, with large, irregularly-shaped structures shown in the image in Figure 32(b). The EDS analysis showed that some of the bigger irregular-sized structures were not only gold, but there were also significant presence of impurities such as Fe and Ni. The small and round structures showed did not indicate the presence of gold.



(a)

(b)

Figure 32: SEM images of Au-Si Deposits at 500mJ and 900 shots of gold but at different silicon deposition shots a) image at 6000 shots, b) image at 900 shots.

#### d) Various Deposition Conditions

The following compilation of SEM images in Figure 33 show some of the typical Si-Au deposition results that were obtained by varying not only the gold and silicon content, but also the energy of the pulse. The image in Figure 33 (a) shows irregularlyshaped gold rich agglomerates at the edge of pits on the silicon substrate. The origin of these pits is not clear. One possible explanation might be due to the consumption of silicon substrate during the eutectic with gold, and its subsequent movement about the silicon surface due to high temperature. The energetic plume is known to cause sputtering, but the presence of the gold-rich agglomerate at the edge of pits seems to eliminate this possibility. The SEM image in Figure 33(b) is the most typical result from depositing silicon on the gold deposited silicon substrate at the elevated temperature. The image shows the transitions from a round gold-rich droplet to subsequent lateral crystallization of silicon at its tail. Despite the image seemingly showing a common vector, the direction of the gold-rich round ball is generally much more random. The reason for their occurrences is not clear, but it may be caused by the non-uniform temperature profile created by the radiant heater. The rotation of the substrate during the high temperature deposition is done to improve the uniformity of the temperature profile, but the shape of the radiant heater is rectangular, and its limited dimension does not heat the entire substrate surface. Consequently, there is a temperature variation across the substrate. Also, the rotation rate of the substrate heating assembly is likely to cause additional fluctuation in the temperature profile. For the non-rotating substrate, the fluctuation in temperature profile across the substrate would be the greatest. Based on these conditions, the most stable temperature region is probably at the center and at the edge of the substrate.

The SEM image in Figure 33 (c) shows the close-up view of the silicon substrate with the gold-rich balls seemingly embedded. The surface of the silicon substrate is rough, but unlike the previous image in Figure 33 (a), there are some rectangular-shaped pits. The image seems to show the transferring of materials onto the gold-rich balls. The image in Figure 33 (d) shows the tilted-view of the silicon substrate after the gold and silicon depositions. There are various "hill-like" structures popping out above the substrate. The EDS analysis on these structures only showed silicon. These are not the evidence of nanowire growth however. The reasons being unknown, these features seem to show up quiet commonly. One possible explanation is that these are the remnants of

droplets that have been ablated from the silicon target. In general however, the droplets splashing onto the silicon substrate are flatter and occupy larger surface area than these, and there is no evidence of axial growth, as these seem to do.



a) Au-900, Si-6000 (500mJ)

b) Au-300, Si-6000 (500mJ)



c) Au-900, Si-3000 (500mJ)

d) Au-900 (500 mJ), Si-54,000 (200 mJ)

Figure 33: SEM images at various deposition conditions.

# 3) Ge Depositions

This section describes the usage of germanium in place of silicon to grow germanium nanowires via VLS growth mechanism. It is not clear why silicon nanowires were not observed. One possible explanation is that the temperature of the substrate was not high enough. In Chapter I, the influence of temperature in the growth behavior of nanowire was discussed. Such factors as adatom mobility and the supersaturation are critically dependent on the temperature. The melting point of silicon is about 1400 °C. In order to observe greater influence of temperature, two experimental options are available: 1) increase the temperature of the substrate even further, and 2) use different material with lower melting point. The first option calls for the incorporation of entirely different heating system, since the maximum achievable temperature based on the existing radiant heater is about 930 °C. Based on time and cost-effectiveness, the second option presents a better choice. The requirements are that the material in question should adhere to same eutectic and solubility conditions as silicon with gold.

The melting point of germanium is 936 °C, and its melting point is lower than silicon by about 500 °C. It has a very similar eutectic temperature and behavior like silicon. Based on the existing radiant heater system, the usage of germanium should shed better understanding in the role of temperature on the growth behavior of nanowires.

The procedure for depositing germanium was the same as for the silicon case. The gold was first deposited onto the germanium substrate at the room temperature. The temperature of the substrate was then varied from 500 °C to about 800 °C. The energy of the pulse was kept at 500 mJ for all three cases, but the repetition rate was varied
depending on the number of pulses desired. The resulting SEM images at various temperatures and deposit conditions are shown below.

a) 500 °C

The SEM image of the Au-Ge deposition at the temperature of about 500 °C is shown in the Figure 34 below. The histogram showing the size distribution of the Au-Ge dots is shown in Figure 35. The number of pulses used for this experiment was 450 and 6000 for gold and germanium, respectively at the pulse energy of 500 mJ. The repetition rate of gold deposition was 5 Hz, while 10 Hz was used for the germanium deposition.



Figure 34: SEM image of the Au-Ge deposits at Au (450), Ge (6000), 500 mJ, 500 °C.

The SEM image as seen from the top did not show any evidence of nanowire growth. The image only showed germanium-rich dots scattered about the germanium substrate. The substrate was also viewed from the angled position, but any evidence of axial growth was not observed. The average diameter of the Au-Ge dots was about 500 nm, with some as small as 140 nm and some as large as 1.1  $\mu$ m were found. The density of the Au-Ge dots was about 0.26/ $\mu$ m<sup>2</sup>.



Figure 35: Histogram showing the size distribution of Au-Ge dots.

b) 700 °C

The SEM image of the germanium deposition at the temperature of about 700 °C is shown in the Figure 36 below. The evidence of germanium nanowires growth was not found. The histogram showing the size distribution of the Au-Ge dots is shown in Figure 37. The number of pulses for gold and germanium deposits was 450 and 6,000 respectively at the pulse energy of 500 mJ. The repetition rate of the gold deposition was 5 Hz, while 10 Hz was used for the germanium deposition. The SEM image shows a markedly different result than obtained from the deposition at the temperature of 500 °C. Upon closer examination of the SEM image, the gold dots seem to "swim" on the germanium substrate with lateral germanium crystallization at its tail. This has been witnessed previously, but unlike the silicon case, the lateral crystallization is much smoother. The EDS analysis as shown in Figure 38 was obtained for the bright dot locations and indicates the presence of gold and germanium. The average diameter of the Au-Ge dot is about 2.1 µm. The smallest diameter was about 510 nm, while the largest was about 3.18 µm. The density of the Au-Ge dots was about 0.13/µm<sup>2</sup>.



Figure 36: SEM image of the Au-Ge deposits at Au (450), Ge (6000), 500 mJ and 700 °C.



Figure 37: Histogram showing the size distribution of Au-Ge dots.



Figure38: EDS analysis of the Ge deposition.



c) <u>800 °C</u>

The SEM image of the germanium deposition at the elevated temperature of 800 °C is shown in the Figure 39 below. The temperature of the substrate was kept below the temperature of about 900 °C to prevent any substrate melting. The EDS obtained on the deposition is shown in Figure 40, and the histogram showing the size distribution of the Au-Ge is shown in Figure 41. The number of pulses for gold and germanium deposits was 450 and 18,000, respectively at the pulse energy of 500 mJ and 15 Hz. The SEM image shows the similar result as in 700 °C case. The lateral crystallization as seen previously still exists, but seemed to have become more diffusive. Despite the rise in temperature, there wasn't any indication of nanowire growth. The sporadic dark patches on the gold-Ge molten alloy seem to indicate the mutual diffusion of Ge and gold. The EDS analysis was measured on the dots, and showed the presence of germanium and gold. The average size of the Au-Ge molten alloy was about 1.7 µm and was scattered about the Ge substrate with a density of about  $0.013/\mu m^2$ . The smallest diameter was about 690 nm, and the largest was about 2.01 µm. This deposition with Ge indicated that the temperature was probably sufficient to cause nanowire growth. The substrate holder, however, melted, possibly caused by forming a eutectic with the Ge substrate.

93



Figure 39: Au (450), Ge (18,000), 500 mJ, 800 °C.



Figure 40: EDS analysis of the Ge deposition.





Figure 41: Histogram showing the distribution of Au-Ge dots.

## **C)** Summary

In this chapter, various deposition attempts have been employed to grow silicon nanowires perpendicularly to the silicon substrate in the UHV condition using PLD. The deposition was PVD with the growth based on the VLS growth mechanism. The approximate number of pulses for gold deposition in relation to the size of the gold-rich dots was first determined. The deposition of silicon has caused various types of results, but the experiment however, did not yield any nanowires. At the low temperature of about 500 °C, the gold-rich dots seemingly buried in the silicon deposit was found, while at temperature higher than about 700 °C, a lateral crystallization of silicon appeared.

## CHAPTER IV: GROWTH OF SI WIRES IN UHV SYSTEM BY DEPOSITING ADDITIONAL LAYER OF SI AT ROOM TEMPERATURE

## A) Procedures

This chapter describes the growth of silicon wires after depositing additional or "overlayer" of silicon at room temperature over the gold thin film. The experiment was used to help test the validity of the modified VLS growth mechanism using the overlayer hypothesis as proposed in Chapter I, section D. The resulting silicon structures are designated as "wires" due to their large diameter. The same experimental procedure as described in Chapter III was used, except for the deposition of overlayer of silicon on the gold thin film at room temperature.

Following is a chronological order of experiments that were performed in the growth of silicon wires. The first observation of silicon wires growth was made with 12,000 shots of silicon at the temperature of 900 °C. The effect on silicon wires growth with silicon content was observed by increasing the number of silicon shots at the same temperature. To understand the role of temperature on the growth of silicon wires, the depositions then took place at the temperature of 500 °C and 700 °C, respectively. With unsuccessful growth of silicon wires at lower temperatures, the deposition temperature was once again increased to 900 °C to fully explore the growth at this temperature region by not only varying the number of shots for gold and silicon overlayer, but also pressure by introduction of ambient gas. At this point however, the inadvertent presence of oxygen during the flow of Ar gas caused the exposed filament to burn out, and the system broke down. Several attempts to remedy this problem were carried out, but they

were unsuccessful. This chapter thus constitutes the limited results prior to system breakdown.

#### B) Comparisons of Au Only and Au-Si

The initial experiment to observe the effect of an overlayer of silicon on the gold film was done by annealing the respective samples without high temperature laser ablation of silicon. The samples consisting of a gold thin film deposited on silicon (111) substrate both with and without the overlayer of silicon on top of the gold film were raised to the processing temperature of 900 °C, held there for about 10 minutes, then brought back down to room temperature. Prior annealing had been done as described in Chapter III, but the temperature was increased only to 600 °C.

The first sample consists of gold deposition only, and the resulting image from annealing is shown in the SEM image in Figure 42 (the scale bar is 5  $\mu$ m). The EDS analysis is shown in Figure 43. The number of pulses for the gold deposition was 300, and for silicon overlayer was 150.



Figure 42: SEM image of a Au film on a Si(111) without silicon overlayer after annealing to 900 °C.





Figure 43: EDS analysis at a bright location of Figure 42.

The SEM image shows two large "spotty" round ball-like structures. These were found near the center of the substrate where the temperature was the highest. The EDS was measured on these structures and shows the presence of gold and silicon as indicated in Figure 43. At the elevated temperatures, it is expected that the alloy formed with silicon and gold is uniformly mixed, however upon cooling, there could be segregation of the silicon and gold as suggested by the darker regions within the ball-like structures in Figure 42. For the second sample consisting of overlayer of silicon on the gold film, the density of the "spotty" round ball-like structures was much lower than the first sample.

### C) Growth of Silicon Wires

This section describes the resulting SEM images from implementing an overlayer of silicon on the gold thin film deposit. The gold was initially deposited onto the silicon substrate at the room temperature, subsequently followed by the deposition of thin layer of silicon also at room temperature. The number of pulses for the gold deposition was 40-300, while 150 pulses were used for the overlayer of silicon at room temperature. Based on the results of the gold sputtering, the thickness of the gold and silicon overlayer is estimated to be about 5-7 nm each. The number of silicon pulses at high temperature was 6,000-24,000 at 500 mJ. The temperature of the substrate was varied from about 500-900  $^{\circ}$ C.

## 1) 900 °C: Silicon (12,000 shots)

In this experiment, the temperature of the substrate was set to 900 °C. The number of pulses used for gold and silicon overlayer depositions was 300 and 150 respectively. For silicon deposition at high temperature, 12,000 shots were used. The energy of the laser pulse was 500 mJ. The resulting SEM images are shown in the Figure 44. The SEM images in Figure 44 (a) (b) (c) shows the silicon wires as seen from the angled view, while the Figure 44 (d) shows the top view. The scale bar is  $3.8 \mu m$ ,  $4.3 \mu m$ ,  $4.2 \mu m$ , and  $15 \mu m$ , respectively. The images represent the first evidence of silicon wire growth. Despite the small height, the tilted SEM image confirms the growth of these wires in the direction perpendicular to the silicon substrate. These wires were primarily found at the edge of the substrate, where the temperature was found to be about 800 °C as measured by the pyrometer. The center of the substrate was higher by about 50 degrees. The lateral crystallization typically seen in other images are visibly absent.

