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FABRICATION AND CHARACTERIZATION OF DIAMOND FIELD EMITTERS FOR FIELD EMISSION DISPLAYS

presented by

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has been accepted towards fulfillment of the requirements for

PhD degree in Electrical Engineering

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FABRICATION AND CHARACTERIZATION OF DIAMOND FIELD EMITTERS FOR FIELD EMISSION DISPLAYS

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By

Dongsung Hong

A DISSERTATION

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

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ABSTRACT

FABRICATION AND CHARACTERIZATION OF DIAMOND FIELD EMITTERS FOR FIELD EMISSION DISPLAYS

By

Dongsung Hong

New materials, with low work function and high chemical immunity, are needed to produce low-cost and stable field emission display (FED). The unique intrinsic properties of diamond make it an excellent material for field emitter.

In the present work, using an IC-compatible fabrication process, a field emission testchip was designed, fabricated, and tested. The chip contains a number of test devices including a 1x4 pixel triode FED which was demonstrated for the first time. The testing of the chip revealed that it is important to enhance field emission current density for further development of FED.

Using different film growth conditions and post-deposition carbon implantation, the effect of defect on the field emission current density was systematically studied. The CH₄/ H_2 ratio, grain size, resistivity, and implantation dose in the ranges of 0.5-2%, 0.3-1.5 μ m, 1.7-189 Ω cm, and 5x10⁵-5x10⁶ cm⁻², respectively, were used to vary the defect density in the film.

Based on the field emission data collected from a variety of samples, it was found that emission from diamond is enhanced when (i) sp^3/sp^2 is low, (ii) peak at 1332 cm⁻¹ is wider, (iii) grain size and the roughness of film are small, (iv) film is highly doped, and (v) ion implantation dose is high while energy is low. The results seem to suggest that field

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electron

emission from polycrystalline diamond is affected by (i) defects and (ii) field enhancement at the grain tips. As all samples were treated in hydrogen at 900 °C, the electron affinity may be same for all samples.

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I can not forget all the support from Korean EE students and their family when I need help. Many friends whom I have known for years and whom I became to know here at Michigan State helped me in many occasions.

Finally but not least, I would like to thank my parents and family in Korea. Their patience, unconditional support, and love gave me the strength to finish this work.

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A. 1	Schematic of RFCVD system

LIST OF A

F-N Fowler

[C:Integrate

Mo: Molybd

FED: Feid E

LCD: Liquid

S: Silicon

CVD: Chem

NEA: Negat

RGA: Residu

996: Spin C

VPCVD: M

HFCVD: Ho

RFCVD: Ra

SiC: Silicon

AFM: Atom

SEM: Scann

DPLF: Dian

CRT: Catho

SiO: Silicor

Gr. Chrome

.TO: Indian

Zn Zinc

LIST OF ABBREVIATIONS

- F-N: Fowler-Nordheim
- IC: Integrated Circuit
- Mo: Molybdenum
- FED: Feid Emission Display
- LCD: Liquid Crystal Display
- Si: Silicon
- CVD: Chemical Vapor Deposition
- NEA: Negative Electron Affinity
- RGA: Residual Gas Analyzer
- SOG: Spin On Glass
- MPCVD: Microwave Plasma Chemical Vapor Deposition
- HFCVD: Hot Filament Chemical Vapor Deposition
- RFCVD: Radio Frequency Chemical Vapor Deposition
- SiC: Silicon Carbide
- AFM: Atomic Force Microscopy
- SEM: Scanning Electron Microscopy
- DPLF: Diamond Powder Loaded Fluid
- CRT: Cathode Ray Tube
- SiO_{2:} Silicon Dioxide
- Cr: Chrome
- ITO: Indium Tin Oxide
- Zn: Zinc

ZnO: Zii

J-V: Cur

W: Tuny

ZnO: Zinc Oxide

I-V: Current versus Voltage

W: Tungsten

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CHAPTER 1

RESEARCH MOTIVATION AND GOALS

1.1 Introduction

The theory for field emission was first proposed by Fowler and Nordheim (F-N) in 1928 [1], but its realization in the field of vacuum microelectronics could be possible through the development of modern integrated circuit (IC) technologies. Despite its advantage of vacuum transport of electrons over electron transport in solid, solid state devices have substituted major part of vacuum devices since technological development in early fifties mainly due to compactness. Ironically vacuum microelectronics area is revitalized thanks to the technological development of IC fabrication that helps make it possible to produce small vacuum devices.

Fabrication of microtip made of molybdenum (Mo) by Spindt *et al.* [2] in the mid seventies opened a new era for field emission devices. A variety of materials and structures were attempted by a number of research groups thereafter to improve the performance of devices with respect to their application needs [3, 4, 5]. Application possibilities of field emitter devices range from ultra fast switches, microwave amplifiers and generators, flat panel display devices, intense electron/ion sources, multiple electron sources, new electron beam lithography tools to miniature electron excitation devices [3, 4]. Mainly due

ie its perfo jeld d L jan Se açul. in i im <u>li</u>tt H.g. **L**ic 381 F.O.C. R ten li k ៍ខ្មែង . J: 1 12 Ę to its colossal market prospect, applying field emission devices to low cost and high performance flat panel display of modern information society has been major thrust of field emission research.

Low power consumption; wide viewing angle; and bright, fast, and high contrast image qualities are the advantages of field emission displays (FED) over the conventional liquid crystal displays (LCD). The first prototype FED, based on metal microtip emitters first fabricated by Spindt *et al.*, was reported in 1991 [6]. Si based prototypes have also been reported. However, in a silicon (Si) or metal FED, high work function (which means high supply voltage) and phosphor contamination of the tip are some of the problems. High work function (typically 4 eV) makes the field enhancement necessary which is achieved by using microtip emitters. The microtip fabrication increases the processing cost. New materials, with low work function and high chemical immunity, are needed to produce low-cost and stable FED.

Recent advances in diamond film technology have led to inexpensive polycrystalline chemical-vapor deposited (CVD) diamond films on non-diamond substrates [7,8]. Due to its negative electron affinity (NEA) [9], immunity to chemical attack, hardness and very high thermal conductivity (highest at 300 K), diamond is an excellent material for field emitters, especially for FED. Field emission was demonstrated from diamond or diamond-like materials [10, 11, 12, 13, 14, 15]. Although a diode-based diamond-like FED has been demonstrated [12], many issues, related mainly to the diamond quality and process technology, must be resolved before any reliable diamond FEDs can be realized.

1.2 Objective of This Work

Early works on diamond field emitters have successfully demonstrated the excellent

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emission properties of diamond field emitters. Being in an early stage of diamond field emission research, these studies are mainly focused on initial measurement of field emission from various diamonds itself leaving some unanswered questions mainly associated with the mechanism of field emission from diamond. To be able to answer these questions, it is necessary to study correlation between emission characteristic and diamond properties such as sp³/sp² ratio, doping concentration and grain size. To apply diamond's unique properties to real world application, it is important to develop fabrication technology for diamond field emitters, compatible to standard IC process. Thus, in order to achieve these two main objectives, one has to address following issues.

- The development of a fabrication technique for diamond field emitter compatible with standard IC fabrication processes using testchip approach.
- (2) Design and systematic execution of a series of experiments to collect emission data from a number of different film growing conditions and post growth treatments.
- (3) Demonstration of application of the developed fabrication technology into diamond FED in triode mode.

Figure 1.1 illustrates a number of essential tasks to be done in order to realize diamond FED in triode configuration. Work covered in this research is limited to those tasks with solid frame.

1.3 Dissertation Organization

Research motivation and goals are defined in Chapter 1. In Chapter 2, a complete derivation of the F-N theory of field emission, diamond properties, the current technologies of diamond field emitters, and suggested models are described. Brief review




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of CVD diamond infrastructure is given as well. Chapter 3 deals with the design and construction of two diamond CVD systems and characterization system including anode design. Chapter 4 focuses on the development of IC compatible diamond field emitter fabrication technology. Characterization of various samples and qualitative effort to explain the measurement results are discussed in Chapter 5. In Chapter 6, two applications of diamond field emitter are demonstrated, namely, diamond FEDs in triode mode and pressure sensor. Summary and conclusions are given in Chapter 7.

CHAPTER 2

BACKGROUND

2.1 Introduction

In this chapter, derivation of F-N equation will be presented in detail. Later, diamond field emitters reported so far by others and some explanations of emission process from diamond will be summarized. Nucleation, patterning, doping, and metallization technologies are reviewed briefly.

2.2 Derivation of Fowler-Nordheim Equation

Let's consider the surface potential energy barrier shown in Figure 2.1 denoted by the solid curve. This curve includes the image potential component $e^2/4z$ and applied field effects component eFz with respect to how they affect a step barrier when combined. The potential energy barrier can be approximated by

$$V(z) = E_F + \phi - \frac{e^2}{4z} - eFz \qquad (2.1)$$
$$= 0 \qquad \qquad for z > 0$$

for z < 0

The peak of the barrier described by Equation 2.1 occurs at z_{max} , where z_{max} is defined by

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Figure 2.1. Surface potential barrier of a metal-vacuum system.

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$$\frac{dV}{dz} = 0 \tag{2.2}$$

If E_F and ϕ are independent of z, Equation 2.2 gives:

$$\frac{dV}{dz} = \frac{e^2}{4z_{max}^2} - eF = 0$$
(2.3)

which gives

$$z_{max} = \left(\frac{e}{4F}\right)^{1/2} \tag{2.4}$$

At $z=z_{max}$, Equation 2.1 becomes:

$$V_{max} = V(z_{max}) = E_F + \phi - \frac{e^2}{4\left(\frac{e}{4F}\right)^{1/2}} - eF\left(\frac{e}{4F}\right)^{1/2}$$
(2.5)

$$V_{max} = E_F + \phi - \frac{e^{3/2}F^{1/2}}{2} - \frac{e^{3/2}F^{1/2}}{2}$$
(2.6)

$$V_{max} = E_F + \phi - (e^3 F)^{1/2}$$
(2.7)

For a theory of electron emission from metal surfaces, it is necessary to consider (i) the number of electrons with energy between W and W + dW normal to the surface impinging on the surface barrier, N(W), and (ii) the tunneling probability of electron through the barrier, D(W). Then P(W)=N(W)D(W) will be the number of electrons per area per second per energy range dW, that penetrate the barrier. Hence, the emitted current density, i.e. the number of electrons emitted per unit area per unit time, in the energy range W and W+dW is given by:

$$J = eN(W)D(W)dW$$
(2.8)

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If the electron energy range extends from $-\infty$ to ∞ , Equation 2.8 becomes:

$$J = e \int_{-\infty}^{\infty} N(W) D(W) dW$$
 (2.9)

Let's start to evaluate N(W) first. Assuming the electron follows Fermi-Dirac statistics, N(W) is given by [16]

$$N(W) = \frac{4\pi m}{h^3} \int_W^\infty f(E) dE$$
(2.10)

where W is the energy of tunneling electron and f(E) is Fermi-Dirac distribution function. Using the Fermi-Dirac distribution function

$$N(W) = \frac{4\pi m}{h^3} \int_{W}^{\infty} \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]} dE$$
(2.11)

Let

$$\frac{(E-E_F)}{k_BT} = x \tag{2.12}$$

then

$$\frac{dE}{k_B T} = dx \tag{2.13}$$

$$dE = k_B T dx \tag{2.14}$$

Limits of integration change according to Equation 2.12:

$$\infty \to \infty$$
 (2.15)

$$W \to \frac{W - E_F}{k_B T} \tag{2.16}$$

Then Equation 2.11 becomes

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$$N(W) = \frac{4\pi m}{h^3} \int_{\frac{W-E_F}{k_B T}}^{\infty} \frac{k_B T}{1 + \exp[x]} dx$$
(2.17)

which, using standard form from integration table [17]

$$\int \frac{dx}{1+e^x} = \ln \frac{1}{1+e^{-x}}$$
(2.18)

becomes

$$N(W) = \frac{4\pi m k_B T}{h^3} \ln \frac{1}{1 + e^{-x}} \bigg|_{\frac{W - E_F}{k_B T}}$$
(2.19)

$$N(W) = \frac{4\pi m k_B T}{h^3} \left[\ln \left(\frac{1}{1 + e^{-\infty}} \right) - \ln \left(\frac{1}{1 + e^{-\frac{W - E_F}{k_B T}}} \right) \right]$$
(2.20)

$$N(W) = \frac{4\pi m k_B T}{h^3} \left[\ln(1) - \ln(1) + \ln \left(1 + e^{-\frac{W - E_F}{k_B T}} \right) \right]$$
(2.21)

$$N(W) = \frac{4\pi m k_B T}{h^3} \ln \left[1 + \exp\left(-\frac{W - E_F}{k_B T}\right) \right]$$
(2.22)