The EDS analysis was obtained on these silicon wires as shown in Figure 45. The bright round spots correspond to the "full" grown wires, while the duller spots seem to

correspond to wires that have yet to grow. The EDS analysis clearly shows the presence of gold at the tip. The height of the silicon wires wasn't large enough to perform separate EDS analysis.

The histograms in Figures 46 and 47 show the diameter and height distributions of the grown silicon wires. The average dimensions of the grown wires were about 540 nm in diameter and 270 nm in height which places these structures slightly above the commonly accepted nanostructure (<100 nm) category, and into the submicron regime.



a)

b)











Figure 45: EDS analysis showing the presence of gold and silicon

There were some structures with bright spots in the image, and it appears that those regions correspond to the initial stage of the wire growth. The histogram in Figure 48 shows the width-height relationship, where the blue series (1) corresponds to width distribution, while the red series (2) correspond to height distribution. Due to the small height of the wires and their low density, any conclusions on the diameter-growth rate relationships can only be estimates, however, based on the evidence collected, it appears that growth rate of these wires seem independent of the diameter.

The SEM images also show the presence of some triangular silicon structures scattered throughout the image. It is not clear the origin of these structures, but the shape seems to have formed in accordance to the substrate crystal orientation. In the background, the large micron-sized droplets resulting from the hydrodynamic ablation of silicon is visible.



Figure 46: Histogram showing the diameter distribution of the silicon wires



Figure 47: Histogram showing the height distribution of the silicon wires



Figure 48: Graph illustrating the width-height relationship in the silicon wires: (Series 1: Wire diameter) (Series 2: Wire height)

### 2) 900 °C: Silicon (24,000 shots)

The previous section described the first evidence of silicon wires growth on the silicon substrate. In this section, the same experimental conditions were used, except the number of pulses for the silicon deposition at high temperature was increased from 12,000 to 24,000. The resulting SEM images of the silicon wires grown on the silicon substrate are shown in the Figures 49 through 53. The EDS analysis is shown in Figure 54. The histograms showing the diameter distribution, height distribution, and diameter-height relationship are shown in Figure 55, 56, and 57 respectively.

In analogy to the previous discovery of silicon wires at lower number of pulses, these silicon wires were also primarily found at the edge of the substrate. In accordance with the increase in the number of pulses for the silicon deposits at high temperature, the height of the silicon wires also increased. There were some evidence of growth toward the center of the substrate, but the height of these structures was negligible. The height of the wires is believed to be enhanced also from the migrating adatoms since the edges are the lowest energy site. The SEM images in Figure 49 and Figure 50 shows the angled and top view of the same growth regions, respectively. These images verify the direction of the grown silicon wires, namely perpendicular to the substrate. The scale bar for both images is  $10 \ \mu m$ . The large droplet-like features are remnants from the hydrodynamic ablation of silicon target.



Figure 49: Oblique view SEM image of the grown silicon wires on the Si(111).



Figure 50: Plane view SEM image of the grown silicon wires.

The image in Figure 49 shows the variation in the shape of the grown silicon wires, with some wires gradually tapering off to the wires with clear bright ball-like feature at the tip. The differences in the wire shapes are more evident in Figure 51, where transition of wire shapes seems to take place with the steady decrease in the bright balllike feature at the tips of some of the structures. For the "pointed" wires, the ball-like feature is completely absent. In Figures 52 and 53, a close view (angled and top views respectively) of one of the silicon wires seen in Figure 51 with clear ball-like feature at the tip is shown. The angled view in Figure 52 shows the faceting of the wires, and the Figure 53 shows the hexagonal base of the grown wire indicative of the Si(111) growth. The shape of the bright ball-like feature was somewhat round suggesting it is formed by the molten alloy of silicon and gold. The EDS was measured on this bright ball-like feature, and the result as shown in Figure 54 clearly indicates the presence of both gold and silicon. The pointed wires did not show any gold at the tips. The presence of gold at the tip is the direct confirmation of the wire growth via VLS growth mechanism. The absence of gold content as seen in the pointed wires does not preclude the VLS growth mechanism however. During the growth process, as discussed in the theory section, such factors as evaporation (perhaps enhanced by unwanted impurities) could have caused the absence of the gold at the tip. This seems logical since the evidence of decreasing gold content has been found in the image. The other parts of the silicon wires only indicated silicon in EDS analysis. The trigonal pyramid base of the wire should also be noted and is believe to have been formed as some of the Si adatoms bond at the lower energy sites located at the interface between the growing wire and the substrate. The large droplets found in the SEM images are the residual from the laser ablation of the silicon target,

107

where the density of the droplets increases with the deposition time due to the erosion of the silicon target from the continual bombardment by the laser beam.



Figure 51: SEM image showing the variation in the grown silicon wires shapes.



Figure 52: Close side-view of one silicon wire which is also shown in Figure 51.



Figure 53: Close view of the silicon wire in Figure 52 as seen from the top.



Figure 54: EDS analysis on the tip of the wire shown in Figures 52 and 53.

The histogram of the widths and heights of the silicon wires are shown in Figures 55 and 56 respectively. The average diameter of these wires was approximately 543 nm with the corresponding average height of about 1  $\mu$ m. The approximate density of the silicon wires was  $0.05/\mu$ m<sup>2</sup>. The growth of these large diameter silicon wires can be attributed to the growth at high temperature condition.



Figure 55: Histogram showing the diameter distribution of silicon wires

Generally, as discussed in Chapter I, the axial growth rate of silicon wires in CVD has been known to depend on the diameter of the wires, i.e., thin wires grow slower than the thick ones. An exception to this is the reported growth of silicon wires in the Gas Source Molecular Beam Epitaxy (GS-MBE) where the correlation between the wire diameter and the axial growth rate was not found and was attributed to the lower gas pressure compared to conventional CVD. The histogram showing the relationship between the diameter and the corresponding height of 80 silicon wires measured by SEM are shown in Figure 57. Based on these results, there does not appear to be a

correlation between the diameter and height of the grown silicon wires in this experiment.

.



Figure 56: Histogram showing the height distribution of silicon wires



a)



b)

Figure 57: Histogram showing the diameter-height relationship a) samples 1-40 b) samples 41-80. Blue Series= width, Red Series=height of the silicon wires.

## 3) <u>500 °C</u>

The SEM image resulting from the deposition of silicon at the temperature of  $500 \,^{\circ}$ C is shown in Figure 58 (scale bar is 2.5 µm). The number of pulses for gold deposition was 40, and the silicon overlayer was also 40. The number of pulses for the high temperature deposition of silicon was 6000. No evidence of nanowire growth on the surface was found. The image instead shows the gold-rich dots seemingly buried within the silicon layer, in what appears as ubiquitous deposition of silicon on the silicon substrate. The EDS analysis is shown in Figure 59, and indicates the presence of gold and silicon in these gold-rich dots. The evidence of silicon deposition outside these gold-rich regions is the appearance of somewhat rougher surface of the substrate and the absence of gold from EDS analysis. Dark craters surround these gold-rich dots, possibly indicating the assimilation of silicon deposits into the gold-rich dots at the higher temperatures. Two conspicuous features of the resulting SEM image from the previous annealing results without the overlayer of silicon is the drastic decrease in the appearances and the brightness of these gold-rich dots.

The histogram showing the size distribution of these gold-rich dots is shown in Figure 60. The density of the gold-rich dots from the SEM image is calculated to be about  $0.19/\mu m^2$ , but the appearance of these gold-rich dots throughout the sample was actually scarcer than this number would indicate. The brightness of the gold-rich dots also had considerably dimmed. The average size of these gold-rich dots is about 150 nm. Based on the number of gold pulses used, namely 300, the evidence of gold depositions was expected to have been much more apparent. For some reason, it appears as if the

114

deposition of additional silicon at room temperature had caused most of the gold to be buried and thus diminished in view.



a)

b)

Figure 58: SEM image of Au (300 pulses)/Si (150 pulses at room temp.)/Si (12,000 pulses at 500 °C), 500 mJ a) Gold-rich dots b) Closer view of gold-rich dots



Figure 59: EDS analysis of the buried gold-rich dots



Figure 60: Histogram of the size distribution of gold-rich dots

# 4) <u>700 °C</u>

The same parameters as described above for the deposition temperature of 500 °C were used in this section; however the temperature of the silicon substrate was raised to 700 °C. The resulting SEM image is shown in Figure 61, where evidence of silicon wire growth was not found. The SEM image shows bright round, ball-like structures seemingly gliding against the rough background. The EDS as shown in Figure 62 shows the presence of gold and silicon on these structures. The gliding or lateral crystallization has also been seen before in the case of deposits in the absence of room temperature silicon overlayer. This seems to be a common feature at this temperature range. The

probable cause of this is the increase in the temperature, along with the non-uniform temperature profile on the silicon surface. Also in one of the gold-rich ball on the lower left corner of the SEM image, there is a darker patch within the structure, perhaps indicating the phase segregation of silicon from the gold alloy upon cooling.



Figure 61: SEM image of the deposits at Au (300 pulses)/Si (150 pulses at room temp.),/Si (12000 pulses at 700 °C). The laser beam energy of 500 mJ was used for all pulses.



Figure 62: EDS analysis on the deposition shown in Figure 61.

### 5) 900 °C: Other Deposition Conditions

To decrease to size of the silicon wires, the number of pulses for the gold and room temperature silicon deposition were decreased from 300 to 200, and 150 to 100 respectively. The number of pulses for the high temperature deposition of silicon was 24,000. Other experimental conditions remained the same as before as in section 2) of this chapter. The angled SEM image in Figure 63 shows a limited amount of silicon wire growth. The density of the wires was quite low, and they were found only at local regions. Most of the wires found seem to show a bright, round structure at the tip, but in decreased content.



Figure 63: Angled SEM image of the silicon wires: scale bar 5 µm.

The SEM image in Figure 64 shows a different area where the silicon wires were found. The SEM image in Figure 65 shows the close view of one of the wires also located in Figure 64, and bright round structure is clearly visible.



Figure 64: Tilted SEM image of the silicon wires



Figure 65: Close view of the silicon wire in Figure 64.

The EDS analysis on this round structure indicated the presence of gold and silicon as shown in Figure 66. The decreasing gold-silicon molten alloy has been seen before, but seems to be more conspicuous in these SEM images.



Figure 66: EDS analysis of the Au/Si tip of the wire shown in Figure 65.

### **D)** Summary

This chapter has described the first growth of silicon wires on the silicon substrate by applying the modified VLS growth mechanism using the overlayer of silicon. This is the first observation of silicon wires growing perpendicularly not only in the UHV, but also PVD-PLD. In so doing, various temperature ranges and deposition conditions have been investigated. The best growth of silicon wires have been found at the temperature of 900 °C with gold and silicon room temperature depositions of 300 and 150 pulses, respectively. The number of pulses for high temperature deposition of silicon was 24,000. The height of the silicon wires increased in accordance with the increased number of high temperature silicon pulses as expected.

## **CHAPTER V: GROWTH OF SILICON NANOWIRES IN FURNACE SYSTEM**

The following chapter describes the growth of silicon nanowires from annealing various thicknesses of gold deposited silicon substrate inside the furnace at a given temperature. The design and the implementation of the furnace system apart from the UHV system arose due to one primary reason, namely to explore the usage of ambient gas during the laser deposition to enhance the growth of silicon nanowires. The consequences of the furnace system usage are not only in the availability of higher pressure but also higher temperature regimes as well.

Initially, in analogy to the growth of silicon wires in the UHV system using PLD, laser ablation was also employed for the growth of silicon nanowires in the furnace system. But throughout the series of results showing the growth of silicon nanowires independent of number of laser pulses, it was soon determined that the silicon nanowires were growing just from annealing the gold deposited silicon substrate at a given temperature. Consequently, the result then led to the inquiry into the role of oxygen, and possibly the oxide-assisted growth method that has emerged in recent years.

## A) Procedures

The steps to growing the silicon nanowires in the furnace system consist of depositing a gold film on a Si(111) substrate, and subsequently annealing the samples at the given temperature. Four samples with different gold film thickness were used including 5, 10, 18, and 112nm. The gold films were obtained by sputtering gold onto the Si(111) substrate in a EMSCOPE SC 500 gold sputter coater. The gold sputter coats

approximately 7 nm per minute at the voltage of 20 kV. The sputtering time and the corresponding gold film thicknesses that were used are shown in the Table 9 below.

Approximate Sputtering Time	Approximate Thickness(nm)
45 seconds	5
1 minute 30 seconds	10
2 minutes 30 seconds	18
16 minutes	112

Table 9: Gold thin film sputtering parameters

The samples were then loaded into the furnace, and the furnace was then purged with argon gas for about 30 minutes at room temperature with the flow rates of 50 sccm for the first ten minutes, and 200 sccm for twenty minutes. After the room temperature purging, the pressure inside the furnace was varied from the pressure level of  $1.6 \times 10^{-1}$  Torr to 500 Torr depending the desired annealing condition.

The approximate amount and uniformity of the sputtered gold thin films is verified by annealing the gold deposited silicon substrate at the lower temperature at which the nanowire did not grow. The samples were raised to a temperature of 800 °C and then were subjected to one of two annealing times. The first case involved lowering the temperature immediately once the temperature reached 800 °C, while the second case involved an additional annealing time of about 8 minutes at 800 °C. The annealed samples were taken out of the furnace once it reached about 500 °C.

For the growth of silicon nanowires, the temperature of the furnace was raised to approximately 1100 °C. The ramp time to reach this temperature was about 1.5 to

2 hours. In analogy to the annealing at lower temperature, the samples were subjected to two separate annealing times. The first case involved lowering the temperature immediately once the temperature reached 1100 °C, and the second case involved an additional annealing time varying from 8 minutes to 3 hours. The annealed samples were taken out of the furnace once it reached about 500 °C.

Using a pyrometer, the temperature inside the furnace was found to be 1100 °C. The emissivity of silicon used for pyrometer measurement was 0.6. The PID controller showed similar temperature once the correct thermocouple was programmed into the controller. JEOL scanning electron microscope (SEM) operating at 20 KV was used to obtain the images of the silicon nanowires. Energy Dispersive X-ray Spectroscopy (EDS) was used to analyze the elements present in the grown nanowires.

## **B) Results**

## 1) Lower Temperature Annealing (800 °C)

## a) <u>5 nm Thick Gold Film</u>

This section describes the annealing of samples with a 5 nm thick gold film at 800 °C. The power to the furnace was immediately turned off once the temperature reached 800 °C, and the temperature subsequently decreased. The SEM image in Figure 67 shows the result from annealing (the scale bar is 0.2  $\mu$ m). The image shows fuzzy dots scattered about the substrate. The EDS analysis was made on these structures, but it was inconclusive due to its fuzziness and small diameter. The Figure 68 shows the histogram of the approximate diameter of these fuzzy dots. The average diameter was

about 21 nm, however due to the fuzziness in the image, the error was about 10 nm. The approximate density was about 375/µm<sup>2</sup>.



Figure 67: SEM image of the annealed gold film thickness of 5 nm




### b) <u>10 nm Thick Gold Film</u>

This section describes the annealing of 10nm thick gold on Si(111) at 800 °C. In analogy to the 5 nm thick gold film, the procedure to the temperature decrease was the same. The SEM images in Figure 69 shows the annealed result at the scale bar of 5 and 1  $\mu$ m, respectively. The image shows irregularly-shaped dots. Unlike the 5 nm thick gold film results however, the dots can be seen with clarity. The EDS analysis, shown in Figure 70, indicates the presence of gold in these dots. In Figure 71, the histogram shows the diameter distribution of the dots. Despite the face that they were not round, the dots were approximated as round during the size measurement. The size of the dots ranged from approximately 20 nm to 100 nm. The density of the dots was about  $60/\mu$ m<sup>2</sup>. Increasing the annealing to 8 more minutes did not seem to cause any change to the appearance of these dots.



Figure 69: SEM images of the annealed gold film thickness of 10 nm at 800 °C. a) Scale bar 5  $\mu m,$  b) Scale bar 1  $\mu m.$ 



Figure 70: EDS analysis of the gold dots

# Average Diameter: 55 +/- 5 nm 3.5 3 2.5 2 Count 1.5 1 0.5 0 0 20 40 60 80 120 100 Diameter of the Dots (nm)

Total Sample SIze: 10

Figure 71: Histogram showing the diameter distribution of the dots

### c) 18 nm Thick Gold Film

This section describes the results from annealing 18 nm thick gold film at 800 °C. The same procedure as in the previous annealing cases at lower gold film thicknesses was also used in this section. The SEM images in Figure 72 show the results. The scale bar is 5 and 1  $\mu$ m, respectively. The image shows larger-sized dots than the 10 nm case. The irregular shape of the dots is more apparent in this image. The EDS analysis measured on these dots showed gold and silicon, and the histogram in Figure 74 shows the diameter distribution of these dots. During the size measurements, these dots were approximated as round. In comparison to the previous annealing cases, the size of these dots was larger as expected for this thicker gold film. Some dots as small as 30 nm and large as 300 nm were found with an average diameter of approximately 114 nm. The density of these dots was  $30/\mu m^2$ . The sample annealing time was increased an 8 additional minutes, but there wasn't any evidence of any changes in the appearance of the dots.



b)

Figure 72: SEM image of the annealed gold film thickness of 18 nm at 800 °C. a) Scale bar 5 µm b) Scale bar 1 µm.



Figure 74: Histogram showing the diameter distribution of dots

# d) 112 nm Thick Gold Film

This section describes the results from annealing 112 nm thick gold film on Si(111) at 800 °C. The same annealing procedure was used in analogy to the previous studies. The SEM images in Figure 75 show the results at scale bar of 20 and 2  $\mu$ m, respectively. The images show the shapes varying from round dot-like to strand-like structures. The EDS analysis, shown in Figure 76, for these structures showed the presence of primarily

gold as expected. The larger sized of the resulting gold structures was due to the larger amount of initial gold film thickness.



a)



b)

Figure 75: SEM images of the annealed gold film thickness of 112 nm at 800 °C. a) Scale bar 20  $\mu$ m b) Scale bar 2  $\mu$ m.

The 112 nm thick gold film was then annealed for 8 minutes longer at 800 °C, followed by lowering the temperature as before. The SEM image in Figure 76 shows the result. The scale bar is 50, 2 and 10  $\mu$ m, for the images a), b), and c) respectively. Figure 77 shows the results from the EDS analysis. Unlike the previous case, the image shows a drastically different picture. Image in Figure 76 a), large rectangular blocks of gold rich region is shown, surrounded by darkening regions with decreasing gold content as verified by the EDS analysis. The EDS showed trace amounts of gold in the darkest regions of the image. The image in Figure 76 b) shows a closer view of the gold-rich rectangular block, and Figure 76 c) shows the closer view of the regions outside these rectangular blocks.





b)

c)



# 2) <u>High Temperature Annealing (1100 °C)</u>

This section describes the annealing of 5, 10, 18, and 112 nm thickness of gold film at the temperature of about 1100 °C. The ramp time of temperature reaching 1100 °C was about 1.5 hours. The annealing time was varied from 0-3 hrs at the 1100 °C. The pressure inside the furnace was varied from approximately  $1.6 \times 10^{-1}$  to 500 Torr using argon gas and adjusting the pressure by controlling the vacuum valve on the system. The substrate was taken out of the furnace typically near 500 °C. Same procedure that was used in previous studies was also used to prepare the silicon substrate for these experiments.

#### a) <u>5 nm Gold Thick Film</u>

The temperature of the furnace was raised to  $1100 \,^{\circ}$ C, then the power to the furnace was immediately turned off, and the temperature subsequently decreased. The pressure inside the furnace was about  $1.6 \times 10^{-1}$  Torr. The results from annealing 5 nm thick gold films are shown in the SEM images in Figure 77, with scale bars of 5, 1 and 0.5  $\mu$ m for images a), b), and c) respectively. The SEM image in Figure 77a) shows a dark-grayish substrate, with black pits occurring randomly. The EDS analysis in Figure 78 shows only silicon content in these black pits, while the dark-grayish regions showed silicon and trace of gold. At higher magnification, most of these black pits did not show significant structure as indicated in the SEM image in Figure 77b). On a very limited number, however, there were some black pits that actually showed some content inside the region. The SEM image in Figure 77c) seem to show some indication of wire-like

134

growth, or remaining ledges that bridge the silicon that remained. At higher magnification, the dark-grayish region also showed what appear to be faint gold dots embedded in the silicon substrate. It is not known how these wire-like growths are occurring, but these seem to branch out from the bright dots. Oxygen was not detected in any of the EDS analysis for this sample.





c)

Figure 77: SEM images of the 5 nm thick gold film at 1100 °C. a) image at the scale bar of 5 mm, b) image of the empty black pits c) image of the black pit showing some wire-like growth



Figure 78: EDS analysis on the black pits shown in Figure 77c).

The 5nm thick gold film was then annealed for 3 additional hours at  $1100^{\circ}$ C. The pressure remained the same at about  $1.6 \times 10^{-1}$  Torr. The following SEM images in Figure 79 show the results. The scale bars are 10 and 0.5 µm, for images a) and b) respectively. Figure 79a) shows the result very similar to the images in Figure 77a) where no additional annealing time was used. Unlike the previous case however, the contour around the black pits are unusually bright. At higher magnification as shown in the Figure 79b), the black pits seem to show some wire-like growth. The appearance of these black pits with these growths seems more common than the previous annealing case with zero additional annealing time. The increase in the annealing time seems to show some changes, but the effect seems minor.





b)

Figure 79: SEM images of the 5 nm thick gold film with 3 additional hours of annealing at 1100 °C a) Image at the scale bar of 10 mm, b) Image at the scale bar of 5 mm showing wire-like growth inside the region.

## b) <u>10 nm Thick Gold Film</u>

The results of annealing the 10 nm thick gold film on Si(111) at 1100 °C is shown in Figure 80. The temperature of the furnace was immediately decreased once it reached 1100 °C. The pressure was about  $1.6 \times 10^{-1}$  Torr, and the scale bars are 5 and 1 µm for images a) and b) respectively. SEM image in Figure 80a) shows a surface of the substrate being considerably rougher than the 5 nm case. There is no apparent indication of any wire-like growth anywhere. At higher magnification as shown in Figure 80b), the image shows bright dots scattered in the silicon substrate, but at a higher density and brightness than the 5 nm case. Within the black pits, there seem to be some evidence of wire-like growth. But unlike the 5 nm case, the wire-like growth seems to occur also in the dark-grayish regions. The EDS analysis, as shown in Figure 81, shows primarily silicon in most of the areas, with some presence of gold. The black pits showed a negligible amount of gold content. Oxygen was not detected in all cases.





b)

Figure 80: SEM images of the 10 nm thick gold film annealed at 1100  $^oC.$  a) Scale bar 5  $\mu m,$  b) Scale bar 1  $\mu m.$ 



Figure 81: EDS analysis on the regions outside the black pits

The 10 nm thick gold film was then annealed for an additional 3 hours at 1100 °C. The experimental conditions remained the same as before. The results are shown in Figure 82. The scale bars for images a)-d) are 50, 5, 1, and 0.2  $\mu$ m, respectively. The SEM image in Figure 82a) shows significant changes caused by the additional annealing time. Against the somewhat rough surface, round "sunflower-like" regions are found. These structures seemed to have extended out from the surface. This is more apparent in the SEM image of Figure 82b). At higher magnification as shown in the SEM image in Figure 82c), these sunflower-like regions show nanowires with a diameter of about 20 nm bridging across what appears to be tubular structures. The length of the nanowire is as long as 1.7  $\mu$ m. Outside these regions, bright dots are found against a much smoother surface. These bright dots are gold as indicated by the EDS analysis.









c)



d)



### c) 18 nm Thick Gold Film

The thickness of the gold film was increased to 18 nm, with the pressure inside the furnace remaining at about 1.6x10<sup>-1</sup> Torr. The temperature was increased to 1100 °C. and then immediately lowered by turning off the power as before. The resulting SEM images are shown in Figures 83-85. The SEM images in Figure 83 show the surface of the annealed gold film at the scale bar of 50 and 10  $\mu$ m. The surface appears rough as in 10 nm case, but there now exist regions with irregular shaped boundaries. The closer view of these surfaces is shown in Figure 84. The SEM image shows bright dots dispersed throughout the boundaries. EDS analysis was obtained on these bright dots, and showed the presence of gold, silicon, and oxygen. The result is shown in Figure 86. Outside the bright boundaries, silicon nanowires are seen growing randomly in high density. SEM images in Figure 85 shows nanowire growth in other parts of the surface, and the structure of the grown nanowires are more apparent. The EDS analysis showed the presence of silicon and oxygen in these nanowires, but generally did not show any gold. The result is shown in Figure 87. The diameter of the silicon nanowires range from about 20-160 nm, with length as long as several micrometers.

144





b)

Figure 83: SEM images of the 18 nm thick gold film annealed at 1100 °C a) Scale bar of 50 $\mu$ m, and b) Scale bar of 10  $\mu$ m.