Each of these electrons has a probability D(W) to be transmitted through the surface potential barrier. Transmission coefficient for the potential barrier shown in Figure 2.1 is given by [16],

$$D(W) = \exp\left(-\int_{z_1}^{z_2} \sqrt{\frac{32\pi^2 m}{h^2} [V(z) - W]} dz\right)$$
(2.23)

when $W < V_{max}$, z_1 and z_2 are two real roots of V(z)-W=0 as shown in Figure 2.1. Using Equation 2.1 which expresses the potential energy in terms of the applied field and image force effect, the above equation can be written as:

$$D(W) = \exp\left(-\int_{z_{1}}^{z_{2}} \sqrt{\frac{32\pi^{2}m}{h^{2}} \left[E_{F} + \phi - W - \frac{e^{2}}{4z} - eFz\right]} dz\right)$$
(2.24)

Let's find two real roots of the V(z)-W=0

$$V(z) - W = E_F + \phi - W - \frac{e^2}{4z} - eFz = 0$$
 (2.25)

$$(E_F + \phi - W)z - \frac{e^2}{4} - eFz^2 = 0$$
(2.26)

$$z^{2} - \frac{(E_{F} + \phi - W)}{eF} z + \frac{e}{4F} = 0$$
 (2.27)

$$z = \frac{\frac{(E_F + \phi - W)}{eF} \pm \sqrt{\frac{(E_F + \phi - W)^2}{e^2 F^2} - \frac{4e}{4F}}}{2}$$
(2.28)

$$z = \frac{\frac{(E_F + \phi - W)}{eF} \pm \sqrt{\frac{(E_F + \phi - W)^2}{e^2 F^2} - \frac{(E_F + \phi - W)^2}{e^2 F^2} \frac{e^3 F}{(E_F + \phi - W)^2}}{2}$$
(2.29)

$$z = \frac{\frac{(E_F + \phi - W)}{eF} \pm \frac{(E_F + \phi - W)}{eF} \sqrt{1 - \frac{e^3 F}{(E_F + \phi - W)^2}}}{2}$$
(2.30)

$$z = \frac{(E_F + \phi - W)}{2eF} \left[1 \pm \sqrt{1 - \frac{e^3 F}{(E_F + \phi - W)^2}} \right]$$
(2.31)

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$$\binom{z_2}{z_1} = \frac{(E_F + \phi - W)}{2eF} \left[1 \pm \sqrt{1 - \frac{e^3 F}{(E_F + \phi - W)^2}} \right]$$
(2.32)

The above defines the limits of integration for the transmission coefficient expression. These limits correspond to the distance the electron must travel in tunneling through the potential barrier. The shorter the distance, the higher the probability of tunneling.

Let

$$y = \frac{\sqrt{e^3 F}}{\phi + E_F - W}$$
(2.33)

and the integration variable:

$$u = \frac{2eF}{\phi + E_F - W}z \tag{2.34}$$

Then

$$z = \frac{\phi + E_F - W}{2eF}u \tag{2.35}$$

$$dz = \frac{\phi + E_F - W}{2eF} du \tag{2.36}$$

Using Equation 2.32 and 2.33

$$z_{2} = \frac{(E_{F} + \phi - W)}{2eF} [1 + \sqrt{1 - y^{2}}]$$
(2.37)

$$z_1 = \frac{(E_F + \phi - W)}{2eF} [1 - \sqrt{1 - y^2}]$$
(2.38)

Substituting Equation 2.37 and 2.38 into Equation 2.34

$$u_2 = (1 + \sqrt{1 - y^2}) \tag{2.39}$$

Then **R**₁ in E

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$$u_1 = (1 - \sqrt{1 - y^2}) \tag{2.40}$$

Then R_1 in Equation 2.24 becomes:

$$R_{1} = \sqrt{\frac{32\pi^{2}m}{h^{2}}} \left[E_{F} + \phi - W - \frac{e^{2}}{4\left(\frac{\phi + E_{F} - W}{2eF}u\right)} - eF\left(\frac{\phi + E_{F} - W}{2eF}u\right)} \right]$$
(2.41)

$$R_{1} = \sqrt{\frac{32\pi^{2}m}{h^{2}}} \left[E_{F} + \phi - W - \frac{e^{3}F}{2(\phi + E_{F} - W)u} - \frac{\phi + E_{F} - W}{2}u \right]$$
(2.42)

$$R_{1} = \sqrt{\frac{16\pi^{2}m}{h^{2}}} \left[\frac{2(\phi + E_{F} - W)u - \frac{(\phi + E_{F} - W)e^{3}F}{(\phi + E_{F} - W)^{2}} - (\phi + E_{F} - W)u^{2}}{u} \right]$$
(2.43)

$$R_{1} = \sqrt{\frac{16\pi^{2}m}{h^{2}} \left[\frac{2(\phi + E_{F} - W)u - (\phi + E_{F} - W)y^{2} - (\phi + E_{F} - W)u^{2}}{u} \right]}$$
(2.44)

$$R_{1} = \frac{4\pi}{h} \sqrt{m(\phi + E_{F} - W) \left[\frac{2u - y^{2} - u^{2}}{u}\right]}$$
(2.45)

Then I₁ becomes:

$$I_{1} = \int_{u_{1}}^{u_{2}} R_{1} \frac{(\phi + E_{F} - W)}{2eF} du$$
(2.46)

$$I_{1} = \frac{2\pi \sqrt{m(\phi + E_{F} - W)^{3}} \int_{(1 - \sqrt{1 - y^{2}})}^{(1 + \sqrt{1 - y^{2}})} \sqrt{\frac{-u^{2} + 2u - y^{2}}{u}} du$$
(2.47)

Using the substitution $\eta^2 = u$ in Equation 2.47 brings the integral I₂ to standard form which can be evaluated by an elliptical integral:

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$$2\eta d\eta = du \tag{2.48}$$

$$u_2 \to 1 + \sqrt{1 - y^2} \tag{2.49}$$

$$\eta_2 \to \sqrt{1 + \sqrt{1 - y^2}} \tag{2.50}$$

$$u_1 \to 1 - \sqrt{1 - y^2} \tag{2.51}$$

$$\eta_1 \to \sqrt{1 - \sqrt{1 - y^2}} \tag{2.52}$$

$$I_{2} = \int_{\sqrt{1-\sqrt{1-y^{2}}}}^{\sqrt{(1+\sqrt{1-y^{2}})}} \sqrt{\frac{-\eta^{4}+2\eta^{2}-y^{2}}{\eta^{2}}} 2\eta d\eta$$
(2.53)

$$I_{2} = 2 \int_{\sqrt{1 - \sqrt{1 - y^{2}}}}^{\sqrt{1 + \sqrt{1 - y^{2}}}} \sqrt{-\eta^{4} + 2\eta^{2} - y^{2}} d\eta$$
(2.54)

Add and substract $\sqrt{1-y^2}$, $\eta\sqrt{1-y^2}$, and 1 to R₂ to get:

$$R_2 = -\eta^4 + \eta^2 + \eta^2 + \sqrt{1 - y^2} - \sqrt{1 - y^2} + \eta \sqrt{1 - y^2} - \eta \sqrt{1 - y^2} - 1 + 1 - y^2$$
(2.55)

which after factorization becomes:

$$R_2 = (1 + \sqrt{1 - y^2} - \eta^2)(\eta^2 - (1 - \sqrt{1 - y^2}))$$
(2.56)

$$b = \sqrt{1 - \sqrt{1 - y^2}}$$

$$a = \sqrt{1 + \sqrt{1 - y^2}}$$
(2.57)

$$R_2 = (a^2 - \eta^2)(\eta^2 - b^2)$$
(2.58)

Equation 2.54 now becomes:

$$I_2 = 2 \int_b^a \sqrt{(a^2 - \eta^2)(\eta^2 - b^2)} d\eta$$
 (2.59)

Equation 2.47 now becomes:

$$I_{1} = \frac{4\pi\sqrt{m(\phi + E_{F} - W)^{3}}}{heF} \int_{b}^{a} \sqrt{(a^{2} - \eta^{2})(\eta^{2} - b^{2})} d\eta$$
(2.60)

Using elliptic integral table [17]

$$I_{1} = \frac{4\pi\sqrt{m(\phi + E_{F} - W)^{3}}}{heF} \frac{2a}{3} \left[\frac{(a^{2} + b^{2})}{2} \int_{0}^{\pi/2} \sqrt{1 - k^{2}\sin^{2}\theta} d\theta - b^{2} \int_{0}^{\pi/2} \frac{d\theta}{\sqrt{1 - k^{2}\sin^{2}\theta}} \right]$$

$$I_{1} = \frac{8\pi\sqrt{m(\phi + E_{F} - W)^{3}}}{3heF} a \left[\frac{(a^{2} + b^{2})}{2} E(k) - b^{2}K(k) \right]$$
(2.61)

where 'K(k)' and 'E(k)' are elliptic integrals of the first and second kind respectively:

$$K(k) = \int_{0}^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}}$$
(2.62)

$$E(k) = \int_{0}^{\pi/2} \sqrt{1 - k^2 \sin^2 \theta} d\theta \qquad (2.63)$$

And,

$$k^2 = \frac{a^2 - b^2}{a^2} \tag{2.64}$$

$$V_1 = \sqrt{1 + \sqrt{1 - y^2}} \left[\frac{1 + \sqrt{1 - y^2}}{2} (E(k) - (1 - \sqrt{1 - y^2})K(k)) \right]$$
(2.65)

$$V_1 = \sqrt{1 + \sqrt{1 - y^2}} [E(k) - (1 - \sqrt{1 - y^2})K(k)]$$
(2.66)

where:

$$v(y) = 2^{-1/2} \sqrt{1 + \sqrt{1 - y^2}} [E(k) - (1 - \sqrt{1 - y^2})K(k)]$$
(2.67)

Then I₁ becomes:

$$I_{1} = \frac{8\pi \sqrt{2m(\phi + E_{F} - W)^{3}}}{3heF} v(y)$$
(2.68)

The transmission coefficient can then be expressed as:

$$D(W) = \exp\left(-\frac{8\pi\sqrt{2m(\phi + E_F - W)^3}}{3heF}\nu(y)\right)$$
(2.69)

Equation 2.9 can be written as

$$J = e \int_{-\infty}^{\infty} \frac{4\pi m k_B T}{h^3} \ln \left(1 + e^{-\frac{W - E_F}{k_B T}} \right) \exp \left[-\frac{8\pi \sqrt{2m(\phi + E_F - W)^3}}{3heF} v(y) \right] dW \qquad (2.70)$$

Let's evaluate the above expression at (or near) absolute zero temperature.