Figure 84: SEM image of the 18 nm thick gold film annealed at 1100 °C.





b)

Figure 85: SEM images of the 18 nm thick gold film annealed at 1100 °C at various locations in the substrate.



Figure 86: EDS analysis on the bright regions.



Figure 87: EDS analysis on the grown silicon nanowires.

The 18 nm thick gold film was annealed for an additional 3 hours at the temperature of 1100 °C. Other experimental conditions remained the same as before. The result is shown in Figure 88. The SEM image shows a much clearer image of silicon nanowires growing randomly. The bright dots of gold can also be seen with better clarity. The improved quality in the images is due to better SEM manipulation. The increase in the annealing time did not seem to improve the structure or the density of the silicon nanowires. EDS analysis on the different regions of the surface showed similar results as before.





b)

Figure 88: SEM image of the 18 nm thick gold film annealed for additional 3 hours at 1100  $^{\rm o}C.$  a) Scale bar of 50  $\mu m$  b) Scale bar of 2  $\mu m.$ 



a)

b)



c)

Figure 89: SEM images of the silicon nanowires growing randomly on the substrate.

## d) 112 nm Thick Gold Film

The thickness of the gold film was increased to 112 nm. The pressure inside the furnace was about  $1.6 \times 10^{-1}$  Torr, and the temperature was increased to 1100 °C. The following SEM images in Figures 90a) and 90b) show the results with 0 and 3 additional hours of annealing time at 1100 °C respectively. The results are combined since the increase in the annealing time at the given temperature did not appear to produce any significant changes in the density or the dimension of the silicon nanowires. The scale bars for images a) and b) are 200 and 50 µm, respectively. The SEM images show large trapezoidal and triangular blocks, with a perimeter consisting of a thick layer of brighter regions. The shapes of these structures seem to adhere to the (111) silicon substrate orientation. EDS analysis was measured on these brighter layer regions and found considerable amount of gold and silicon as shown in Figure 91. The EDS analysis was also obtained on other areas and found gold content inside the rectangular and triangular regions to be high as well. Outside these regions, the amount of gold presence varied from complete absence to minute amounts.





b)

Figure 90: SEM images of the 112 nm thick gold film at 1100  $^{\rm o}C$  a) Scale bar of 200  $\mu m$  b) Scale bar of 50  $\mu m.$ 



÷

Figure 91: EDS analysis on the bright rectangular boundary.

The images at higher magnification are shown in Figure 92 where the the growth of silicon nanowires outside the gold-rich boundary layer is shown. The high density of randomly directed growth of silicon nanowires is conspicuous in the image. The EDS analysis showed silicon and oxygen, but gold was usually not present in this region of the sample. The SEM images in Figure 93 show the close view of the grown silicon nanowires. The diameter of the grown silicon nanowires was 20-160 nm, with some small as 10 nm. The length was several micrometers long. The branching and kinking in the nanowires were seen throughout the region in high density. As seen with the whisker growth, branching and kinking are typical morphological instabilities. Generally for the VLS growth mechanism using gold as the metal catalyst, these occurrences are attributed to the spontaneous breaking of the gold rich regions into droplets with the new droplet giving rise to other branches. In this case of nanowire growth based on annealing with oxygen usually present instead of gold, it is not clear what is actually causing the branching and kinking. Some nanowires with long, straight shapes were also found throughout the regions.



Figure 92: SEM image of the silicon nanowires growth outside the gold-rich boundary layer for 112 nm thick gold film annealed at 1100 °C.





b)

c)



Figure 94 shows the SEM images of the silicon nanowires showing bright dots at its tips. The scale bar is 1  $\mu$ m for both images. Generally, EDS analysis on these bright dots show silicon and oxygen, but on a very limited basis, the EDS analysis did show traces of gold along with silicon and oxygen. Such brightness could indicate the presence of gold at the tips, or simply the charging up of the structures at the tips while collecting the SEM image.



a)



 b)
Figure 94: SEM images of the various silicon nanowires with bright dots at the tips.



The SEM image in Figure 96 shows the bright dot within the ring-like nanowire. The scale bar is 0.5 µm. The EDS analysis on the dot showed only silicon along with oxygen, but it does not seem conclusive. The bright dot might be due to kinking of the nanowire.



Figure 96: SEM image showing a bright dot within the ring-like nanowire.

The SEM Images in Figure 97 shows the growth of silicon nanowires at the gold-rich boundary layer. The scale bar is 2  $\mu$ m. The silicon nanowires seem to randomly sprout out of the gold-rich boundary layer. The EDS showed primarily gold and some silicon and oxygen. The SEM images in Figure 98 show the growth of silicon nanowire in other gold-rich boundary layers. The variation in the dimension of the silicon nanowires is much more apparent. The pressure inside the furnace was increased to as much as 400 Torr by flowing argon gas, but it did not seem to have noticeable effect on the nanowire growth. The silicon nanowires were also observed inside the gold-rich boundary layer, but they were very similar to the growth of silicon nanowires outside as
seen in Figure 92. One difference was the presence of gold, in addition to silicon and oxygen in the silicon nanowires grown inside. In comparison to the growth of silicon nanowires in 18 nm case, the further increase in the thickness to 112 nm do not seem to show any noticeable differences in terms of silicon nanowire density and their dimensions. One noticeable difference is the presence of thick gold-rich boundary layer at higher gold thickness, and the growth of silicon nanowires in these regions.



Figure 97: SEM images of the 112 nm thick gold film at 1100  $^{\circ}$ C. at the edge of the gold-rich boundary layer.





a)





Figure 98: SEM images of the silicon nanowires growing at the gold-rich boundary layer.

# C) Summary

In this chapter, the growth of silicon nanowires in the furnace based system has been observed by simple annealing of gold-coated Si(111) substrates at the temperature of approximately 1100 °C. Four different thicknesses of gold films were investigated, including 5, 10, 18, and 112 nm. The results from our experiments showed there was a critical gold film thickness above which the nanowires spontaneously grew with a rapid increase in density. This critical thickness is in the range of 10 to 18 nm of gold film. Increasing in the gold film thickness beyond 18 nm and increasing the annealing time only had minor effects on the density and the dimensions of the nanowires. The pressure of the argon gas likewise did not seem to affect the growth density significantly. The dominating factors in nanowire growth seem to be the initial gold film thickness and the temperature.

## **CHAPTER VI: DISCUSSIONS & CONCLUSIONS**

## **A) Discussions**

In this research, the growth of silicon nanowires have been investigated in two separate growth systems: an ultra high vacuum chamber, and a high temperature, high pressure furnace. The employment of two growth systems allows investigation of silicon nanowires in various growth regimes, namely in temperature regions as high as 1100 °C and pressure from 10<sup>-9</sup> to 500 Torr. Most of the nanowires grown by other researchers have been in furnace systems under high pressure conditions using ambient gas such as argon. The investigation of nanowire growth, in the ultra high vacuum condition in particular, should further the understanding in the control and growth of nanowires.

In the ultra high vacuum system, the silicon wires were grown using the gold mediated VLS growth mechanism. The growth occurred only when an additional layer of silicon was deposited on top of the gold film at room temperature. This is the first observation of silicon wires growth with the growth direction perpendicular to the Si(111) substrate not only in the UHV, but also PLD without resorting to CVD growth. The source of axial growth of silicon wires was provided by the ablation of the silicon target using the KrF excimer laser at the substrate temperature of about 800 °C. The base pressure inside the ultra high vacuum chamber was 10<sup>-8</sup> Torr. This result does not preclude the possibility of silicon nanowire growth without using the overlayer of silicon; the evidence of growth based on such a method was not investigated in this research. The growth conditions without using the overlayer of silicon might prove to be more stringent. Various shaped silicon wires were observed, ranging from wire with clear molten gold-silicon alloy at the tip of the wire to those with diameters gradually tapering off with height. The presence of gold at the tip of the wire, as verified by EDS analysis, confirmed the VLS growth mechanism. The absence of any molten gold-silicon alloy at the tip can be attributed to various factors. Based on the decreasing dimension of the nanowires with increasing height in some of the wires, it is possible that evaporation, or absorption of gold into the lattice of the growing nanowire, is a cause of their gradual disappearance. One interesting aspect in the EDS analysis of these wires is the absence of oxygen.

The orientation of the grown silicon wires was primarily in the direction perpendicular to the Si(111) substrate. It was found that the height of the silicon wires increased in accordance to the number of pulses. The typical dimension of the silicon wires was about 500 nm in diameter and 1  $\mu$ m in height. The grown silicon wires showed faceting with hexagonal base reflecting the Si(111) substrate, thus indicating the high crystalline quality of the wires.

In the furnace system, silicon nanowires were formed simply by annealing the gold coated Si(111) substrate at the temperature of 1100 °C. Four different thicknesses of gold films were investigated, namely 5, 10, 18, and 112 nm. The pressure was varied from about  $1.6 \times 10^{-1}$  to 500 Torr. The dimensions of the silicon nanowires were 10-150 nm in diameter and several microns in lengths. The silicon nanowires were observed only when the thickness of the gold film exceeded 18 nm and the samples were raised to the growth temperature of about 1100 °C. The axial growth of nanowires up from a substrate requires an additional silicon source, regardless of which growth mechanism is

employed. The case of silicon nanowire growth just by annealing the gold deposited silicon substrate at high temperatures, to this author's knowledge, has not been seen before. There was one interesting case however, where silicon fibers were formed just by annealing the silicon substrate deposited with silicon crystalline particles followed by deposition of monolayer-equivalent gold atoms<sup>109</sup>. The growth conditions were 1000 °C annealing for several hours under ultra high vacuum condition. In the efforts of this research, however, annealing did not yield nanowires below 18nm.

A rapid increase in the density of the silicon nanowires was observed above the 18 nm thick gold film. Among the samples that did form nanowires, the density of silicon nanowires formed did not appear to deviate significantly with changes in factors such as pressure, thicker gold films, and longer annealing times. Based on these results, there seems to be a critical thickness of gold with corresponding amount of silicon substrate that participates in the growth of the silicon nanowires. While there was clearly a distribution of diameters of the nanowires formed, this distribution also appeared to be insensitive to pressure, gold film thickness, and annealing times.

The EDS analysis was measured on the grown silicon nanowires, and always showed the presence of oxygen in addition to silicon for the samples grown in this furnace based system. Gold was present only in some nanowires, namely those that grew at the edge of the gold-rich boundary layer and inside. In analogy to the UHV grown silicon wires, the absence of gold in some furnace grown silicon nanowires might be attributed to evaporation of the gold-silicon molten alloy. If the nanowire dimension was defined by the diameter of the gold-silicon molten alloy, as is typically the case for the VLS growth mechanism, then the absence of gold in some silicon nanowires due to evaporation seem

166

very probable not only due to the smaller dimension of the grown silicon nanowires, but also due to the higher growth temperature.

One interesting feature in the growth of these silicon structures in the two growth system is the differences in the growth rate of silicon wires in UHV without the presence of oxygen and the rapid growth rate of silicon nanowires in the furnace with the presence of oxygen. Any endeavor to compare the silicon structures that have been grown under these different systems should also address the role of oxygen especially in the size and growth rate of the nanowires. The view of enhancement of the growth rate due to oxygen in this research would then conform to the concept of oxide-assisted growth of silicon nanowires where higher densities of nanowires have been seen in comparison to the metal-catalyst based nanowires. Further study needs to be done to understand the role of oxygen and the combination of oxygen with a metal-catalyst in the growth of nanowires.

# **B)** Conclusions

In this study, silicon structures have been formed by using two separate growth systems: a UHV chamber and a tube-furnace based system. In the UHV chamber, following results have been obtained.

- 1) Silicon wires a typical diameter of about 500 nm and height of about 1  $\mu$ m were grown at the temperature of about 800 °C under ultra high vacuum condition.
- 2) The silicon wires primarily grew perpendicular to the Si(111) substrate.
- 3) VLS growth mechanism was employed to grow the silicon wires in conjunction with a deposition of additional layer of silicon over gold thin film at room temperature.

- 4) The VLS growth mechanism was verified by the EDS detection of gold in the goldsilicon molten alloy at the tip of the wire.
- 5) The source of silicon for the subsequent axial growth of silicon wires was provided by the laser ablation of silicon target.
- This is the first observation of silicon wires with the growth direction perpendicular to the Si(111) substrate without resorting to CVD.

In the furnace, following results have been obtained.

- Spontaneous growth of silicon nanowires was observed simply by annealing the Si(111) substrate covered with various thickness of gold. This is the first observation of silicon nanowires growth based on annealing alone.
- The dimensions of the silicon nanowires were about 10-150 nm in diameter and several μm in length.
- 3) The growth temperature was about 1100 °C and the pressure was about  $1.6 \times 10^{-1}$  Torr.
- 4) There was an explosive increase in the density of the nanowires from 10 nm to 18 nm gold film. The further increase in the gold thickness, pressure, and annealing time does not seem to show drastic differences in the density of the nanowires.
- 5) The EDS showed the presence of oxygen in all the silicon nanowires that were grown. Gold was detected in those nanowires that grew at the edge or inside the gold-rich boundary layer.
- 6) The source of silicon for the rapid growth of silicon nanowires was provided by the silicon substrate itself.

### APPENDIX:

#### A) Systems/Components Specifications

This section describes the components that have been used during the research. It is separated into several categories according to the list shown below. Components that relates to vacuum are treated entirely under Vacuum Technology in section E.

- 1) KrF Excimer Laser
- 2) UHV Chamber and Mullite Tube

3) Optics

4) Control

### 1) KrF Excimer Laser

The Lamda Physik LPX 210i KrF Excimer Laser is shown below in Figure 99. The laser is used to ablate the targets either inside the UHV chamber or furnace. The specifications for this laser are listed below in Table 10.



Figure 99: Photograph of the LPX 200 KrF excimer laser

Wavelength (nm)	248
CDRH Class	IV
Maximum Repetition Rate (Hz)	100
Average Power (W)	65
Pulse Duration (ns)	25
Beam Dimension (mm <sup>2</sup> )	5-12 x 23
Manufacturer	Lamda Physik

Table 10: Specifications for Lamda Physik 210i KrF Excimer Laser

# 2) UHV Chamber and Mullite Tube

# a) UHV Chamber

The nanowire growth experiments under UHV condition have been performed inside the UHV chamber. The Figure 16 in Chapter III shows the photograph of the UHV chamber. The specifications for the chamber are shown in Table 11.

Table 11: Basic specifications for UHV chamber

Material	Stainless Steel
Dimension (DxH)*	18 x 24

<sup>•</sup> DxH: D = Diameter, H = Height

### b) Mullite Tube

The mullite tube, as shown in Figure 100 below, was used to house the substrate/target in the furnace system. The average diameter of the tube used in this study was about 3.75 inches. Some of the key properties of the mullite tubes are good thermal shock and stress resistance, low thermal conductivity, good strength, wear resistant, and most importantly, usable at high temperature. Some other properties are listed below in Table 12.



Figure 100: Mullite tube

Table 12: Properties of Mullite

Density	2.8 g/cm <sup>3</sup>
Hardness	1070 Kg/mm <sup>2</sup>
Thermal Conductivity	6 W/m•°K
Coefficient of Thermal Expansion	5.4x10 <sup>-6</sup> /°C
Maximum Use Temperature	1650 °C
Manufacturer	Zircar

The section describes the optics used in the UHV chamber and furnace systems. It comprises of a UV-graded optical materials which includes plano-convex lens, laser mirror, fused silica optics window and Plexiglas beam box. The photograph of the lens, laser mirror and the optics stand inside the beam box is shown below in Figure 101. In the background, the furnace system is shown.



Figure 101: Lens and mirror configuration

### a) Plano-Convex Lens

The round UV-graded fused silica plano-convex lens is used to direct and focus the laser beam onto the target. The specifications are shown in Table 13.

# Table 13: Specification for the plano-convex lens

Material	UV-grade fused-silica
Wavelength (nm)	248
Diameter (Inches)	2
Surface Quality	60-40
Manufacturer	Oriel Optics

# b) Laser Mirror

The laser mirror was used to redirect the laser beam in the experiments conducted in the furnace system. The specifications are shown below in Table 14.

Material	UV grade fused silica
Dimension (diameter x thickness)	2 x 0.375 inches
Surface finish	20-10 laser grade polish
Reflectance (248 nm)	> 97 % (45° AOI)*
Manufacturer	Acton Research Corp

Table 14: Specification for the high power UV laser mirror

\* AOI: angle of incidence

c) Optics Window

Deep UV optics window was used to couple the laser into the UHV chamber.

The Figure 102 shows the CF flange type optics window. The specifications are shown in Table 15.



Figure 102: UV-graded CF flange optical window

Material	Deep UV graded fused silica
Nominal Flange Diameter	3.75 inches and 2.75 inches
Wavelength (nm)	0.2 μm – 2 μm
Surface Quality	40-20
Manufacturer	Insulator-Seal

Table 15: Specifications for the optical window

#### d) Plexiglas Beam Box

The purpose of the UV-graded beam box is to protect the researchers during the laser ablation. The photograph of the beam box is shown in the previous section in Figure 101. The specifications are shown in Table 16.



Table 16: Beam box specifications

Material	UV blocking Plexiglas
Dimension (inches) (LxW)	48 x 7 ¼ x 14 ¼

e) Optics Stand

The two aluminum optics stand was used to support the lens and the mirror. A single piece of the optics stand is shown in Figure 103. The specifications for the optics stand are shown in Table 17.



Figure 103: Aluminum optics stand

Table 17: Specifications for the aluminum optics stand

Material	aluminum
Dimension (inches) (LxH)	24 x 2.65

### 4) Control

This section describes the components that were employed for mechanical and temperature manipulations in the UHV chamber system.

### a) Target Holder/Manipulator

The ablation target manipulator used in the UHV chamber is shown in Figure 104. It is capable of holding up to six 1" targets. Clocking of the target into appropriate positions and the continuous rotation of the targets can be done either manually or by using the Stepping Motor Controller. The manipulator is cooled by the water from the recirculating chiller. The assembly can also be cooled by the liquid nitrogen if desired. The spent targets can be replaced either by shutting down the system completely and doing it manually or mechanically by using the transfer arm without breaking the vacuum condition and transferring samples through the load lock region. The entire target manipulator can be manipulated in the transverse direction in accordance with the alignment with the laser beam and the substrate by using the built-in linear translator.



Figure 104 : Thermionics ablation target manipulator a) with a cover b) without the cover

## b) Sample Holder/Heater

The sample holder/heater assembly from Thermionics is shown in Figure 105. It is used to heat the substrate using the radiant heater quartz lamps. The temperature control and the heating unit for this assembly are provided by the SPS Sample Heater Power Supply as discussed in the following section. The sample can also be rotated using the Stepping Motor Controller as discussed in section d).



Figure 105: Thermionics substrate holder/heater assembly

#### c) SPS Sample Heater Power Supply

The SPS sample heater supply, as shown in Figure 106, provides the necessary power for the sample heating. The PID controller provides the automated temperature control and reading. The maximum output is 10 A at 80 VDC.



Figure 106: Thermionics sample heater power supply.

#### d) Stepping Motor Controller

The Figure 107 shows the Stepping Motor Controller and the hand-held control keypad. It is capable of driving up to six motors that are used for sample manipulations with output currents up to 3.5 amps. One primary use of the stepping motor controller is

in the rotation of the target during the laser ablation. By programming the appropriate parameters into the hand-held control keypad, the rotation rate can be varied. The operating procedure for the hand-held keypad, and the programming of the rotation rate of the target is discussed in the section.



Figure 107: Thermionics stepping motor controller.

e) Chiller

The CFT-33 Neslab Chiller is shown in Figure 108. The function of the chiller is to provide the continuous cooling water both to the ultra high vacuum chamber and the furnace system. It is capable of providing cooling water as low as 0 °C and the flow rate of 100 psi. Only the filtered water should be used in the chiller. In the ultra high vacuum chamber, the target and the substrate heater assembly is cooled. The flow rate should be such that the pressure is between 60psi and 100 psi. The typical operating flow pressure is about 75psi. The temperature should be set between 10-15 °C. Care must be taken to insure that there is no leak in the tube prior to each run. During the experiment, the outlet tube will get warm and the tube diameter will expand. Depending on the room condition, condensation will form in the tube. Care must be taken to insure that the condensed water do not drip onto the experimental equipments. Wiping with paper towel should be

sufficient. For the furnace system, the Al endcaps are cooled. The water flow rate can be set at the minimum. The temperature of the water should be set about 15-20 °C.



Figure 108: NESLAB CFT-33 recirculating chiller.

### **B) Vacuum Technology**

#### 1) Pressure Units

The System Internationale (SI) pressure unit is pascal (Pa). It corresponds to  $1 \text{ N/m}^2$ . Another acceptable unit of pressure is bar, which is  $10^5 \text{ N/m}^2$  or  $10^5 \text{ Pa}$ . A unit of pressure unit commonly used is torr, where pressure of one atmosphere at the sea level (0 °C) corresponded to 760 mm in height of mercury column. The following relationships are used for pressure conversion from one unit to another.

> 1 Pa = 7.5 x 10<sup>-3</sup> torr 1 torr = 133.3 Pa 1 bar = 1 x 10<sup>5</sup> Pa = 750 torr 1 atm = 1.013 x 10<sup>5</sup> Pa = 760 torr

#### 2) Vacuum Pumps

This section briefly describes several different types of vacuum pumps. The section is divided into three sections as listed below.

a) Dry Roughing Pump

b) Turbo Pump

c) Ion Pump

### a) Dry Roughing Pump

The Dry scroll roughing pump, as shown in Figure 109, provides the initial pumping down of the chamber from the atmosphere pressure to the medium vacuum level about  $10^{-2}$  torr. The dry roughing pump is turned on by connecting the plug into the wall outlet. There are some other types of vacuum pumps available in the market such as diffusion pumps that will achieve similar vacuum condition, but the dry vacuum pump has the advantage of eliminating the contamination of the chamber with the oil contaminants.



Figure 109: TriScroll 300 dry roughing pump.

### b) Turbo Pump

Turbomolecular or Turbo Pump provides the vacuum condition from medium vacuum level of  $10^{-2}$  torr to ultra high vacuum level to  $10^{-10}$  torr. The photograph of the

pump is shown in Figure 110. This pump is used in series with the roughing pump described above. In order to operate the turbo pump, the chamber is first pumped down by the roughing pump. Once the vacuum level is about  $10^{-2}$  torr, the turbo pump is then turned on. The normal ramp up time is about 40 minutes in reaching the 42,000 rpm, but it can be as short as a few minutes if the pump has a low lifetime. The reduced pumping speed of 28,000 rpm can also be used. The condition of the pump can be estimated by the increase in the noise of the pump during the operations.



Figure 110: Turbo 551 pump.

### c) Ion Pump

Ion Pump shown in Figure 111, provides the vacuum level from the medium range to about ultra high. It is also used in conjunction with the roughing pump. In this study, the ion pump (2 l/sec) from Thermionics is used to pump down the RNN Rotary Seal as shown in Figure 112. The function of the RNN Rotary Seal is to provide the continuous vacuum when the substrate holder is rotated during the loading/unloading of the substrate. This is done by first roughing pumping the RNN Rotary Seal, lowering the pressure to about  $10^{-2}$  torr. Then the valve is closed and the ion pump is turned on.



Figure 111: Ion appendage pump from Thermionics.



Figure 112: RNN rotary seal.

### 3) Vacuum Systems

Following figures in Figure 113 and 114 shows the general schematic of the vacuum systems that have been implemented in the UHV chamber and furnace systems. The UHV vacuum system is comprised of the dry roughing pump connected in series with the turbo pump.



Figure 113: General schematic of the UHV chamber vacuum system.



Figure 114: General schematic of the furnace vacuum system.

# 4) Pressure Measurement

The instruments that are used to measure the pressure is called vacuum gauges. Several different types of vacuum gauges are available to measure the pressure at various pressure ranges. Two types of vacuum gauges were used in this studythermocouple and ionization gauges.

# a) Vacuum Gauge Controller

The senTorr<sup>™</sup> vacuum gauge controller, as shown in Figure 115, was used to monitor the pressure level inside the UHV chamber as well as the furnace. Prior to its use, the controller needs to be calibrated. This is done by using the ConvecTorr thermocouple gauge. The thermocouple is first exposed to the atmosphere and the data is entered. By using the roughing pump-turbo pump dual system, the high vacuum level is recorded.



Figure 115: Varian senTorr<sup>™</sup> vacuum gauge controller.

# b) Thermocouple Gauge

Thermocouple gauges are rated to measure the pressure in the range of atmosphere down to 10<sup>-3</sup> torr. In this study, ConvecTorr<sup>TM</sup> thermocouple gauge from Varian is used as shown in Figure 116.



Figure 116 : ConvecTorr<sup>TM</sup> gauge tube.

c) Ionization Gauge

Ionization gauges are used to measure the high vacuum pressure level from  $10^{-3}$  to  $5 \times 10^{-12}$  torr. In this type of gauge, the pressure or the ion density is derived from the degree of ionization of the gas atoms. In this study, UHV-24 Nude Bayard-Alpert ionization gauges from Varian are used as shown in the Figure 117.



Figure 117: UHV-24 nude Bayard-Alpert type ionization gauge.

# C) Cleanroom Wet Station

The Figure 118 shows the wet station in the cleanroom where the wafer cleaning is done. It mainly consists of filtered water gun, drying rack, glassware cleaning accessories, bottles of methanol and acetone placed under the exhaust fume hood.