First consider the exponent, G(W) in the transmission coefficient portion of Equation 2.70:

$$G(W) = -\frac{8\pi\sqrt{2m(\phi + E_F - W)^3}}{3heF}v(y)$$
(2.71)

with

$$y = \frac{\sqrt{e^3 F}}{\phi + E_F - W}$$
(2.72)

Since electrons have energies in the neighborhood of the Fermi level E_{F} , using Taylor's expansion theorem:

$$G(W) = G(E_F) + G'(E_F)(W - E_F) + \frac{G''(E_F)}{2!}(W - E_F)^2 + \dots$$
(2.73)

Only first two terms will be considered here.

$$G(W) = G(E_F) + G'(E_F)(W - E_F)$$
(2.74)

Using Equation 2.71, G(W) at $W=E_F$ is given by

$$G(E_F) = -\frac{8\pi\sqrt{2m\phi^3}}{3heF}v\left(\frac{\sqrt{e^3F}}{\phi}\right)$$
(2.75)

G'(W) in the second term is given by:

$$G'(W) = \frac{d}{dW} \left[-\frac{8\pi \sqrt{2m(\phi + E_F - W)^3}}{3heF} v \left(\frac{\sqrt{e^3F}}{\phi + E_F - W} \right) \right]$$
(2.76)

Using

$$(uv)' = u'v + uv'$$
(2.77)

u'v is given by

$$\frac{-8\pi}{3heF} \left[\frac{1}{2} (2m(\phi + E_F - W)^3)^{-1/2} 2m3(\phi + E_F - W)^2 \nu(y) \right]$$
(2.78)

and uv' is given by

$$\frac{-8\pi}{3heF} \left[\sqrt{2m(\phi + E_F - W)^3} \frac{d}{dW} \nu(y) \right]$$
(2.79)

Equation 2.76 becomes:

$$G'(W) = \frac{-8\pi}{3heF} \left[\frac{-3(\phi + E_F - W)^2 m}{\sqrt{2m(\phi + E_F - W)^3}} v(y) + \sqrt{2m(\phi + E_F - W)^3} \frac{d}{dW} v(y) \right]$$
(2.80)

Using

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$$\frac{dv}{dW} = \frac{dv\,dy}{dydW} \tag{2.81}$$

$$\frac{dv}{dW} = \frac{dv}{dy} \frac{\sqrt{e^3 F}}{\left(\phi + E_F - W\right)^2}$$
(2.82)

$$G'(W) = \frac{-8\pi}{3heF} \left[\frac{-3(\phi + E_F - W)^2 m}{\sqrt{2m(\phi + E_F - W)^3}} v(y) + \sqrt{2m(\phi + E_F - W)^3} \frac{\sqrt{e^3F}}{(\phi + E_F - W)^2 dy} \frac{dv}{(2.83)} \right]$$

$$= \frac{-8\pi\sqrt{2m(\phi + E_F - W)}}{3heF} \left[\frac{-3}{2}v(y) + \frac{\sqrt{e^3F}}{(\phi + E_F - W)}\frac{dv}{dy}\right]$$
(2.84)

$$= \frac{4\pi\sqrt{2m(\phi + E_F - W)}}{heF} \left[v(y) - \frac{2ydv}{3dy} \right]$$
(2.85)

Let $t(y) = v(y) - \frac{2}{3}y\frac{d}{dy}v(y)$ then

$$G'(W) = \frac{4\pi \sqrt{2m(\phi + E_F - W)}}{heF} t(y)$$
(2.86)

$$G'(E_F) = \frac{4\pi\sqrt{2m\phi}}{heF}t(y)$$
(2.87)

Equation 2.74 becomes

(2.88)

$$G(W) = -\frac{8\pi\sqrt{2m\phi^3}}{3heF}v\left(\frac{\sqrt{e^3F}}{\phi}\right) + \frac{4\pi\sqrt{2m\phi}}{heF}t(y)(W-E_F)$$

As the temperature approaches absolute zero,

$$k_{B}T \ln \left(1 + e^{-\frac{W - E_{F}}{KT}}\right) = 0 \qquad \text{when } W > E_{F}$$

$$= E_{F} - W \qquad \text{when } W < E_{F}$$
(2.89)

Thus, from Equation 2.70, it follows that:

$$J = 0 \quad \text{when } W > E_F$$

$$J = \frac{e4\pi m}{h^3} \int_{-\infty}^{E_F} (E_F - W) \exp[G(W)] \, dW \quad \text{when } W < E_F$$
(2.90)

As at T=0 K the highest energy is E_F , the limit of integral in Equaion 2.90 changed to $-\infty$ to E_F .

Using Equation 2.74:

$$J = e \frac{4\pi m}{h^3} \int_{-\infty}^{E_F} \exp[G(E_F) + G'(E_F)(W - E_F)](E_F - W)dW$$
(2.91)

$$J = \frac{e4\pi m}{h^{3}} \exp[G(E_{F}) - G'(E_{F})E_{F}] \int_{-\infty}^{E_{F}} \exp[G'(E_{F})W](E_{F} - W)dW$$
(2.92)
$$C_{1}$$

$$I_{3}$$

$$I_{3} = \int_{-\infty}^{E_{F}} E_{F} \exp[G'(E_{F})W]dW - \int_{-\infty}^{E_{F}} W \exp[G'(E_{F})W]dW$$
(2.93)
$$I_{4} \qquad I_{5}$$

First integral I₄ becomes

$$I_4 = \left. \frac{E_F}{G'(E_F)} \exp[G'(E_F)W] \right|_{-\infty}^{E_F}$$
(2.94)

For second integral I_5 , let's use integration by part

$$\int u'v = uv - \int uv' \tag{2.95}$$

Let
$$u' = \exp[G'(E_F)W]$$
, $= \frac{\exp[G'(E_F)W]}{G'(E_F)}$, $v=W, v'=1$

Then second integral becomes

$$I_{5} = -\frac{\exp[G'(E_{F})W]W}{G'(E_{F})} \bigg|_{-\infty}^{E_{F}} + \int_{-\infty}^{E_{F}} \frac{1}{G'(E_{F})} \exp[G'(E_{F})W]dW$$
(2.96)

$$= -\frac{\exp[G'(E_F)W]W}{G'(E_F)}\bigg|_{-\infty}^{E_F} + \frac{1}{G'^2(E_F)}\exp[G'(E_F)W]\bigg|_{-\infty}^{E_F}$$
(2.97)

Let's combine the first integral and second integral

$$I_{3} = \frac{E_{F}}{G'(E_{F})} \exp[G'(E_{F})W] \bigg|_{-\infty}^{E_{F}} - \frac{\exp[G'(E_{F})W]W}{G'(E_{F})}\bigg|_{-\infty}^{E_{F}} + \frac{1}{G'^{2}(E_{F})} \exp[G'(E_{F})W]\bigg|_{-\infty}^{E_{F}}$$
(2.98)

$$= \frac{E_F}{G'(E_F)} \exp[G'(E_F)W] \bigg|_{-\infty}^{E_F} - \frac{1}{{G'}^2(E_F)} \exp[G'(E_F)W][WG'(E_F) - 1] \bigg|_{-\infty}^{L_F}$$
(2.99)

$$= \frac{E_F}{G'(E_F)} \exp[G'(E_F)E_F] - \frac{1}{{G'}^2(E_F)} \exp[G'(E_F)E_F][E_FG'(E_F) - 1]$$
(2.100)

$$= \frac{1}{{G'}^2(E_F)} \exp[G'(E_F)E_F][E_FG'(E_F) - E_FG'(E_F) + 1]$$
(2.101)

$$I_{3} = \frac{\exp[G'(E_{F})E_{F}]}{{G'}^{2}(E_{F})}$$
(2.102)

Then J becomes:

$$J = \frac{e4\pi m}{h^3} \frac{e^{G'(E_F)E_F}}{{G'}^2(E_F)} \left(e^{G(E_F) - G'(E_F)E_F}\right)$$
(2.103)

$$= \frac{e4\pi m}{h^3 {G'}^2(E_F)} \exp[G(E_F)]$$
(2.104)

Substituting $G(E_F)$ from Equation 2.75 and $G'(E_F)$ from Equation 2.87

$$J = \frac{e^{3}F^{2}}{8\pi h \phi t^{2}(y)} \exp\left[-\frac{8\pi \sqrt{2m} \phi^{3/2}}{3heF} v(y)\right]$$
(2.105)

where

$$t(y) = v(y) - \frac{2}{3}y \frac{d}{dy}v(y)$$
(2.106)

and

$$v(y) = 2^{-1/2} \sqrt{1 + \sqrt{1 - y^2}} [E(k) - (1 - \sqrt{1 - y^2})K(k)]$$
(2.107)

Substituting all numerical parameter of

m=9.11x10⁻³¹ kg
k_B= 1.38x10⁻²³ J/K
h=6.63x10⁻³⁴ Js
e=1.6x19⁻¹⁹ C

$$J = \frac{1.54 \times 10^{-6} F^2}{\phi t^2(y)} \exp\left[-6.83 \times 10^7 \frac{\phi^{3/2}}{F} v(y)\right]$$
(2.108)

2.3 Fowler-Nordheim plot

 $t^{2}(y)$ vs. y and v(y) vs. y curves are shown in Figure 2.2. At (or very near) absolute zero temperature, y value is close to 0 since electron enegry is close to E_F. In this case, we can approximte $t^{2}(y)=v(y)=1$ for ease of discussion. Let d = the emitter-to-gate



Figure 2.2. t(y) and v(y) as a fuction of y.

3] çU 01 Nev 0ŗ Clear often 2.4 Th े भग ich af thiter distance such that F=V/d. Now let A= the emitting area in cm². These two assignments allow us to put the F-N equation in Equation 2.113 in terms of the physically tractable quantities of current, I and voltage V. So

$$J = 1.54 \times 10^{-6} \frac{V^2}{\phi d^2} \exp\left[-6.83 \times 10^7 \frac{\phi^{3/2} d}{V}\right]$$
(2.109)

or

$$\frac{I}{V^2} = 1.54 \times 10^{-6} \frac{A}{\phi d^2} \exp\left[-6.83 \times 10^7 \frac{\phi^{3/2} d}{V}\right]$$
(2.110)

Now take the log of both sides

$$\log \frac{I}{V^2} = \log \left(1.54 \times 10^{-6} \frac{A}{\phi d^2} \right) - 6.83 \times 10^7 \frac{\phi^{3/2} d}{V} \log e$$
(2.111)

or

$$\log \frac{I}{V^2} = \log \left(1.54 \times 10^{-6} \frac{A}{\Phi d^2} \right) - 2.97 \times 10^7 \frac{\Phi^{3/2} d}{V}$$
(2.112)

Clearly, a plot of the $\log \frac{l}{v^2}$ vs. $\frac{1}{v}$ will have straight line. This plot is called F-N plot and often used to confirm field emission.

2.4 Diamond Field Emitters

The chemical, thermal, and electrical properties of the emitter material play an important role in the design of on-chip vacuum tubes. To achieve high current density at low applied voltages, two approaches are feasible. One approach is to sharpen the emitters to enhance the electric field, resulting in a greater field effect. Another approach

5 ċ 13 ja: 101 **7**0 ť.t. WD qui ¢mi ion cond "ite UNI Va.11 of the anviro D; Si 270 iciocity acilitate is to use emitter materials with low work function. Thus less energy is required to emit electrons into vacuum. In other words, the emitters (if semiconductors are used) should have a low (or even negative) electron affinity so that lower electric fields are required for emission.

Low electron affinity is just one of many desired emitter properties. In addition to a low electron affinity, the ideal emitter would have a high carrier concentration and high mobility, and thus a high electrical conductivity (from $\sigma=nq\mu$). It would also have a high electric field breakdown strength so as to withstand the locally high fields. The thermal conductivity should be high so the heat generated by the high current densities could be quickly dissipated. Finally, the emitter should be chemically inert since impurities in the emission surface can increase the material work function. Early metal emitters suffered from impurity contamination [18] and structural fragility, although their high electrical conductivity made them promising emitter candidates. Si microtips have been shown to withstand high current densities (J > 1000 A/cm⁻²), but work function raising impurities continue to be a problem, along with current instability and the need for an ultra high vacuum environment [19]. Diamond, however, has the possibility of overcoming many of these obstacles and greatly improving device performance, particularly in harsh environments.

Diamond's high electric field breakdown coefficient of 10^7 Vcm^{-1} is 30 times that of Si and 1.5 times that of GaAs [20], meaning locally high electric fields could be produced and the device would continue to function properly. The electron saturation velocity in diamond is nearly twice that of silicon at $2.7 \times 10^7 \text{ cms}^{-1}$ [20], which would facilitate high speed device applications. Diamond is nearly impervious to chemical

attack and therefore work function raising contamination encountered in metals and Si would be of a lesser concern. The resistance of diamond to chemical attack means that the device may be operated in a lower vacuum environment, thus relaxing fabrication demands. The thermal conductivity of diamond is unmatched at 20W/cm-K (for type IIb) [19] and is nearly 5 times that of copper, so it should be able to quickly dissipate the power induced by the high current densities. In the (111) direction, the electron affinity of diamond is very small and perhaps even negative [9], so emission could be realized at lower applied fields. For type IIb diamond the electrical resistivity is on the order of 10-1000 ohm-cm [21], so conductivity of type IIb diamond is resonably high.

Recently, the research activity in field emission from diamond has seen an exponential growth [10, 11, 12, 13, 14, 15] which is due mainly to its NEA [9] and immunity to chemical attack. Low anode voltages, simplified fabrication process, less stringent vacuum requirements, and high stability are some of the consequences of diamond's unique properties. The simplified fabrication process is expected to result in lower cost.

The field emission has been demonstrated from a diamond junction device [10], homoepitaxial diamond [11], amorphous diamond [12], polycrystalline diamond [13,15] and diamond coated Si tip [14]. The emission was observed for electric fields in the range of 0.03 - 0.5 MV/cm which is two orders of magnitude lower than that for typical Si or metal emitters. Current densities of up to 10 Acm⁻² have been reported. Prototype FED based on diamond and carbon have been reported [12, 22] as well. Carbon based field emitters reported are summarized in Table 2.1.

Material & structure	Current I or Current densigy J	Applied potential V or field E	Deposition method	Reference
Cone shaped glassy carbon	50 µ.A	V~1350 V		[23]
DLC coated Si tip	І _а =8µА	V_{a} =300V V_{g} =120V	PECVD	[24]
DLC film on glass or Si	I=65μA	E=22V/μm	PECVD	[25]
Tetrahedral amor- phous Carbon film	I~20 μA	E~21 V/µm	Filtered cathodic vacuum arc plasma	[26]
Diamond coated Si tip			CVD	[27]
Diamond coated Si tip array	I _{max} = 80 mA at pulse mode J _{max} =320mA/cm ²	V _{max} =960V E _{max} =6.4V/μm	HFCVD	[28]
Diamond coated Si tip array			HFCVD	[29]
N doped DLC film	I ~ 70 µA	E ~ 20V/µm	PECVD	[30]
DLC coated Si tip	Ι~45 μΑ	I _a ~ 350V	RFCVD	[31]
Pyramidal diamond microtip			PECVD	[32]

Table 2.1 Summary of various diamond field emitters

Material & structure	Current I or Current densigy J	Applied potential V or field E	Deposition method	Reference
Diamond wedge arrays by transfer mold technique	J=800 μA/cm ²	V= 600 V	PECVD	[33]
Matrix carbon				[34]
CVD diamond film	J=10mA/cm ²	E=30V/μm	MPCVD	[35]
Amorphous carbon coated Si tip	I~1μA	V~1500V	Filtered cathodic arc technique	[36]
Diamond coated Si tip	I~ 2μA		HFCVD	[37]
Diamond coated Si tip	I ~ 500 μA		HFCVD	[38]
CVD diamond film			HFCVD	[39]
Diamond coated Mo			CVD	[40]
CVD diamond film	Ι~100 μΑ	E=100MV/m	HFVCD	[41]
Diamond grit		E=0~1V/µm	Electrophoresis	[42]
Pyramidal diamond tip	I ~ 0.1 mA	E~ 10 V/µm	PECVD	[43]

Table 2.1. Continued

Material & structure	Current I or Current densigy J	Applied potential V or field E	Deposition method	Reference
Thin film nanofila- ment carbon struc- ture	I~1.8mA	V 009∽V		[44]
ZrC films on Si and Mo	I~100 μA	V~ 130V	E-beam bombard- ment evaporation	[45]
Diamond coated Si tip			HFCVD	[46]
Diamond coated Si spikes	I∼a few µA		HFCVD	[47]
Diamond coated Si tip			MPCVD	[14]
CVD diamond film	Ι~15 μΑ	E<20MV/m	HFCVD	[15]
Ion-milled diamond films on Si	I~ 32 µА	V ~700 V	MPCVD	[48]
Nanotube carbon structure film	J~70mA/cm ²	V ~ 450 V		[49]
Graphite caron based field emitter				[22]
Carbodization of Si tip				[50]

Table 2.1. Continued
Table 2.1. Confined

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Material & structure	Current I or Current densigy J	Applied potential V or field E	Deposition method	Reference
SiC on Si	Ι~12.5 μΑ	E=0.95V/Å		[51]
Metal carbide emit- ter	I ~ 48.7 mA	V=12 kV		[52]

Table 2.1. Continued

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2.4.1 Models

Presently, the physics of electron emission from diamond is not well understood. First theoritical study by Huang *et al.* [53] found that emission from surface states is shown to be capable of producing the current density with field magnitudes comparable to experiments. The question of how these electrons are transported to the surface states needs to be answered. One possible mechanism they propose is that the elecron transport can take place through the defect states.

If defect concentration is significant, the electron states in these defects could form a band or bands. In their model, two subbands in the intrinsic band gap are postulated, which may be generated, for example, by defects or impurities. Band structure they postulated is shown in Figure 2.3. It is suggested that the defect bands can transport electrons to the unoccupied surface band located 1 eV below the conduction band, which, if occupied under applied field, can emit electrons to vacuum.

Givargizov *et al.* [37] proposed a model for electron emission from Si tip coated with thin diamond. They assumed that diamond is perfect crystal with low doping concentration. The proposed emission process is illustrated in Figure 2.4 for a Si/diamond interface, assuming that properties of a heavily doped Si/diamond heterojection are similar to metal/diamond Schottky junction. At $n<10^{15}$ cm⁻³, the bend bending effect at the Si/ diamond interface is small and may be neglected. Electrons tunnel through the bent band gap of the diamond, and drift to the surface and escape for vacuum. NEA of diamond surface was assumed in a model.

Choi *et al.* [40] proposed a model similar to Givargizov's model for electron emission from diamond coated Mo emitter. They consider an undoped or slightly doped diamond layer on Mo. The band bending effect at the metal/diamond interface is so small that it can be neglected. The energy barrier height at the metal/diamond (intrinsic) interface is very nearly $E_g/2$. They assume that diamond has a NEA surface, as a result, the emission would



Figure 2.3. Band diagram including the hypothetical bands in the energy gap [53].



Figure 2.4. Emission models for a Si/diamond system: tunneling of electrons through the bent band gap and escaping into a vacuum from the surface under NEA conditions [37].

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depend only on tunneling of electrons through the Mo/diamond Schottky barrier into the conduction band of diamond. The resultant energy band diagram for metal/diamond/ vacuum is shown in Figure 2.5.

Geis *et al.* [42] and Lerner *et al.* [54] explained the emission performance of their device by the stable NEA of diamond, which allows for injection of electrons from diamond into vacuum. They argue that emitter operation is limited by the injection of electrons into the diamond at the back metal-diamond interface, which depends upon the doping of the diamond and the roughness of that interface. They consider the case in which the diamond is doped with an electron donor. Substitutional nitrogen, for example, forms a deep trap 1.7 eV below the conduction band. Figure 2.6. shows the energy levels for synthetic-type Ib diamond containing substitutional nitrogen, which forms a comparatively shallow trap. Since the donor energy is well above the Fermi energy of most metlas, a depletion region will from in equibrium. When diamond is positively biased, electrons can tunnel into the conduction band of the diamond, due to NEA of diamond electrons can escape into the vacuum with little to no electric filed, 0-1 V μ m⁻¹. This concept is shown in Figure 2.8.

2.5 CVD Diamond Infrastructure

2.5.1 Nucleation

To grow diamond films effectively on non-diamond substrates, the substrate is usually treated to enhance nucleation density. Abrasive polishing of the substrate with various grain sizes of diamond [55, 56], c-BN, or SiC [57] powder is one of the commonly utilized methods. Ultrasonic agitation of the substrate with diamond powder suspension [58, 59, 60, 61] is another most commonly used pre-treatment technique. Bias enhanced







Figure 2.6. For substitutional nitrogen. Donors are ~1.7eV below E_c . In equilibrium a depletion region forms at the metal-diamond interface. The circles represent the energy position of the donors [42].



Figure 2.7. Energy levels for a metal-diamond interface with the metal biased to -6V with respect to the diamond [42].



Figure 2.8. Schematic diagram of a diamond cathode in a diode structure [42].

nucleation (BEN) has also been reported for effectively creating nucleation sites on silicon substrates [62] and preparing highly oriented diamond films [63, 64]. Although these methods successfully enhanced the nucleation density up to 10cm^{-2} [55, 59, 65] most of these techniques cause surface damage and have a poor uniformaity [57].

Nucleation method used in this experiment is an IC-compatible nucleation technique which does not cause surface damage [66]. Diamond Powder Loaded Fluids (DPLF) with different carrier fluids, mean powder sizes and densities are applieded on substrates by various means to enhance the nucleation density. The idea of this method is to spread diamond crystals, suspended in carrier fluids, on the substrate surface. During the diamond deposition process, the carrier fluids are evaporated at initial stages leaving behind the diamond particles which act as seeds for diamond growth. DPLFs are applied to substrates through direct writing, spinning, spraying or brush-painting. The technical details of two different DPLFs are summarized in Table 2.2. Further detail can be found in Ref. [67].

The DPLF1 are commercially available diamond powder suspensions, 1/40 SQG, from Du Pont Chemicals-Repauno Plant, NJ. The DPLF2 is prepared by suspending diamond powders into photoresist [68, 66]. In contrast to other nucleation procedures, DPLF method does not cause any damage to the substrate surface. This method is highly compatible with standard integrated circuit (IC) processes and amenable to patterning, doping, and coating of 3-D samples.

2.5.2 Patterning

In order to fulfil a variety of applications and desirable structures, growth of patterned diamond thin films is desired. Patterning techniques are, in general, distinguished into two categories, selective deposition and selective etching.

The selective deposition is achieved by pre-deposition nucleation on the desired area, or by masking the undesirable area during the diamond deposition. Hirabayashi et al. used

	DPLF1	DPLF2
Carrier Fluid	Water	Photoresist
Mean powder size	0.038 μm	0.101 µm
Density	40 Carats/liter	12 Carats/liter
Nucleation density	$\sim 10^{11} \text{ cm}^{-2}$	10^{8} cm^{-2}
Application methods	Spary, brushing, or direct writing	Spray, spin, or direct writing
Patterning	Photolithography, spray with shadow mask, or direct writing	Photolithography, spray with shadow mask, or direct writing

Table 2.2. Comparison of two types of diamond powder loaded fluids.

Ar sputtering in undesired growth regions to suppress nucleation after substrates were pretreated by ultrasonic method [61]. Ma *et al.* reported selective deposition onto SiO_2 stripes patterned on a Si substrate [58]. The Ar⁺ ion beam was used to suppress the nucleation on both Si and SiO₂ except in the shadows cast by the downwind edge of the SiO₂ stripes. The selective nucleation was successfully achieved by masking substrates during the ultrasonic treatment by Masood *et al.* [66]. Leksono and coworkers reported successfully the patterning of diamond films by lift off process on Si wafer. Thin ZnO film and amorphous silicon were used as sacrificial layers for lift off processes [69]. SiO₂ or Si₃N₄ as a masking layer during the diamond deposition was successfully reported by Masood *et al.* [66] and Roppel and coworkers [70].

The patterning of continuous diamond films by selective etching method was reported by Masood *et al.* [71,66]. Using a rapid thermal processor (RTP), diamond films were successfully etched in oxygen environment at 700 °C. The SiO₂ or Si₃N₄ were used as masks to block the undesirable area during etching process. ECR etch of diamond using O₂ plasma was performed as well [72].

However, most of these techniques, which involve selective etching or selective deposition, either cause damages on substrate surfaces or have poor reproducibility. Recently, a novel patterning process, photolithographic patterning techniques, has been developed at Michigan State University to selectively deposit high quality polycrystalline diamond films through standard photolithographic processes [66]. This technique not only achieves excellent selectivity without surface damages, but is also compatible with the existing integrated circuit fabrication technology. This technique is adopted in the present research to pattern CVD diamond films.

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2.5.2.1 Photolithographic Methods

The mostly used patterning technique in this research was to prepare samples coated with DPLF2. In this technique, DPLF2 is spin-coated on substrates, Si or oxidized Si wafer in most cases, and is patterned by standard photolithography. The spin rate was in the range of 2000 - 4000 rpm. An enhanced diamond nucleation density was observed at lower spin rate, however, the seeding uniformity seems inferior. When higher nucleation density is required, DPLF2 was coated multiple times. An optimal spin speed of 3000 rpm was found to possess a nucleation density on the order of 10^8 cm⁻² with good uniformity. The ratio of nucleation density in the undesired area and that in the desired area is in the range of 7.57 x 10^{-3} - 3.38 x 10^{-4} [67].

2.5.2.2 Direct-write Patterning Method

In direct-write patterning technique, DPLF1 are used as seeding materials and are applied to substrate surfaces via a fine spray nozzle. The minimum pattern size can be varied by selecting the opening sizes of nozzles. In initial experiments, a capillary of wire bonder, with an opening of ~40 μ m (1.5 mils) was fixed in front of syringe needle and was used as a spray nozzle. The width of lines manually created on Si or oxidized Si wafers are in the range of 125 - 600 μ m. A substrate temperature of 65 - 75 °C is found optimal to dry the seeding fluid, DPLF1, before it spreads out. In case of DPLF2, spary gun with compressed air was also used with shadow mask. G. Yang has designed and built computerized direct writing system [67].

2.5.3 Doping

As a wide band gap semiconductor material, Eg=5.5 eV, CVD diamond films deposited without intentional doping are usually good insulators. As a result use of

diamond as an electronic material requires a control over the ability to dope it p- and ntype. In general, doping of semiconductors is achieved by diffusion, ion implantation, or in situ doping. Because of the low diffusibility of most elements in diamond, diffusion is impractical. Although ion implantation can achieve active doping, the damages of crystal structure were introduced [73]. Therefore, in situ doping was commonly utilized in preparing semiconducting diamond films. Boron (B), aluminum (Al), phosphor (P), lithium (Li), and nitrogen (N) are potential dopants of diamond. Although the $NH_4H_2PO_4$ and $(CH_3O)_3P$ were reported to produce n-type semiconductive CVD diamond films, the conductivity is too low for electronics application [74, 75]. Other attempts to obtain n-tupe doping were unsuccessful until now [76, 77]. P-type diamond films were successfully prepared by using born as an in-situ dopant.