Figure 118: Cleanroom wet station.

### D) Operating Manual

### 1) Excimer Laser

This section describes the operating procedures of the LPX 210i (F) KrF Lamda

Physik excimer laser. The components to using the excimer laser are divided into the

following categories.

a) Checking the Beam Path b) Laser Cooling c) Starting the Laser d) Gas Lifetime and Replacement e) Laser Operations f) Shutting Down Laser g) Air Filter

a) Checking the Beam Path

The Figure 119 shows the beam aligner that is used to align the beam prior to using the excimer laser.



Figure 119: Beam aligner.

The path of the laser beam must be clear of any obstructions. The beam-target alignment is checked frequently to insure the proper transmission of the beam and the ablation of the target materials. This is done by using a visible diode laser mounted at the rear of the laser. The operating procedure for the visible diode laser is listed below.

- Turn on the visible diode laser by pushing the switch down located at the rear of the diode laser.
- Raise the shutter at both ends of the laser to allow the transmission of the visible laser through the laser.
- 3. Locate the bright reddish spot size.
- 4. Align the spot size so that it is shown on the target.
- 5. Once the target-beam alignment is set, turn off the visible diode laser.
- Close the rear shutter. This is done to avoid the excimer laser beam from exiting the rear of the laser during the operation.

#### b) Laser Cooling



Figure 120: Laser water coolant line.

In Figure 120, the waster coolant assembly is shown. Currently, the laser is cooled by the house tap water. A water filter is used to filter the water. The flow rate of the water should be less than 4 l/min and the temperature of the water flowing out of the laser during the operation should be 15-20 °C. For the water temperature lower than 15 °C, the efficiency of the laser falls. In order to insure the longevity of the laser, the filtered water should be flowing into the laser device. Once every few months, the filter should be replaced.

c) Starting the Laser



Figure 121: Back panel of the laser.

The Figure 121 shows the back panel located at the rear of the laser. To turn on the laser, following instructions are used.

- 1. Turn the key switch on the back panel of the laser head from O to I.
- Laser head is turned from OFF to ON. The laser ON warning lights should light up, with the sound of the laser turning on.

There is a warm up time of 8 minutes before the laser become fully operational. During the delay, the system parameters such as repetition rate, energy, mode of operation, gas partial pressures should be checked.

#### d) Gas Lifetime and Replacement

After the laser warm up period, the next procedure is to check the beam quality. The test should indicate the approximate lifetime of the gases inside the laser. The control keypad for laser operation is shown in Figure 122.



Figure 122: Laser control keypad.

To test the laser beam quality, following commands in the keypad are used.

1. REPRATE

2. Press 1. This should set the repetition rate to 1 Hz.

3. ENTER.

4. EGY

5. Press 5-0-0. The energy of the pulse should now be 500 mJ.

6. RUN/STOP

7. EXE

During the test, the value of the energy should be observed. Initially, the energy of the first pulse should start around 800 mJ, and gradually fall with each pulse until it oscillates at the preset energy value. In situation where the energy does not start at the high value, then the gas inside the laser needs to be changed. Also, if the laser has not been used for about month, then the gas should be changed.

If the gas needs to be changed, then leave the laser running without firing any pulses. Open the gas tanks and set the pressure to about 4 psi. In Figure 123, the gas cabinet is shown.



Figure123: Gas cabinet.

Then proceed to fill new gas by following the commands listed below.

- 1. PURGE line
- 2. select INERT by pushing  $\leftarrow \rightarrow$
- 3. ENTER
- 4. EXE
- 5. repeat the steps 3 more times
- 6. select BUFFER by pushing  $\leftarrow \rightarrow$
- 7. ENTER
- 8. EXE
- 9. repeat steps 3 more times
- 10. NEW FILL
- 11. ENTER
- 12. EXE

After the NEW FILL command has been executed, the pressure of the gas should start to fall immediately, indicating the exhausting of the spent gas. Once the gas pressure has reached about 30-40 mbar, it will automatically start refilling the laser device. The whole flushing and refilling should take several minutes. Once the new gas is filled, the laser is ready for operation. Test the laser by firing a few shots at the dummy target. The initial energy of the laser pulse should begin above 800 mJ.

# e) Laser Operations

To start the laser pulses, follow the commands listed blow.

1. RUN/STOP

2. EXE

With a brief delay of about 1 sec, the laser should start emitting the pulses. The water cooling should be checked quiet frequently during the operation stage of the laser. The temperature of the water flowing through the laser can be estimated by feeling the inlet and outlet hoses connected to the rear panel of the laser with a hand. For laser operations requiring only a few minutes, the water outlet hose should feel the same as the inlet hose, but for laser operations requiring hours or more, the outlet water should feel lukewarm. The flow rate of the water during the operation of the laser device can be increased as long as it is below 4 l/min.

## f) Shutting Down Laser Device

To terminate the laser operations, following commands in the key pad are used.

1. BREAK

- Wait a few minutes prior to turning off the laser completely to allow the water to cool the laser. The laser should be turned off once the temperature of the water outlet hose and the inlet hose feels the same.
- To turn off the laser device, the key switch on the back panel of the laser head is turned from I to O, followed by turning the main switch of the laser head from OFF to ON.

## g) <u>Air Filter</u>

The air filter located on the front panel of the laser device needs to be changed frequently. Any kind of air filter can be used. The lifetime of the filter is conspicuously noticeable by the darkening of the filter. The old filter can be taken out and washed under the running water, dried and reinstall for further use, or new filter can be installed.

## 2) Optical Window Cleaning

One of the inherent problems in pulsed laser deposition is the ablated materials being deposited on the optical window. Some methods can be implemented to reduce the deposits such as using argon as, but the problem cannot be completely prevented. The dirty optical window will not only drastically reduce the transmission of the laser beam, but also alter the beam path. Depending on the severity of the deposit, two cleaning agents are used to clean the optical window. For the lightly deposits on the optical window, an uncoated optical cleaning solution from Oriel is used. Using the special optical tissue, the solution is gently applied either on the tissue or directly onto the optical window. Then the optical window is wiped clean and dry.

For the heavily deposits, the optical window needs to be polished using a Pol metal polisher. Pol is an abrasive polishing compound that is frequently used to clean metal surfaces. Figure 124 shows the photo of the Pol metal polisher purchased from SPI supplies. Apply a small amount of Pol directly on the optical window, and using the special optical tissue, rub with a hand. If the hand polishing does not seem to work well, then Dremel Moto-Drill needs to be used. Applying a small amount of Pol on the soft buffing wheel, proceed to polish the optical window. Always wear a goggle during the polishing. If the compound gets into your eyes, immediately rinse eyes under the running water for about 10 minutes. There isn't any known cancer-forming agent from using this compound. The cleaning process does not completely clean the optical window, and it

194

will also damage the optical window. A new window has about 8% loss in transmission. After cleaning, the loss is about 15-20 %. Before cleaning it's much worse. Thus despite the reduction in transmission due to optical cleaning, it is the best option available in dealing with the deposits on the optical window.



Figure124: Pol<sup>™</sup> metal polisher.

# 3) Radiant Quartz Lamp

The UHV chamber system uses the quartz radiant heater. The power rating for this type is 70 W. With the supply current of about 10 A, the power is about 1000 W. The quartz lamp should always be handled with a glove on. Any finger prints or grease will cause the lifetime of the quartz lamp to reduce drastically. For the case where the bare filament is used in the ultra high vacuum chamber, the quartz housing needs to be cracked to expose the filament. This is done by using the Dremel Moto-Drill to make the necessary cutting at the edge of the quartz tube. Using the drill, make a small cut at the hardest part of the quartz lamp tube. Making a small cut is sufficient. There is no need to cut across the entire edge of the quartz lamp tube. There is some tendency for the drill to cut the filament itself during the cut. Always wear a glove and goggles during the cutting. When the quartz tube is cut, the gas inside the quartz tube is released. The typical gas composition of the inside the quartz tube is mostly Ar, and it should be harmless. Once the incision is made, a pliers can be used to crack open the quartz tube with relative ease.

To install the quart lamp in the gear box, the wires needs to be trimmed, and housed with the available ceramic beads.



### 4) SPS Series Power Supply

Figure 125: Front panel of the SPS power supply.

SPS Power Supply from Thermionics provides the power for the radiant heater quartz lamp. The Figure 125 shows the front panel of the SPS Power Supply. The procedure to raising the temperature of the radiant sample heater in the ultra high vacuum system is described below.

 Familiarize yourself with the control panel. All readings and knob levels should initially be at zero.
- Locate the MAXIMUM and MINIMUM OUTPUTS knobs on the front panel. Do not change the MINIMUM OUTPUT; it should remain at zero. The MAXIUM OUTPUT knob will be used to increase the current in the radiant sample heater filament, and subsequently the temperature of the sample.
- 3. Locate the current OUTPUT reading. The scale is from 0 to 15 AC AMP, but the machine is designed for a maximum current level of 10 AC AMP.
- Turn on the SPS Power Supply and current by pressing the ON buttons on the POWER and OUTPUT. The PID controller should automatically turn on with the SPS power supply.
- 5. Using the MAXIMUM OUTPUT knob, start increasing the current by first setting it at 0.3. This is done by turning the knob clockwise to 3. The number in the middle of the knob should be at zero. At this point, there should not be any changes in the current reading nor the temperature.
- 6. Wait about 5 seconds, and then proceed to turn the knob to 6. Wait about 30 seconds.
- Turn the knob to 9, and wait about a minute or so. During this time interval, the temperature should be increasing.
- 8. Set the knob to 1, and wait about 5 minutes.. The number in the middle of the knob should now read 1 to indicate the knob reading to be 1.2. The increase in the temperature should be quiet noticeable at this point.
- 9. Once the temperature reaches about 200 °C, do not turn the knob. Let the temperature continue to increase to about 300 °C or so. Once it reaches this temperature, start turning the current knob again as before, gradually increasing the current. The time

interval between successive knob turns should be more than 1 minute. Care must be taken so that the temperature does not increase too rapidly.

- 10. Once the temperature reaches about 700 °C or so, the saturation in the temperature increase will be more noticeble. Turn the knob every three units with increase in the temperature of about 8 to 10 degrees.
- 11. The following graphs in Figures 126 and 127 are included as a reference in raising the temperature using the data points from the actual experiment as shown in Table 18. The graphs depict the typical trend in temperature response with time and knob level. The response of the temperature with both the knob level and the time is generally linear at lower temperature of about 400 °C, then steadily saturates with further increase in the temperature. The lifetime of the quartz lamp can be crudely approximated by the steady drop in the temperature at the given knob level, especially above 850 °C.



Figure 126: Graph of the time-temperature response.



Figure 127: Graph of the knob level-temperature response.

Time	Temperature (°C)	Knob Level
Start (0:00)	~23	0
:30 mins	250	1.4
:40 mins	350	1.8
:50 mins	392	2.1
1 hr	457	2.5
1 hr 10 mins	514	3.0
1 hr 20 mins	555	3.3
1 hr 30 mins	603	3.7
1 hr 40 mins	645	4.2
1 hr 50 mins	698	4.9
2 hrs	728	5.2
2 hrs 10 mins	790	5.8
2 hrs 20 mins	833	6.8
2 hrs 30 mins	855	7.4
2 hrs 40 mins	885	7.7
2 hrs 50 mins	900	8.1

# Table 18: Sample temperature control parameters

ļ

Ē

#### 5) Turbo Pump Controller

The Figure 128 shows the front panel of the Varian Turbo-V 550 controller for turbo pump. This section describes the procedure for starting the newer turbo pump attached to the main UHV chamber.



Figure 128: Turbo pump controller.

- Turn on the controller. The display should read READY FOR LOCAL SOFT START.
- Push START button. The ramp up time for the pump with soft start is 80 minutes. The maximum pump speed is 40 KRPM.
- 3. If lower speed is desired at 28 KRPM, then press LOW SPEED.

#### 6) PID Controller/Thermocouples

Type K thermocouples are used both in the ultra vacuum chamber and high temperature furnace systems. The thermocouple in ultra high vacuum system is connected to the PID controller attached to the SPS Power Supply. The PID controller used by the furnace system is based on Fuzzy Logic as shown in Figure 129. This section describes the procedure to using the fuzzy logic based PID controller. All other parameters have been set, so only two steps are needed to operate the PID controller.



Figure 129: Fuzzy logic based PID controller.

- Turn on the PID controller. Wait a few seconds for the display to clear to 0000.
- 2. Set the temperature by pressing << or >>.

#### 7) Scanning Electron Microscope (SEM)

This section describes the operating procedures in using the SEM to image the sample and perform X-ray energy dispersive (EDS) analysis. Two types of SEMs were used to examine the samples in this study-JEOL (Japan Electron Optics Laboratories) 6400V and Hitachi S2500 shown in Figures 130 and 131, respectively. Table shows the comparison in parameters in the two types of SEMs used in this study.