A number of in situ doping techniques involving gaseous, liquid and solid sources to incorporate boron into CVD diamond films have been successfully used to produce the p-type semiconducting diamond films. Solid sources (B_2O_3 [78, 79], boron powder [68]) have the advantages of chemical stability and simplicity. However, non-uniformity of doping are observed and it easily contaminates deposition chamber. Gaseous source (B_2H_6 [80]) has a better controllability, but is poisonous and explosive. Liquid sources ($B(CH_3O)_3$ [78, 81]) is also used to prepare p-type diamond and is reported to be nonpoisonous, stable, and controllable. Due to the safety concern, only solid sources are used in this research.

High purity (5N8) amorphous boron powders and B_2O_3 boron wafers purchased from Techneglas Co., Perrysburg, OH are used to fabricate semiconductive diamond films via in situ doping technique in this work. Specially designed holders, as shown in Figure 3.4 later, made of 1 mm thick Mo plate were used to introduce boron powder into process chamber. The doping sources were placed on substrate holder during the deposition. Although relatively uniform doping profile was confirmed by secondary ion mass

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spectroscopy (SIMS) measurement [71], depending on the relative position of born powder holder, non-uniformity is found. A layer of undoped diamond under the p-type layer was found to enhance the quality of p-type diamond films, measured in terms of sp^3/sp^2 ratio by Raman spectroscopy, even for very high doping levels [71, 82].

2.5.4 Metallization

Metallic contacts are essential for achieving electronic devices. It is desirable that the resistance of devices be determined mainly by the resistivity of the bulk material and that the influence of contact resistance be minimized. In addition, the good adhesion is essential for developing the contact structure.

The contact resistance is found to decrease with an increase in the doping level [83]. Ti/Au, Ta/Au, Ti/Pt, and Ti/Mo/Au were reported by several workers to provide good contacts with diamond films [68, 84, 85, 86].

Since resistance to high temperature is not required for contacts in diamond field emitter research and single target metal evaporation facility was not readily available, Al were tested on the samples which diamond films were synthesized on SiO₂ substrates. Al with a thickness in the range of 0.6 - 1 μ m were thermally evaporated under a pressure less than 10⁻⁶ torr. Patterns were defined either by shadow masks or by photolithographic processes and wet etching.

After the metallization, samples with contact metals of Al were thermally annealed at 500 $^{\circ}$ C for 20 minutes, in N₂ by tubular furnace constructed by G. Yang or rapid thermal processor (RTP). Al contact layers show good adhesion on diamond and SiO₂ (if any). The ohmic contacts of Al with polycrystalline diamond films are confirmed by I-V measurements at room temperature. A Keithley 224 programmable current source along with a Fluke 8840A multimeter are used for I-V characterization. The voltage reading was

taken right after current was applied to minimize the self-heating effect especially at current > 10^{-4} A.

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CHAPTER 3

DEPOSITION AND CHARACTERIZATION SYSTEMS

3.1 Introduction

Prior to the study of field emission (FE) from diamond film, it is necessary to build a film deposition and an automated FE characterization system beforehand. Design and construction of the deposition systems and the characterization system are described in detail. In addition, film characterization techniques are described. Anode designs used in this study are also discussed.

3.2 Deposition Systems

The ability to grow optimum films for FE is essential for the realization of diamond field emitter application. With the exception of some samples, all diamond films used in the present research were prepared by a hot filament chemical vapor deposition system (HFCVD) [87]. In addition to the description of HFCVD system, the modification of RFCVD system are described in this section.

3.2.1 Hot Filament Chemical Vapor Deposition System

The HFCVD reactor used in this work was designed by S. Sahli and A. Masood after a

similar system used at Ford Motor Company's Research Lab. It was constructed at Michigan State university by S. Sahli [88] and D. Hong. Original system at Ford can grow only up to two-inch samples. In the design of new system, consideration was given to grow uniform diamond film up to four-inch wafers. Some modifications and optimizations were incorporated during the course of this work to improve the reproducibility, deposition uniformity, growth rate, and film quality. A simplified schematic diagram of this system is shown in Figure 3.1. Based on the operational function, a HFCVD system can be categorized into the following five major subsystems.

- (1) Chamber
- (2) Filament
- (3) Sample stage
- (4) Vacuum system
- (5) Pressure and flow controls

• Chamber

The HFCVD reactor consists of an 18-inch diameter stainless steel vacuum chamber with a 10 inch diameter access door. 1/4 inch stainless tubing is wrapped around the top portion of the chamber for cooling purpose. When it is in operation, additional cooling by blower is necessary to prevent the chamber from overheating.

Filament

In original design, ten 5-inch long and 0.005-inch thick Ta wires in a parallel configuration were horizontally mounted on a 4.5×5 inch² frame via 20 Mo hooks. The



Figure 3.1. Schematic of HFCVD system constructed.

supporting frame consists of two Mo bars which serve as electrodes. The 4.5 x 5 inch² filament array was utilized to ensure a uniform deposition over a 4 inch wafer. This configuration caused an unacceptable amount of sagging due to lack of tension applied to thin wires. Same configuration with 0.02-inch thick wires was attempted. This new scheme reduced the amount of sagging within tolerable range. However, the total current exceeded the specification of 50 A power supply. The supporting frame had to be modified to the combination of two BN bars and two Mo bars to accommodate filaments in a series configuration such that total current can be reduced down to less than 50 A. The filament typically draws 18 - 22 A current at nominal temperature in the range of 2200 - 2400 °C. The filament temperature is monitored by an optical pyrometer (Williamson 8125PS-G-C) through a 6 inch glass view port. Monitored signal is fed into Yokogawa UT35 controller to maintain filament temperature at specified value. Enhancement efforts are being done to change filament assembly in a vertical fashion that would eliminate sagging of the filament.

• Sample stage

Original sample stage used was 2" diameter heater assembly powered by Research Inc.'s type 663F power supply. Temperature was measured with type K thermocouples at both the top and back side of substrate during deposition process. Sensed signal was feedbacked to Partlow MK2000 controller. It was found that 4.5×4.5 inch² filament array generates enough heat to maintain substrate at normal deposition temperature without heating the substrate. In order to grow diamond film on four-inch wafer, sample stage was changed to four-inch wafer, graphite plate, or graphite column. The supporting frame was specially designed with a vertical movement mechanism to adjust the separation of filament array and substrate in the range of 0.5 - 1 cm. Due to the sagging of the filament, temperature at the surface of the substrate was expected to be non-uniform. A temperature

profile of four-inch substrate was characterized by measuring temperatures at several points of substrate using thermocouples during a test deposition. A ~100 °C difference was found between the temperatures measured at the center and the edge of the top side of substrate. The substrate temperature then was monitored at the edge in the actual deposition to minimize the blocking area by thermocouples. ANSYS simulation of sagging filament also confirmed that difference between simulated temperatures at the center and the edge of the top side of substrate is ~120 °C. This value almost coincides with the measured value. Figure 3.2 shows simulated structure and temperature plot respectively. During the test run, filament temperature was controlled. It later turned out to be inefficient due to the following reasons. First, due to the sagging of the filament as a function of time, focusing aperture of pyrometer didn't measure same area of filament. Secondly, small vibration of the system could change temperature reading drastically which would enormously fluctuate filament current. It was found, after numerous test run, that controlling substrate temperature is better method to achieve more uniform diamond film. Later, machine was reconfigured, so that thermocouple signal of substrate temperature is fed into filament controller.

• Vacuum system

A Varian SD-200 rotary pump is used for evacuation. This configuration is sufficient enough to evacuate chamber down to 10 mTorr within 30 minutes. In addition, N_2 is used to purge and backfill the chamber.

• Pressure and flow controls

The reactant gas mixture consists of ultra-pure grade (99.995%) methane (CH₄) and hydrogen (H₂). The flow rates of these gases are independently controlled by MKS type



(a)



Figure 3.2. (a) ANSYS simulation of temperature profile due to sagging filament. (b) Temperature of the substrate as a function of the distance from the center.

1159B mass flow controllers and read by MKS Model 247C 4 channel readout. The operation pressure is monitored through a MKS type 122A baratron pressure gauge and is controlled by a MKS type 250 pressure controller via a type 248A upstream valve. The base pressure, measured by a MDC thermocouple vacuum gauge, is in the range of 1 - 10 mTorr.

• Deposition parameters

Since CVD growth of diamond is essentially in metastable phase, the selection and consistency of processing parameters are very important in achieving reproducible high quality diamond films [8]. The ranges and typical values of deposition conditions used throughout this research are summarized as follows. Values in the parenthesis are typical values used:

(1)	Gas composition:	$CH_4: H_2 = 0.5\% - 2\% (1\%)$
(2)	Gas flow rate:	CH ₄ : 1 - 5 sccm (4 sccm)
		H ₂ : 200 - 500 sccm (400 sccm)
(3)	Filament temperature:	2200 - 2400 °C (2300 °C)
(4)	Substrate temperature:	850 - 950 °C (900 °C)
(5)	Operation pressure:	40 - 50 Torr (50 Torr)
(6)	Substrate to filament distance:	0.5 - 1.5 cm (1 cm)
(7)	Doping source:	Boron powder or B_2O_3 boron wafer

• Operation procedure

The operation sequence of HFCVD is reported to have a great influence on the deposited film quality [71]. The operation steps used through out this research are described as follows.

Start up procedures:

- Samples to be deposited and doping sources (if any) are loaded on sample holder. The distance of filaments and substrate is adjusted to be ~1 cm. (The distance varies with the sag of filaments.)
- (2) Process chamber is evacuated down to a base pressure of less than 10 mTorr.
- (3) Hydrogen is then introduced into the process chamber.
- (4) When the chamber pressure reaches > 20 Torr, the filament temperature is brought up slowly to the nominal temperature of 2300 °C. The slow adjustment of filament current is desired to avoid any damage and to ensure long life time of the filament.
- (5) CH₄ is switched on only after the substrate temperature reaches desired temperature of 900 $^{\circ}$ C.

Shut down procedures:

(1) The CH₄ is turned off to terminate the deposition processes, while the H₂ remains on for another 5 to 10 minutes. During this period, the hydrogen is believed to be the preferential etchant to remove a thin conducting carbonaceous layer on the surface of CVD diamond films [71]. This step makes the surface H₂ passivated. No conduction is found in the case of undoped films after this treatment. (2) The applied filament current is decreased slowly down to zero. The chamber is then evacuated to vent out process gases. Samples are unloaded after the system is cooled down and backfilled with N₂.

Typical morphology and Raman spectrum of the film grown by HFCVD is shown in Figure 3.3.

3.2.2 Radio Frequency Chemical Vapor Deposition System

A radio frequency chemical vapor deposition (RFCVD) reactor is currently under construction in collaboration with Dr. N. Abu-Ageel (Appendix A). RFCVD systems, used for diamond growth in the late eighties and early nineties, were found to lead to lower quality films [89, 90, 91, 92]. As such films are more appropriate for FE, an existing Plama-Therm system is being modified.

3.3 Film Characterization

The quality of diamond films was monitored by secondary electron microscopy (SEM), Raman spectroscopy, and atomic force microscopy (AFM). The SEM and AFM provided a direct vision of film surface morphology. The Raman spectroscopy provides a direct evidence of existence of diamond through its characteristic peak at 1332 cm⁻¹. Peak values at 1332 cm⁻¹ and 1580 cm⁻¹ were compared to estimate sp3/sp2 ratio. AFM was used to inspect small grain films.

Raman spectroscopy

In Raman effect, discovered by physicist Sir Chandrasekhara Venkata Raman of India, light is scattered by an atom or a molecule that changes its state. There is a corresponding discrete decrease in the frequency of scattered radiation. Raman spectroscopy is widely



Figure 3.3. Typical morphology by SEM (a) and corresponding Raman spectrum (b) of the film grown by HFCVD.

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used in the analysis of materials and the identification of trace elements. In diamond related research, Raman spectroscopy is a powerful tool to identify the presence of sp^2 and sp^3 bonding in diamond films [93]. The wave number shift of 1332 corresponds to sp^3 diamond peak.