	JEOL 6400V	Hitachi S2500
Resolution (nm)	3.5	3.5
Max. Magnification	300,000 X	200,000 X
Max. Accel. Voltage (KV)	40	30
Electron Source	LaB <sub>6</sub> Emitter	Tungsten Filament
Image Type	Digital	Polaroid Film

Table 19: Specifications for the two types of SEMs

Ŀ



Figure 130: JEOL 6400V Scanning Electron Microscope.



Figure 131: Hitachi S2500 Scanning Electron Microscope.

The general steps to using SEM are

- 1. Sample Loading/Unloading
- 2. Start up
- 3. Imaging/EDS Analysis
- 4. Shutting Down/Sample Unloading

The sample to be examined under the SEM needs to be conductive, unless Environmental Scanning Electron Microscope is used. Otherwise, the build-up in charges would drastically reduce the resolution of the image. For the non-conducting metal, this can be done by sputter coating the sample with gold for instance. Care must be taken to insure that the sample that is loaded into the SEM is not volatile, since it would contaminate the detectors. For the silicon substrate that was used in this study, a conductive tape was used. Gloves should be worn at all times during the sample handling. Using the plastic tweezer, the sample then should be carefully placed onto the conductive tape which has been placed on the sample stage. Press the sample lightly at the ends with the plastic tweezer to insure that the sample has been firmly placed. It should withstand tilting of the sample during the SEM examination. After the sample is taped onto the sample stage, following procedures is used to load the sample into the main SEM chamber. Operating procedure for both types of SEMs are very similar. Since the future research will primarily use JEOL 6400V, the procedure pertinent to this type of SEM is described below.

### a) Operating Manual (JEOL 6400V)

### Prior to Turning on the SEM:

- 1. Sign in the logbook.
- 2. Prepare the sample as described above, and proceed to load the sample onto the sample stage. Use appropriate screwdrivers and blades as needed.
- 3. Make sure all the lights are on. Otherwise, contact the supervisor of the SEM.
- 4. The working distance should be at 39 mm, X position at 35, and Y at 25mm.
- The vacuum inside the main chamber in the SEM should read about 1x10<sup>-5</sup> to 1x10<sup>-7</sup> Torr.

## Loading the sample into SEM:

- 6. Evacuate the airlock-exchange area by pressing the red button.
- Once the red button goes out, open the metal door, and proceed to slide the sample stage into the SEM main chamber using the transfer arm.
  8Mount the sample stage onto the sample holder inside the main SEM chamber. Try turning the sample stage left and right to insure the sample stage has been firmly secured.
- 9. Unscrew the sample stage, and pull out the sample transfer arm.
- 10. Close the chamber door, and press the red button.

#### Startup:

Once the sample is inside the main SEM chamber, the accelerating voltage needs to be turned on and increased according to the procedure described below. All the buttons are located at the front control panel.

- 11. Locate the filament current reading indicator. The reading should be at 145.
- 12. On the screen, change the accelerating voltage to 20 KV if it is not at this value initially. This can be done by pressing INS button, followed either by typing in the value from the keyboard or turning the voltage knob. Press ENTER. Other values can be used, but for doing the EDS during the SEM usage, this value needs to be used. The value of the accelerating voltage should NEVER be changed during the SEM usage.
- 13. Press the button ACCELVOLT.
- 14. Press the MODE button. There should be a flat or distorted line in the monitor screen.
- 15. The accelerating voltage needs to be saturated to the desired level. Turn the knob clockwise ½ every 30 seconds. Too rapid increase in the current will damage the filament.
- 16. Increase the current until it reaches the value 220.
- 17. Align the filament gun by turning the x- and y- knobs by watching the monitor and finding the point of maximum current level.
- 18. Once the current is at the desired level, press the button PIC. The line should disappear on the screen, and some image of the sample should appear.

#### Imaging/EDS Analysis:

The procedure to examining the sample is described below.

- 19. The initial magnification should be high. Try turning the MAG and FOCUS knobs back and forth to find some bright object to focus.
- 20. Initially, the condenser lens should be at 9.
- 21. Once the sample is focused, increase the magnification.
- 22. The working distance should be changed to 15mm to increase the resolution.
- 23. Proceed to increase the condenser lens to a value 11 or 12 depending on the resolution by turning the COND knob. Do not operate the SEM below the condenser value of 9.
- 24. Once the desired image is obtained, use the ANALYSIS program in the separate computer to capture the image onto the disk. Three resolutions are available to photograph the image from 1 to 3. The highest number corresponds to the best resolution, but it also not only takes up time in capturing the image, but the file size is over 10Mb. Typically, resolution 1 is used to capture the image of the sample from far away, while the resolution 2 is used to capture the finer details of the sample.
  - 25. To burn the scale into the captured image, click IMAGE-BURN SCALE.
  - 26. To save the images, drag the image files to the icon showing the disk-savecomputer icon. To print the image, click FILE-PRINT.
  - 27. In order to examine the type of elements present in the sample, EDS analysis is performed. This program is located in the third computer.

- 28. When the computer first starts, a window showing the parameters will popup. The accelerating voltage should be 20 KV in accordance to the value used to saturate the filament earlier, and the working distance should correspond to the value currently used at the time of SEM usage. To change any of the values, type in the value on the desired parameter line, then press ENTER, followed by clicking on CLOSE button to close the popup window
- 29. Click on the ANAL icon on the desktop.
- 30. Press the icon showing the person running to start the EDS analysis.
- 31. The deadtime of the detectorshould fall somewhere around 20%. If the deadtime is too low, then the condenser lens value needs to be decreased.
- 32. Click on the icon showing the guy standing still to stop the EDS analysis once the desired graph is obtained. To print out the graph, click on the FILE-PRINT.

#### Shutting Down/Sample Unloading:

The procedures to shutting down the SEM and unloading the sample are described below.

- 33. Accelerating voltage needs to be desaturated. The desaturation is done by turning the knob counterclockwise at the rate of ½ turn every 15 secs. Continue to turn the knob until the current filament reads 145.
- 34. Press the ACCEL VOLT button to turn off.
- 35. Press the red button to evacuate the loading/unloading chamber.
- 36. Once the red button goes out, open the main chamber door and slide in the rod.

37. Screw the rod into the sample stage, and pull out the sample stage from the main SEM chamber.

A REAL PROPERTY OF

- 38. Close the chamber door.
- 39. Press the red button.
- 40. Sign out in the logbook.

#### 8) Wafer Cleaning/Wet Station

This section describes the procedure for cleaning the wafer using Hydrofluoric (HF) Acid.

- Locate the nitrogen gas tank storage area adjacent to the cleanroom. Open the nitrogen tank valve. If the tank is empty, replace the empty tank with the new one from the gas storage located near the loading dock
- 2. Prepare to enter the cleanroom by wearing the appropriate apparel, including gown, gloves, shoe, and hat.
- 3. Once inside the cleanroom, make sure the nitrogen gun is working properly.
- 4. At the wet station, place the wafer gently onto the Teflon wafer holder using a plastic tweezer.
- 5. Turn on the filtered water, and proceed to rinse the wafer for a few seconds.
- 6. Next, rinse the wafer with acetone for about 20 seconds. The wafer can also be dipped in the beaker filled with acetone for the equal amount of time.
- 7. Then immediately, rinse the wafer with methanol for about 20 seconds. Likewise, the wafer can also be dipped in the beaker filled with methanol.

Rinse the wafer with filtered water by holding under the filtered water gun for about 20 seconds. Then dip it in the beaker filled with filtered water.

- 9. While the wafer is in the water in the beaker, proceed to HF etching. This is done by filling the Teflon container first with the measured amount of filtered water, followed by adding HF directly into the water. The amount of HF can vary from as much as 50 % concentration by volume to little as 10 %.
- 10. Take out the wafer from the water, and then dip it in the distilled HF Teflon container for about 5 minutes. This time should be more than enough.
- 11. The native oxide removal however, can be checked during the etching time by leaving the wafer under the running water from the filtered water gun. Water is hydrophilic to oxide, while water is hydrophobic to bare Si substrate. Thus if the water flows smoothly across the Si wafer, then the wafer should be dipped in HF Teflon container longer.
- 12. Once the wafer is clean of oxide, take it out of the Teflon container and rinse it under the filtered water gun. Dry the wafer by blowing gently with the nitrogen gun.
- 13. Once the wafer is completely dry, carefully place it in the Petri dish.
- 14. The used acetone, methanol and distilled HF should be poured into the appropriate chemical hazard container. Fill out the chemical hazard tag.
- 15. Finally, close the nitrogen gas tank.

#### E) Furnace Aluminum Endcap Designs

Following figures show the Autosketch drawings and the photographs for the various water-cooled aluminum endcaps that were designed and made for the furnace system. The Figures 132 and 133 show the drawings and the photographs of the optical-side Al endcaps. It is designed to accommodate the transmission of laser into the furnace as well as gas inlet. The figures in Figure 136 show the design and the photograph of the Right-pusher, where it was designed to accommodate the gas outlet, temperature and pressure measurement gauges, as well as port for sample transfer. Finally, the Figure 137 shows the middle stands which are designed to support the mullite tube and the endcaps.

## 1) Optics Holder/Components



Figure 132: Autosketch drawings of optics side Al endcaps



# **Optics Holder**

Figure 133: Autosketch drawings of optical window holder.



b)

Figure 134: Photographs showing the designed optical-side Al endcaps. a) side view b) front view

## 2) Right Pusher



MENTRAL TO ME

Figure 135: Autosketch drawing of right-pusher Al endcaps



Figure 136: Photograph showing the right pusher Al endcap

# 3) Middle Stands



Figure 137: Middle stands.

#### REFERENCES

- 1. National Nanotechnology Initiative Report, July (2000)
- 2. E. Leobandung, L. Guo, and S.Y. Chou, Appl. Phys. Lett. 67, 938 (1997)
- H. Namastsu, Y. Takahashi. M. Nagase, and K. Murase, J. Vac. Sci. Tech. B 13, 2532 (1995)
- 4. T. Ono, H. Saitoh, and M. Esashi, Appl. Phys. Lett, 70, 1852 (1999)
- 5. P.G. Collins, M.S. Arnold, and P. Avouris, Science, 292 (2001)
- 6. X. Duan, Y. Huang, R. Agarwal, and C. Lieber, Nature, 421, 16 (2003)
- 7. M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science, 8, (2001)
- 8. X. Duan, Y. Huang, Y. Cui, J. Wang, and C. Lieber, Nature, 409, 4 (2001)
- Y. Cui, X. Duan, J. Hu, and C. M. Lieber, Journal of Phys. Chem. B 104, 5213 (2000)
- 10. S.W. Chung, J.Y. Yu, and J.R. Heath, Appl. Phys. Lett. 76, 2068 (2000)
- 11. Y. Cui, Z. Zhong, D. Wang, W.U. Wang, and C.M. Lieber, Nanoletters, 3, 2 (2003)
- 12. Y. Cui and C.M. Lieber, Science 291, 851 (2001)
- 13. L.J. Lauhon, M.S. Gudiksen, D. Wang, and C.M. Lieber, Nature, 420, 7 (2002)
- 14. A. M. Morales and C. M. Lieber, Science, Vol.279, 9 Jan. (1998)
- 15. Y.H. Tang, Y.F. Zhang, N. Wang, W.S. Shi, C.S. Lee, I. Bello, and S.T. Lee, J. Vac. Sci. Tech. B 19(1), Jan/Feb (2001)
- 16. D.D.D. Ma, C.S.Lee, and S.T. Lee, Appl. Phys. Lett. 79, No. 15 (2001)
- 17. Y. Wang, G. Meng, L. Zhang, C. Liang, and J. Zhang, Chem Mater. 14, 1773-1777 (2002)
- 18. G. Gu, M. Burghard, G.T. Kim, G.S. Dusberg, P.W. Chiu, V. Krstic, S. Roth, and W.Q. Han, J. Appl. Phys. Vol 90, No.11, (2001)