Raman system used in this research was built by J. Mossbrucker using monochrometer donated by Ford. It consists of laser, optics, monochrometer, photomultiplier tube, counter, and computer. The 514.5 nm argon laser line (green) is used. It has a laser power of 600mW and a spectral resolution of 9 cm^{-1} . The monochrometer is Czerny-Turner scanning type where both gratings are mounted on the same axis.

• Scanning electron microscopy (SEM)

SEM consists of an electron gun and electron detectors in a vacuum chamber. Images are constructed by collecting the secondary electrons emitted from samples due to the incident electron beam. The image then is displayed on a cathode ray tube (CRT) for direct vision [94]. Because of the large magnification range of 10 X to 300,000 X [95] and great depth of field, SEM is a very powerful tool for studying the morphology and visual analysis of diamond films. It is widely utilized to inspect the surface morphology, crystal orientation, grain sizes, and film thickness. It is also used to monitor the nucleation densities and patterning. The need for a conducting specimen somewhat limits its utility for undoped films on insulating substrates. Three different SEMs were used for this research.

Jeol SEM with W filament at Composite Material and Structure Center was used often. It is simple to operate and it can accommodate large size samples. Jeol SEM at Electron Optics Center is equipped with LaB_6 gun. It makes saturation of filament easy. Another advantage is that it is fully computer controlled. As a result, it is easy to save images into data file. Usage of this machine was hindered by the size limitation of the

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sample that can be loaded. Environmental SEM at Composite Material and Structure Center was also used for some samples. This special SEM allows non-conducting samples. It was beneficial to load samples without conductive layer coating. It was especially useful when testchip is fabricated. After each step of wafer processing, SEM picture could be taken without the need for the conductive layer coating.

• Atomic force microscopy (AFM)

Atomic Force Microscope (AFM), also called as Scanning Force Microscope (SFM), can measure the force between a sample surface and a very sharp probe tip mounted on a cantilever beam having a spring constant of about 0.1-1.0 N/m, which is more than an order of magnitude lower than the typical spring constant between two atoms. Raster scanning motion is controlled by piezoelectric tubes. If the force is determined as a function of samples's position, then the surface topography can be obtained. Detection is most often made optically by interferometry or beam deflection. In AFM measurements, the tip is held in contact with the sample. Spatial resolution is a few nanometers for scans up to 130 μ m, but can be at the atomic scale for smaller ranges. Both conducting and insulating materials can be analyzed without sample preparation.

3.4 Field Emission Characterization System

As field emission characterization systems are commercially not available, characterization system is designed and built. It consists of vacuum chamber, pumps, pressure gauges and readouts, power supply, measurement instruments, and computer system. Schematic of the system is shown in Figure 3.4.

Chamber

8.5-inch diameter vacuum chamber was machined at the Physics shop. It has 8 flange



Figure 3.4. Schematic of automated characterization system built.

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connections and can be accessed from the top. The following ports were attached to the eight flanges.

- (1) Gate valve
- (2) Thermocouple pressure sensor
- (3) Barotron pressure gauge
- (4) Electrical feed through
- (5) Mechanical feed through
- (6) Ion gauge
- (7) N_2 purge
- (8) View port

• Vacuum system

The chamber, equipped with two stage pumping system, is connected to the turbo pump (Ley bold-Heraeus Turbo Tronik NT150/360) through gate valve. Turbo pump is water cooled by closed loop Neslab CFT-33 refrigerated recirculator. Varian SD-200 mechanical pump is connected to the turbo pump in series. With this configuration vacuum chamber can be evacuated down to 10^{-6} Torr range.

• Pressure readout

Four types of vacuum readouts were used to check different ranges of vacuum levels. They are summarized in the Table 3.1.

Readout type	Range		
MKS barotron 122AA-01000AB with PDR-C-	2 - 1000 Torr		
2C MKD power supply readout			
MKS barotron 122AA-00002AB with PDR-C-	1-2000 mTorr		
2C MKD power supply readout			
MDC thermocouple vacuum gauge	1 - 1000 mTorr		
Varian 0571-K2471-303 ionization gauge	10 ⁻⁸ - 10 ⁻⁴ Torr		

Table 3.1 List of pressure readouts.

Table 3.2 List of power supplies.

Model	Rating	Computer controllability	
Hewlett Packard Harrison 6110A DC power	3000V, 5mA	No	
supply			
Keithley model 248 high voltage supply	5000V, 5mA	Yes	
Keithley 230 programmable voltage source	100V, 100mA	Yes	
HP model 712B power supply	500V, 200mA	No	
Universal Electronics regulated power supply model 520A	500V, 200mA	No	
Keithley 220 programmable current source	100mA, 100V	Yes	
Keithley 224 programmable current source	100mA, 100V	Yes	

Model	Computer controllability		
Fluke 8506 Thermal RMS digital	No		
multimeter			
Keithley 181 nanovoltmeter	Yes		
Keithley 169 multimeter	No		
Fluke 77 multimeter	No		
HP 3435 digital multimeter	No		
HP 34757 multimeter	Yes		
Keithley 595 quasistatic CV meter	Yes		
Fluke 8840A multimeter	No		

Table 3.3. List of measurement instruments.

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Power supply units

Various power supply units were used. Two different types of power supplies used were DC volt and DC current. All the power supplies used were listed in the following table 3.2.

• Measurement readout units

Measurement readout was performed by either measuring voltage drop over the resistor or measuring current. Instruments used are listed in Table 3.3.

• Computer system

A computer with IEEE 488 interface card was employed to automate the characterization system. Computer, power supply, and measurement instruments were daisy chained as shown in Figure 3.5. Control program was developed by using BASIC program with built-in library functions furnished with IEEE 488 card vendor, Hewlett Packard. Source code is shown at appendix A. This control program allows automatic measurement.

An effort to build new characterization system is led by C. Koellner. This system is similar to one already discussed. Major addition to this new system is fully computer controlled XYZ stage with a resolution of 1 μ m and microscope with camera for field emission pattern acquisition. This will enable us to map the wafer in a great detail.

3.4.1 Anode Designs

Six different types of anodes were used to characterize samples. Each has its own pros and cons. The best anode type for a particular measurement situation was selected. They are shown in Figure 3.5.

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3.4.1.1 W Probe Anode

Figure 3.5 (a) shows tungsten probe anode used in the characterization of discrete samples, W probe was used often due to its simple setup. Sample is fastened on substrate holder and probe is placed on top of the sample. Advantage of W probe anode is that there is no insulating material involved in but the separation between anode and emitter is not precisely controlled. Two SEM pictures of two W probes used are shown in Figure 3.5 (b).

3.4.1.2 Brass Column Anode

In this type of anode, insulating material is placed between sample and the mirror grade polished brass column. In some cases, Si wafer coated with Al was substituted by brass column. This configuration is shown in Figure 3.5 (c). Its advantage was that we know the separation precisely by knowing the thickness of the insulating material, which is quartz sheet. Usual thickness of the QZ plate used is in the range of ~100 μ m. In some cases, 100 μ m thick plate is etched with a solution of HF mixed with water to get thinner plate such as 50 μ m.

3.4.1.3 Lateral Anode

In this case, MKS mechanical feed through was used. Its maximum travel range is 1 inch and minimal resolution is 25.4 μ m. Sample is mounted on the sample holder with clamp and positioned in a vertical fashion. Detailed setup is shown in Figure 3.5 (d). At first, anode and emitter contact was made. Contact were detected by measuring resistance between anode and cathode. Upon finding contact between anode and cathode, 1 notch of mechanical feedthorugh was moved back to make a separation of 25.4 μ m and another 1 notch of mechanical movement was added to get 50.8 μ m separation.

3.4.1.4 Glass Anode

Figure 3.5 (e) shows that final version of glass anode made in collaboration with Dr. S. Kwon. Samples are placed on top of the glass anode upside down. Two mask fabrication steps were required to make the glass anode. First mask defines the grooves in glass. Depth and width of the groove can be controlled precisely by the etching time. Sodalime glass were used. Next, Al is thermally evaporated on the glass and second mask is used to remove Al outside groove area. With small gap between anode and emitter it was possible to demonstrate low voltage emission. This glass anode was very useful to calculate current density.

3.4.1.5 Phosphor Anode

This type of anode was provided by Zenith Corporation. Transparent conducting layer, Indium-Tin-Oxide (ITO), is coated on 1 x 2 inch sodalime glass. On top of ITO, phosphor material (ZnO:Zn), which transfer electron energy to light emission, was coated. Samples had to be separated by quartz insulator. This phosphor anode is very useful to record emission spot and to check whether or not measured current is emission current quickly. It is expected that we only see visible spots when forward biased, if it were real emission current. If visible spots were found at both same forward and reverse bias, it would be discharge current due to vacuum breakdown. Phosphor anode is shown in Figure 3.5 (f).

3.4.1.6 Built-In Anode

Some discrete samples and field emitters in testchips includes built-in anode, so that no other anode system is necessary. This will be discussed in Chapter 4 in greater detail. One example of built-in anodes, a bridge shaped Al anode over emitter, is shown in Figure 3.5 (g).



(b)



Figure 3.5. Six different anodes used in this study.



Figure 3.5. Continued.





Figure 3.5. Continued.

3.5 Summary

In this chapter, the design and construction of HFCVD system is discussed in detail. Modification of RFCVD for low temperature diamond deposition is described as well. Low temperature deposition is especially important to meet low cost, large area diamond deposition, which is crucial to commercialization of diamond FED in the near term. In section 3.3, an overview of commonly used film characterization tools, SEM, Raman spectroscopy, and AFM is given. In section 3.4, the design and construction of an automated characterization system is explained. Finally, six different types of anodes used in the measurement are introduced.

CHAPTER 4

IC COMPATIBLE FIELD EMITTER TECHNOLOGY

4.1 Introduction

In this chapter, new patterning techniques for DPLF1 and enhanced technique for DPLF2 are beriefly mentioned. Chronological efforts to achieve IC compatible field emitter technology are discussed. Starting from preliminary and simple discrete samples to establish key technologies, three unique testchips were designed and fabricated. Detailed explanations of these three testchips are given.

4.2 New and Ehanced Patterning Technique

This section deals with the modification of photolithographic patterning technique to incorporate patterning of samples coated with DPLF1. In addition, problems, difficulties and proposed solution are also included in this section.

In the case of DPLF1,both a combination of photolithographic methods and direct writing methods are used for patterning. For a photolithographic method for DPLF1, as shown in Figure 4.1, a sacrificial layer of photoresist is uniformly spin-coated on the substrate with a high spin rate of 4500 rpm. This photoresist layer is for preventing diamond powder from touching the substrate directly. The seeding fluid then is manually



Figure 4.1. Process sequence for the patterning of (a) DPLF1 and (b) DPLF2 using photolithographic method.

brushed over. The second layer photoresist is spin-coated at a speed of 4000 - 4500 rpm to prevent the seeding material removed during the developing process. Due to the poor transparence of DPLF1, a fully exposure of the first photoresist layer prior to the coating of seeding fluid is helpful to improve the selectivity. However, it may cause the problem of over developing resulting a poorly defined pattern edge. The schematic of DPLFs patterning procedure by standard photolithography is shown in Figure 4.1. SEM pictures of diamond structures prepared by both patterning procedures are shown in Figure 4.2 for comparison. The wavy edge observed on DPLF1 pattern is mainly caused by the over developing of the first layer photoresist and the non-uniformity of DPLF1 seeding fluid coated by hand brushing. A uniform and well controlled application technique is essential to improve the pattern quality of DPLF1 seeded samples.

As shown in Figure 4.1 (b), there are a number of diamond stray particles in unwanted area when DPLF2 was applied. These are due to remaining diamond particles, which are not washed away completely during the development process of the diamond-loaded photoresist. They can affect the yield if they form a continuous film and if their size becomes too large. A double layer process is developed to prevent diamond particles from reattaching to the surface in undesired areas. Comparison between conventional method and double layer method is shown in Figure 4.3. Essence of double layer process is that pure photoresist is coated underneath DPLF2 to prevent diamond particle from touching the substrate directly.

4.3 **Preliminary Samples**

Early diamond field emitter samples were B-doped polycrystalline films on p-type Si wafers. Nucleation is achieved by spin coating of DPLF2 as described in section 2.5.1. One group of samples are not patterned in order to grow continuous film on the substrate. Another group of samples were patterned using spray method with shadow mask



Figure 4.2. Patterning results of (a) DPLF1 and (b) DPLF2 samples by photolithography.



Figure 4.3. Comparison of (a) conventional patterning method and (b) double layer method.

described in section 2.5.2 to create a collection of diamond dots on the substrate. Cross sectional view of the samples are shown in Figure 4.4. The samples are subsequently placed in the HFCVD reactor. The filament temperature in HFCVD was 2300 °C which maintained the substrate temperature, sensed by a thermocouple, at ~900 °C. The deposition atmosphere consisted of 1% CH₄ in H₂ at 50 Torr. The separation between filament and substrate was approximately 5 mm. Using a diamond deposition rate of approximately 0.25 μ m per hour, a film thickness of 2 μ m was achieved. In-situ doping of boron was accomplished by placing a small container with pure boron powder on the substrate holder as describe in section 2.5.3. Such an arrangement can provide resistivity values in the range of 20-100 Ω cm [96]. Al was thermally evaporated on the backside of Si wafer to provide an ohmic contact. The samples were annealed at 400°C in nitrogen for 30 minutes. With the exception of diamond deposition, all the sample fabrication steps were completed in a class 100 area in the cleanroom.

4.4 Discrete Sample with Built-In anode

Two types of simple samples with built-in anode were fabricated, namely vertical structure and lateral structure. Although it is required to pattern diamond film and Al anode, very crude first sample with built-in anode was made even without any mask or with simple transparency mask, metal shadow mask, or crude shadow mask made by Al foil.

4.4.1 Vertical Structure

Figure 4.5 (a) shows top view and (b) shows magnified cross sectional view along A-A' of the first diamond field emitter structure with built-in anode fabricated on a piece of oxidized Si wafer. Figure 4.5 (b) shows step-by-step coross-sectional view. A 3-micron

Figu



Figure 4.4. Cross sectional views of preliminary samples with (a) continuous film and (b) dot patterned film.



Figure 4.5. (a) Top view, (b) cross-section view, and (c) magnified view of section A-A' of vertical type discrete sample with built-in anode.

thick layer of SiO₂, deposited at 400 °C on p-type (100) Si, is annealed in N₂ at 1000 °C for 30 min to improve its insulating properties. Patterning and nucleation of diamond was achieved by manual direct writing of DPLF1 or DPLF2 using a syringe method described in 2.5.2.2. Structure shown in Figure 4.5 used DPLF2. B-doped and strip-shaped patterned diamond film is grown on top of substrate. Photoresist, patterned by syringe again, was applied on top of the diamond film. Width of this sacrificial photoresist is wider than the width of diamond line. Photoresist is baked at 120 °C for 30 minutes to harden it before putting thin Al layer on it. Using shadow mask, Al layer is evaporated on top of photoresist layer. Width of Al line is narrower than underlying photoresist layer. Thus photoresist underneath Al layer can be removed. To remove photoresist only without attacking Al, either acetone or Shiply photoresist remover was used. After photoresist is removed, bridge shaped Al anode is constructed over diamond film with vacuum equal to the thickness of sacrificial photoresist layer. Al is also selectively evaporated at the ends of each diamond lines to make ohmic emitter contacts. Same structures were also fabricated on top of quartz (QZ) plate as shown in Figure 4.6. Adhesion of diamond film to QZ plate was as good as to oxidized Si wafer. Two vertical devices are on QZ plate, one in the far left and another one in the far right. Color of diamond lines in these two vertical devices are different. One in the left used DPLF1 and one in the right used DPLF2. This simple device enables us to characterize its current versus voltage without any external anode attached. It permits great accuracy of anode to emitter distance and emitting area.

4.4.2 Lateral Device

Figure 4.7 (a) shows cross sectional view along with A-A' and (b) shows top view of the first lateral diamond field emitter structure with built-in anode fabricated on a piece of oxidized Si wafer. B-doped and patterned diamond film is grown on top of oxidized Si wafer. Sample is then covered with thermally evaporated Al. To create the distance







Figure 4.7. (a) Cross sectional view and (b) top view of lateral device.

between anode and emitter, photolithography and subsequent etching was used to pattern Al. It was impossible to use shadow mask due to the difficulty of aligning of small dimension. Transparency mask, which has a gap between dark pattern of ~125 μ m, was used. As shown in Figure 4.7 (b), minimum gap created is in the range of 20 μ m. Emitter contact is Al on part of diamond film and anode contact is Al on SiO₂. Four lateral structures made on QZ are shown in Figure 4.6. Again, two in the left side are nucleated and patterned with DPLF1 and two in the right side were by DPLF2. Compared to vertical structure described in the previous section, immediate advantage of lateral device is its high yield. All the lateral devices fabricated exhibited successful operation while some of vertical structures suffered collapsed bridge partly due to surface tension during sample drying process and partly due to wafer handling error. Another advantage was that it was easy to control the gap between anode and cathode by shifting alignment. In case of vertical device, the gap between anode and cathode was controlled by the thickness of photoresist.

4.5 Testchip I

Encouraged by the work in section 4.4, a 1 x 2 inch² testchip was designed and fabricated. Two chips were placed on 4 inch wafer to check uniformity of diamond film quality over 4 inch wafer from newly built HFCVD system. Each chip consists of eight identical vertical devices. Figure 4.8 (f) shows fabricated 4 inch wafer. Each emitter is fundamentally same as one shown in Figure 4.5 except the fact that size is well controlled in the testchip. Figure 4.8 (a) - (d) show the top view of four masks used in the fabrication.

Layout of masks was done using Framemaker and pattern size at during layout was ten times larger than size appeared on the wafer. Each layer is printed in the high resolution black and white printer. It was reduced two times due to the limitation of reduction lens of the equipment, and printed on transparency at the Instructional Media Center. These







Figure 4.8. Test chip I (a) Diamond pattern (b) Sacrificial photoresist pattern (c) Metatl pattern I (d) Metal pattern II which covers most of diamond with metal (e) Overlapped view (f) completed wafer. transparency masks were cut and pasted on 1.5 mm thick 4 x 4 inch glass. Minimum feature size possible with this transparency mask was in the range of 50 μ m. Although the contrast of the pattern in the trancyparency masks was not as high as Cr mask, use of tranceparency masks in the design rule of > 50 μ m is acceptable and used successfully before [71].

Three mask steps were involved to fabricate this sample. First mask (Figure 4.8a) defines diamond line. Second mask (Figure 4.8b) patterns sacrificial photoresist layer. Third mask (Figure 4.8c and d) cuts Al layer. Two different types of third mask were used. As shown in Figure 4.8 (c), metal pattern I has ohmic emitter contact only at the two ends of diamond strip. Metal pattern II shown in (d) has Al pattern covering almost all the diamond line except emitter area reducing resistance. It is expected that electrons move either bulk or surface of the diamond film from the metal ohmic contact to the emission area when metal pattern I is used. However, in case of metal pattern II, due to high conductivity of metal on top of relatively low conducting diamond, it is expected that electrons and patterning of diamond line was done by photographic method using DPLF2. Figure 4.8 (e) shows overlapped schematic of the original design. Completed wafer is shown in Figure 4.8 (f).

4.6 Testchip II

After confirming uniformity of HFCVD system, 1×1 inch² testchip with three-mask step was designed and fabricated to include lateral device and have emitters in different geometric values such as size of emitter area and anode to emitter distance. Figure 4.9 shows top view of designed pattern and corresponding pictures taken under the optical microscope.



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(c)

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(d)



Figure 4.9. Test chip II (a) Diamond pattern (b), wafer picture corresponding to (a), (c) sacrificial photoresist pattern (d) Metal pattern (e) Overlapped view (f) completed wafer. Identical to masks in testchip I, first mask (Figure 4.9a & b) defines diamond pattern, second mask (Figure 4.9c) sacrificial layer, and third mask (Figure 4.9d) metal layer. Again transparency masks were used for testchip II. Upper left corner has 16 vertical emitters. Widths of diamond lines are 50, 100, 150, and 200 μ m, respectively. Widths of Al lines are same as diamond lines from top to bottom. As a result, nine different combinations of emitter area are created. This matrix combination was intentionally designed to compare current density from different diamond emitter area. In a vertical device, separation between anode to emitter, d, is same for all 16 structures. d is same as thickness of sacrificial photoresist layer.

Other three quarters of the testchip were devoted to the lateral devices. Every lateral emitter has different separation between the anode and emitter structures varying from 10 to 50 μ m. Emitters at upper right corner have wider diamond line with small saw teeth like pattern. Emitter area for lateral type emitter is diamond thickness multiplied by width of diamond line. Emitters at lower right corner have pointed shape. Two saw shaped emitters, one in lower left and another in lower right corner, have largest emission area.

4.7 Testchip III

Upon testing all the necessary components of fabrication technology throughout previous sections, a diamond field emitter testchip III was designed and fabricated. A completed 4 inch wafer is shown in Figure 4.10 (a). Composite chip consists of four different areas, MEMS area, piezoresistive sensor area, thermistor and heater area, and field emitter area. Field emitter area includes two types of vertical emitters, lateral devices, diode type FED, triode type FED, and pressure sensors. FEDs and pressure sensors will be discussed in Chapter 6 in greater detail. Figure 4.10 (b) shows magnified views of all kinds of devices included in the testtestchipchip III. Total number of masks was six. Detailed information is summarized in Table 4.1. Not all layers were was necessary to build each



Figure 4.10. Variety of structures on test chip III.

Mask number	Pattern defined	Type A vertical device	Type B vertical device	Lateral device	Diode FED	Triode FED	Pressure sensor
1	Oxide etch	X		x	x		X
2	Diamond pattern	x	x	x	x	x	x
3	Cr electrode		x			x	
4	Sacrificial layer	x	x			x	x
5	1st Al layer	x	x	x		x	x
6	2nd Al layer						x

 Table 4.1. Summary of mask steps for each structure in test chip III

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structure. For example, mask number 3, Cr electrode patterning and mask number 6, second Al patterning were not necessary for type A vertical structure.

Composite chip was designed by layour editor L-Edit and saved in GDSII format by each member of the group [97]. D. Hong finally combined all the data. This data was later merged together and converted to MEBES format to generate chrome masks using electron beam exposure system. Four inch chrome mask set with minimum feature size of $4 \mu m$ was generated at Samsung (S. Korea).

Although some techniques might have been explained briefly in the previous sections fabrication steps will be explained in greater detail again in this section because this section is one of the main contribution of this research. Two different types of vertical field emitter structures were fabricated. For the type A, targeted for pressure sensor applications, p-type diamond film was grown directly on p-type Si. For the type B, targeted for display applications, the diamond film was grown on oxidized Si and chromium was used as the contact to the diamond film.

The fabrication process for the types A and B is depicted in Figure 4.11 and Figure 4.12 respectively. A 3-micron thick layer of SiO₂, deposited at 400 °C on p-type (100) Si, is annealed in N₂ at 1000 °C for 30 min to improve its insulating properties. For the type A structure, the oxide is patterned using buffered oxide etch and is used as a mask for Si etching (Figure 4.11a). Before the diamond growth, the seeding and patterning is accomplished by photographic method using DPLF2 described earlier. The mixture is spin-coated and patterned using a standard lithographic process. As the diamond is typically deposited at 900 °C, the photoresist evaporates leaving behind the diamond particles which act as seeds for diamond growth by the CVD process [66]. Using HFCVD reactor, p-type polycrystalline diamond is grown on Si for type A devices (Figure 4.11b) and on



Figure 4.11. Top and cross sectional views of type A device in different process steps.

Oxide Si



Figure 4.12. Top and cross sectional views of type B device in different process steps.
SiO₂ for type B devices (Figure 4.12a).

For the type B devices, approximately 2,000 Å thick Cr is thermally evaporated on diamond and patterned. Using wet etching, the thickness of the Cr layer on diamond is reduced. As the diamond surface is rough (Figure 4.12b), part of its surface is exposed after etching. Since some diamond emitters consist of a continuous film while others consist of patterned dots, we show SEM micrographs of a dot patterned film in Figure 4.12(a) and a continuous film in Figure 4.12 (b). Photoresist, serving as a sacrificial layer, is spin coated at a speed of ~1000 rpm and is patterned (Figure 4.11c & Figure 4.12c). Al, thermally evaporated on top of the photoresist layer, is patterned and part of the sacrificial photoresist is now exposed to remove it. After removing the sacrificial layer, the separation between Al and diamond, computed by taking into account the thicknesses of sacrificial photoresist, oxide, etched Si and diamond film, is in the range of 9~10 μ m for type A devices and 2~3 μ m for type B devices. Al is also evaporated on the backside of the wafer to provide an ohmic contact for type A devices (Figure 4.11d). For type B devices (Figure 4.12d), Cr is the cathode contact.