- 19. E. Leobandung, L. Guo, and S.Y. Chou, Appl. Phys. Lett. 67, 938 (1997)
- 20. H. Namastsu, Y. Takahashi. M. Nagase, and K. Murase, J. Vac. Sci. Tech. B 13, 2532 (1995)
- 21. T. Ono, H. Saitoh, and M. Esashi, Appl. Phys. Lett, 70, 1852 (1999)
- 22. B. Xiang, H.Z. Zhang, G.H. Li, F.H. Yang, F.H. Su, R.M. Wang, J. Xu, G.W. Lu, X.C. Sun, Q. Zhao, and D.P. Yu, *Appl. Phys. Lett.* 82, 19 (2003)
- 23. M. W. Lee, H. Z. Twu, C.C. Chen, and C. H. Chen, Appl. Phys. Letts. 79, 22 (2001)
- 24. Y. Yan, P. Liu, M. J. Romero, and M. M. Al-Jassim, J. of Appl. Phys. 93, 8 (2003)
- 25. M.H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, Science, 292, 8 (2001)
- 26. J. Westwater, D.P. Gosain, S. Tomiya, S. Usui, and H. Ruda, J. Vac. Sci. Tech. B. 15, 3 (1997)
- 27. R.S. Wagner and W.C. Ellis, Appl. Phys. Lett. 4, 89 (1964)
- 28. E.I. Givargizov, J. Cryst. Growth 31, 20 (1975)
- 29. Y.H. Tang, Y.F. Zhang, N. Wang, C.S. Lee, X.D. Han, I.Bello, and S.T.Lee, J. of Appl. Phys., 85, 11 (1999)
- 30. Y.H. Tang, Y.F. Zhang, N. Wang, W.S. Shi, C.S. Lee, I. Bello, and S.T. Lee, J. of Vac. Sci. Tech B, 19, 1 (2001)
- 31. Z. Zhang, X.H. Fan, L. Xu, C.S. Lee, S.T. Lee, Chem Phys. Lett. 337, 18-24 (2001)
- 32. Z.W. Pan, Z.R. Dai, L. Xu, S.T. Lee, and Z.L. Wang, J. Phys. Chem. B, 105, 2507-2514 (2001)
- 33. Duan, and C.M. Lieber Advanced Materials, 12, (4), p. 298, (2000)
- 34. D. Dijkkamp et al., Appl. Phys. Lett. 51, 619-621 (1987)
- 35. F. Beech, and I.W. Boyd, "Photochemical Processing of Electronic Materials", Academic Press, New York, pp.387-429
- 36. X. D. Wu, B. Dutta, M. S. Hegde, A. Inam, T. Venkatesan, E. W. Chase, C. C. Chang, and R. Howard, *Appl. Phys. Letts.* 54, 179 (1989)

- 37. G.K. Hubler, *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey, and G.K. Hubler, Chapter 13, John Wiley & Sons Inc., (1994)
- 38. X. Mao, and R. Russo, Appl. Phys. A: Mater. Sci. Process. 64, 1 (1997)
- 39. M.A. Shannon, X.L. Mao, A Fernandez, W. Chan, and R.E.Russo, Anal. Chem. 67, 4522 (1995)
- 40. D.B. Geohegan, in *Pulsed Laser Deposition of Thin Films*, edited by E. Fogarassy and S. Lazare, North Holland, Amsterdam, (1992)
- 41. G. Han, and P.T. Murray, J. of Appl. Phys., 88, 2 (2000)
- 42. A. D. Akhsakhalyan, Y. A. Bityurin, S. V. Gaponov, A. A. Gudkov, and V. I. Luchin, Sov. Phys. Tech. Phys., 27, 969 (1982)
- 43. A. D. Akhsakhalyan, Y. A. Bityurin, S. V. Gaponov, A. A. Gudkov, and V. I. Luchin, Sov. Phys. Tech. Phys. 27, 973 (1982)
- 44. R. Kelly, J.J. Cuomo, P.A. Leary, J.E. Rothenberg, B.E. Braren, and C.F. Aliotta, Nucl. Instum. Meth, B9, 329 (1985)
- 45. R. Kelly and J.E. Rothenberg, Nucl. Instum. Meth. B7/8, 755 (1985)
- 46. M.W. Chase, C.A. Davies, J.R. Downey, D.J. Frurip, R.A. McDonald, and A.N. Syverud, JANAF, *Thermochemical Tables*, 3d ed. American Chemical Society, New York
- 47. R.L. Fleischer, P.B. Price, and R.M. Walker, J. of Appl. Phys. 36, 3645 (1965)
- 48. N. Itoh, and T. Nakayama, Appl. Phys. Lett. 92A, 471 (1982)
- 49. Y. Nakai, K. Hattori, A. Okano, N. Itoh, and R.F. Haglund, Nucl Instr. Meth. B58, 452 (1991)
- 50. H. Helvajian, and R. Welle, J. Chem Phys. 91, 2616 (1989)
- 51. N. Bloembergen, in Laser Ablations: Mechanisms and Applications-II, Proceedings of the Second International Conference Laser Ablation (Ref. 5), p.3
- 52. A. Vertes, R.W. Dreyfus, and D.E. Platt, IBM, J. Res. Dev. 38, 3 (1994)
- 53. J.C.S. Cools, *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey and G.K.Hubler, Chapter 19, Wiley, New York, (1994)
- 54. A. Vertes, R.W. Dreyfus, and D.E. Platt, IBM, J. Res. Dev. 38, 3 (1994)

- 55. G.E. Jellison Jr., and F.A. Modine, Appl. Phys. Lett. 41, 2 (1982)
- 56. H.J. Scheibe, A.A. Gorbunov, G.K. Baranova, N.V. Klassen, V.I. Konov, M.P. Kulakov, W. Pompe, A.M. Prokhorov, and H.J. Weiss, *Thin Solid Films*, 189, 283 (1990)
- 57. X. Zhang, S.S. Chu, J.R. Ho, C.P. Grigoropoulos, Applied Physics A 64, 545-552, (1997)
- 58. R. Kelly, and A. Miotello, *Pulsed Deposition of Thin Films*, edited by D.B. Chrisey, and G.K. Hubler, Wiley, New York (1994)
- 59. F.F. Chen, Introduction to Plasma Physics, Plenum, New York, Chapter 1 (1974)
- 60. D.B. Geohegan, *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey, and G.K. Hubler, Chapter 5, Wiley, New York (1994)
- 61. S. Metev, *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey, and G.K. Hubler, Chapter 3, Wiley, New York, (1994)
- 62. S. Metev, S. in *Laser Processing and Diagnostics (II)*, D. Bauerle, K.L. Kompa and L. Laude, eds. European Materials Research Society Symposium Proceeding Les Ulis Cedex, France, p. 143 (1986)
- 63. R.K. Singh, O.W. Holland, and J. Narayan, J. Appl. Phys. 68, 233 (1990)
- 64. F. P. Gagliano, and U. C. Paek, Appl. Opt., 13, 274 (1974)
- 65. D. B. Geohegan Mater. Res. Soc. Symp. Proc. 285, 26, (1993)
- 66. D. Lubben, S. A. Barnett, K. Suzuki, S. Gorbatkin, and J. E. Greene, J. Vac. Sci. Tech., **B3**, 968 (1985)
- 67. H. Dupendant, J. P. Gavigan, D. Givord, A. Lienard, J. P. Reborillat, and Y. Souche, *Appl. Surf. Sci.*, 43, 369 (1989)
- 68. K. Murakami, Laser Ablation of Electronic Materails: Basic Mechanisms and Applications (E. Fogarassy and S. Lazare, eds.) North Holland, Amsterdam, p. 125 (1992)
- 69. D. Lubben, S.A. Barnett, K. Suzuki, S. Gorbatkin, and J.E. Greene, J. Vac. Sci. Tech. B3, 968-974
- 70. M. Hanabusa, M. Suzuki, and S. Nishigaki, Appl. Phys. Lett. 38, 385-387 (1981)

- 71. S.M. Green, A. Pique, K.S. Harshavardhan, and J.S. Bernstein, *Pulsed Laser* Deposition of Thin Films, edited by D.B. Chrisey and G.K. Hubler, Chapter 2 (1994)
- 72. F. Beech, and I.W. Boyd, "Photochemical Processing of Electronic Materials", Academic Press, New York, pp.387-429, (1991)
- 73. Q. Lu, S. S. Mao, X. Mao, and R. E. Russo, Appl Phys. Lett. 80, 17 3072 (2002)
- 74. K.H. Wong, S.K. Hau, P.W. Chau, L.K. Leung, C.L. Choy, and M.K. Wong, J. *Mater. Sci. Lett.* **10** 801-803 (1981)
- 75. H. Sankur, W. J. Gunning, J. DeNatale, and J. Flintoff, Appl Phys Lett. 65, (1989)
- 76. E.G. Gamaly, A.V. Rode, and B. Luther-Davies, J. of Appl. Phys. 85, 8 (1999)
- 77. X. Xu, J. Appl. Phys. 77, 12 (1995)
- 78. Kennedy, R. J. Thin Solid Films, 214, 223 (1992)
- 79. Y. Wu, P. Yang, J. Am. Chem Soc, Published on Web (2001)
- 80. J.R. Arthur, and R.S. Wagner, US Pat. 3, 505 127 (1970)
- 81. M.K. Sunkara, S. Sharma, R. Miranda, G. Lian, and E.C.Dickey, Appl. Phys. Lett, Vol. 79, No. 10, (2001)
- W.G. Moffatt, Handbook of Binary Phase Diagrams (Genium, Schenectady, NY. 1976)
- 83. J.L. Liu, S.J. Cai, G.L. Jin, S.G. Thomas, and K.L. Wang, J. of Crystal Growth, 200, 106-111 (1999)
- 84. J.S. Horwitz and J.A. Sprague, *Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey, and G.K. Hubler, Chapter 8, Wiley, New York, (1994)
- 85. S. Metev, and M. Sendova, in *Trends in Quantum Electronics*, volume 1033, SPIE, Bellingham, p. 260
- 86. Y. Vui, L.J. Lauhon, M.S. Gudiksen, J. Wang, and C.M. Lieber, *Appl. Phys. Lett.* 78, 15 (2001)
- T. Yoshida, S. Takeyama, Y. Yamada and K. Mutoh, Appl. Phys. Lett. 68, 1772 (1996)
- 88. T. Makimura, Y. Kunii, and K. Mutoh, Jpn. J. Appl., Part I 35, 4780 (1996)

- 89. H. Z. Zhang, D. P. Yu, Y. Ding, Z. G. Bai, Q. L. Hang, and S. Q. Feng, Appl. Phys. Lett. 73, 3396 (1998)
- 90. Le Lay, Surface Science 132 169-204, (1983)
- 91. A.K. Green, and E. Bauer, J. of Appl. Phys. 47, 4 (1976)
- 92. A. Hiraki and M. Iwami, Japn J. Appl. Phys Suppl. 2, Part 2 (1974) 749
- 93. T. Narusawa, S. Komiya, and A. Hiraki, *Appl. Phys. Lett.* 20, 272 (1972); 22, 389 (1973)
- 94. L. Braicovich, C.M. Garner, P.R. Skeath, C.Y. Su, P.W. Chye, I. Lindau and W.E. Spicer, Phys. Rev. B20 (1979) 5131
- 95. A. Cros, J. Derrien, C. Moulettet, J.P. Gaspard, P. Lambin and F. Salvan, J. Physique 41, C8 (1980) 795
- 96. A. Hiraki, and E. Lugujjo, J. of Vac. Sci. Tech, 9, 1 (1971)
- 97. Kirakosian et al J. Appl. Phys. Vol. 90, No. 7, (2001)
- 98. J. Nogami, A.A. Baski, and C.F. Quate, Phys. Rev. Lett. 65, 1611 (1990)
- 99. P. Predecki, B.C. Giessen, and N.J. Grant, Trans. Metall. Soc. AIME 233, 1438 (1965)
- 100. T.R. Ananthraman, H.L. Luo, and W. Klement, Jun Nature, 210, 1040 (1966)
- 101. G.A. Anderson, J.L. Bestel, and A.A> Johnson, and B. Post, Mater. Sci. Eng. 7, 83 (1971)
- 102. L.H. Allen, J.R. Phillips, D. Theodore, C.B. Carter, R. Soave, J.W. Mayer, and G. Ottaviani, *Physical Review B*, **41**, 12 (1990)
- 103. G.D. Wilk, R.E. Martinez, J.F. Chervinsky, F. Spaepen, and J.A. Golovchenko, *Appl. Phys. Lett.* 65, 7 (1994)
- 104. X.H. Fan, L. Xu, C.P. Li, Y.F. Zheng, C.S. Lee, S.T. Lee, Chem Phys. Lett. 334, 229-232 (2001)
- 105. H.Y. Peng, Z.W. Pan, L. Xu, X.H. Fan, N. Wang, C.S. Lee, and S.T. Lee, Adv. Mater. 13, 5 (2001)
- 106. W. Shi, Y. Zheng, N. Wang, C.S. Lee, and S.T. Lee, Adv Mater. 13, 8 (2001)

- 107. Y.F. Zhang, Y.H. Tang, N. Wang, C.S. Lee, I. Bello, and S.T. Lee, *Phys Rev. B* 61, 4518 (2000)
- 108. Y.F. Tang, N. Wang, Y.F. Zhang, C.S. Lee, I. Bello, and S.T. Lee, *Appl. Phys. Lett.* **75**, 2921 (1999)
- 109. T. Takami, and I. Kusunoki, J. of Applied Phys. 91, 12 (2002)  $107^{24}$