The fabrication process for the lateral device is depicted in Figure 4.13. Oxide and Si in the lateral device area is also etched at the same time, Cross sectional view and SEM picture of lateral device is shown in Figure 4.13. In the previous section, ohmic contact to emitter in the lateral device is provided by Al only on top of diamond film. In testchip III, ohmic contact to emitter can be achieved either from Al layer on top of diamond or Al at the backside of wafer. This variation enables us to study the effect of metal to diamond interface on the emission characteristics.

4.8 Summary

In this chapter, the development of diamond field emitter devices using testchip method is described in chronological order. By integrating all the technologies available



and newly developed, IC compatible diamond field emitter fabrication technology has been achieved.

CHAPTER 5

FIELD EMISSION RESULTS

5.1 Introduction

In this chapter, measurement data on a variety of samples described in Chapter 4 will be presented. Up to section 5.6, factual data will be presented without trying to answer the questions raised. In section 5.7, some questions are raised and additional experiments, which may help answer the questions, are executed. Combining all the data, preferred conditions for field emission from diamond film are summarized. An interpretation of these observations is discussed qualitatively.

5.2 **Preliminary Samples**

The main aim of the first measurement experiment was to qualify the functionality of characterization system and characterization method itself.

5.2.1 Setup

Figure 5.1 depicts a setup for sample testing for a preliminary sample described in section 4.3. Setup for continuous film sample is shown in Figure 5.1 (a) and setup for dot patterned film sample is shown in Figure 5.1 (b), respectively. For continuous film sample, the voltage drop across the resistor R, measured by a nanovoltmeter, is used to



Figure 5.1. Test configuration of the samples; continuous film (a) and patterned film (b).

compute the emission current at switch position 1 using sharp and blunt tungsten (W) anodes described in section 4.4. To protect the measurement instrument, two resistors were connected in series. One has at least an order of magnitude higher value than another one. Voltage was read at the smaller resistor. In case there is arc or sudden vacuum breakdown, which makes all the applied potential across the resistors, at least only one tenth of applied potential is dropped at the measuring resistor. At position 2, phosphor anode is used to record emission pattern. This phosphor anode is very useful to record emission spot and to check quickly whether or not measured current is emission current. It is expected that we only see visible spots in forward bias, if it were real emission current. If visible spots were found for the same forward and reverse bias, it would be discharge current due to vacuum breakdown. For dot patterned film, emission pattern was inspected only by using phosphor anode.

5.2.2 Results

The field emission current was studied as a function of anode geometry, anode-tocathode separation, and pressure. Figure 5.2 shows the emission current for sharp and blunt anodes shown in Figure 3.5 (b); the corresponding F-N plot is shown in the inset. The difference in the current for the two anode types is more pronounced in upper anode voltage range where the emission current shows a F-N behavior. The deviation from F-N behavior in the lower voltage range may indicate the presence of non-emission currents. It may also be due to the fact that emission area is larger when blunt anode was used. The reverse current was an order of magnitude lower than the values shown in Figure 5.2.

Figure 5.3 shows the emission currents for anode to cathode separations of 50 and 100 μ m for the sharp anode. The F-N curve becomes steeper with increasing separation indicating a smaller geometric factor. Part of the emission current may be from tiny grain tips on the polycrystalline diamond surface. The distance dependence of F-N field



Figure 5.2. I-V curves of diamond field emitter for blunt and sharp anodes; emitter to anode separation is 50 μ m and the measurement pressure is 10⁻⁷ torr. The inset shows the corresponding F-N plot.

d=50 μ m, p=10⁻⁷ torr



Figure 5.3. I-V curves for different anode to cathode distances for the sharp anode at 10^{-7} torr .

emission current affecting the geometric factor has been observed for microtip emitters [98, 99]. The emission was reported for anode-to-cathode separation of 60 μ m for tungsten-coated silicon pyramid [99] and up to 500 μ m for diamond field emitter [13].

The pressure dependence of field emission current for hydrogen ambient is shown in Figure 5.4. The test chamber was evacuated and flushed with H₂ many times and the pressure was kept at 10^{-7} or 10^{-2} Torr during the measurement. Field emission behavior is continued even though absolute value of current density is decreased as the pressure inside vacuum chamber is raised up to 10^{-2} Torr range. The field emission at a pressure of 10^{-2} Torr in H₂ environment may be due to diamond's chemical immunity to residual gases which are known to be adsorbed to the surface of other materials and raise their work functions. This may also be related to the enhancement of field emission found for H₂ and hydroxide (OH) ambient [100]. Kim *et al.* [33] have also measured constant emission current for pressure range of $10^{-6} \sim 10^{-4}$ Torr from diamond wedge fabricated by mold technique. Emission from Si tip dropped very sharply at pressure higher than $2x10^{-4}$ Torr [101].

Using a phosphor anode, the field emission from diamond was confirmed by light emission observed in position 2 (Figure 5.1) of continuous sample and dot patterned sample. The anode-to-emitter separation was kept at 100 μ m using thick quartz sheet. As shown in Figure 5.5, the bright spots, caused by electrons impinging upon the phosphorcoated anode, indicate emission only from certain points from the diamond film. In case of dot patterned film, the light emission pattern does not correspond to that on the film. An increase in anode voltage caused an increase in the number of emission sites and the spots became brighter. For negative anode voltages, no light emission was observed. This proves that measured current is not discharge current. Bright spots can be seen at emission current as low as 50 nA. Although emission area for dot patterned film was smaller than that of continuous film, number of emission sites was higher and larger current was



Figure 5.4. I-V curves for two different pressures; the emitter to anode separation is 200 μ m and the sharp anode is used.

SHARP ANODE, d=200 µm



(a)



Figure 5.5. The field emission pattern measured (a) for continuous film in position 2 of Figure 5.1(a) and (b) for patterned film. detected.

It is not clear why the emission is non-uniform. Discussion about non-uniform emission from diamond film will be deferred until section 5.7.

5.3 Discrete Samples with Built-in Anode

Figure 5.6 depicts a setup for sample testing for discrete samples with built-in anodes described in section 3.4.1.6. Setup for vertical device is shown in Figure 5.6 (a) and setup for lateral device is shown in Figure 5.6 (b), respectively. Figure 5.7 shows I-V data of vertical devices on oxidized wafer. Since sacrificial photoresist was not spin coated, gap between anode and emitter is in the range of 100 μ m as shown in Figure 4.5 (c). Due to manual diamond patterning, different photoresist thickness, and non-uniform Al width, there are some variation among data. Different turn-on voltages reflect different anode to emitter distances and variation on current at the same voltage may be from the variation of emitter size. Figure 5.8 shows I-V data for lateral devices on oxidized Si wafer. For lateral devices, turn-on voltage is much lower than vertical devices because anode to emitter distance is in the range of $\sim 25 \,\mu\text{m}$. Also, data shown in Figure 5.8 is close to each other than data shown in Figure 5.7. It may be due to the fact that anode to emitter distance was well controlled for lateral device by using precise aligner. Figure 5.9 shows I-V data for vertical devices on QZ sample (Figure 4.6). Nucleation densities for two different devices were $\sim 10^{11}$ cm⁻² and $\sim 10^8$ cm⁻², respectively. Diamond film seeded with high nucleation density exhibits slightly higher current and low turn-on voltage. As shown in Figure 5.10, for lateral devices on QZ substrate higher emission current is again found in case of high nucleation density film. These measurement data is promising to future application of built-in structures. The main purpose of this study was the successful implementation of built-in anode and technological development for field emission testchip.









Figure 5.7. I-V and F-N data for four different vertical devices.



Figure 5.8. I-V and F-N data for two different lateral devices.



Figure 5.9. I-V and F-N data for two different vertical devices seeded with low and high nucleation density.



Figure 5.10. I-V and F-N data for two different lateral devices seeded with low and high nucleation density.

5.4 Testchip I

Figure 5.11 depicts a setup for sample testing for testchip I. Cell notation in the form of "XYZ" are used to identify a cell in a wafer. The "X" specifies the chip number of the wafer. The "Y" denotes row number of each chip. The "Z" denotes column number of each chip. For example, the 224 denotes the chip No. 2, row No. 2, column No. 4 which is connected to the test circuit in Figure 5.11. In Figure 5.12 (a) I-V data is shown for cells marked circle in Figure 5.11, which are away from the center of the wafer. Although there is a variation in current level, it can be said that diamond quality, grown by newly built HFCVD, is similar and uniform over 4 inch wafer. When compared I-V data taken from cells marked in circle to data taken for cells marked in square, cells close to the center exhibit a little bit larger current at the same voltage. As marked on the center of the wafer, two boron powder holder were located at the center of the wafer. Resistivity of cells close to the center is smaller than cells away from the center due to non-uniform doping. **Reduced** resistivity might have played a role in higher current. This will be investigated further in section 5.7. Figure 5.13 shows data for samples made by using metal pattern I and metal pattern II. The wafer where diamond film covered with metal on the top of the **diam**ond line (metal pattern II shown in Figure 4.8d) shows higher current than the wafer where diamond pattern with metal only on the pad (metal pattern I shown in Figure 4.8c). For the samples using metal pattern I, electrons have to move through diamond to reach to emission site from the pad. But in case of sample by using metal pattern II, electrons are likely to move through metal just before the emission site. Sample using metal pattern II shows higher current at lower voltage.

5.5 Testchip II

To include lateral devices, testchip II is designed and fabricated. Figure 5.14 shows measurement setups for vertical devices and lateral devices. In Figure 5.15, I-V curve for



Figure 5.11. Measurement setup for cell 224 of testchip I. Eight marked cells were measured.



Figure 5.12 (a) I-V and F-N data of cells marked circle in Figure 5.11. (b) I-V and F-N of a cell from square marked and one cell from circle marked in Figure 5.11.



Figure 5.13. I-V and F-N data for samples with metal pattern I and metal pattern II in test chip I.

vertical devices with different emission area are shown. Since sacrificial photoresist layer was spin-coated for the testchip II, vacuum gap is believed to be same for all sixteen devices. It is found that measured currents don't grow in proportion to the emitting area. Ermission from diamond seems to be non-uniform. Figure 5.16 shows, I-V for lateral device with same emission area but different anode to emitter distance. At same field, it seems that emitter with large distance to anode draws slightly larger current than emitter with smaller distance.

Figure 5.17 shows lateral device with same anode to emitter distance but different emitter shape.

5.6 Testchip III

Using the setups shown in Figure 5.18 (a) for type A and in Fig. 5.18 (b) for type B, the current-voltage (I-V) measurements are taken by placing the samples inside a vacuum chamber with a pressure of 10⁻⁶ Torr. The current density J measured as function of field strength F for the diode structure is shown in Figure 5.19 for type A and B devices. The current density measured at 0.2MV/cm is approximately 0.5A/cm² for type A device and 0.1 A/cm² for type B device. A number of factors may have contributed to the difference in the current densities for devices A and B. First, the diamond film is partly covered with Cr for type B devices, reducing the effective emission area. Secondly, the emitter contact resistance might have affected the emission at high emission current values, as the emitter with smaller contact resistance was found to exhibit higher current density [6]. It may be noted that for the type A device, the metal semiconductor contact is ohmic. Lastly, the different anode-to-emitter spacing for type A and B may affect the field at the emitting surface. The diamond surface consists of tiny tips of diamond due to the surface roughness. It was found [102] that, for the same field, a larger anode-to-emitter spacing results in a higher current. It is argued that as the anode is moved away from the emitter,





Actual area=2500:5000:10000:20000 μm² Area ratio=1:2:4:8 Current ratio=1:1.12:1.36:3.5



Figure 5.15. I-V and F-N data for vertical devices with different emitter area.



Figure 5.16. I-V and F-N data for lateral devices with different emitter to anode distances.



Figure 5.17. I-V and F-N data for lateral devices with different emitter shape with same distance.

the area of relatively uniform electric field under the probe expands, and more emitters can
ontribute to the measured current. Our simulation studies and measurements, which will
be discussed later in detail, support this argument.

The testchip contains a number of type A and B device structures a consisting of continuous or patterned diamond film as the emitter. As shown in Figure 5.20, for both types of emitters, the current density for an array of dots is higher than that of a continuous film for equal areas of the emitters. As the continuous and patterned films are prepared under similar deposition conditions, their doping level, surface morphology, sp³/sp² ratio and surface termination are expected to be similar. Using a phosphor-coated glass plate as an anode, it was found that the emission from doped diamond films is non-uniform [15]. In another study [103], the emission from isolated diamond particles showed a higher current density than that from a continuous film. Although our results seem to suggest a larger number of emission sites for the patterned emitter, it is not clear whether the enhanced emission takes place at edges.

In Figure 5.21 measurement setup for lateral device is shown. Two different emitter **contacts** were possible. One from the top and another from the backside of the wafer. In **Figure 5.22**, I-V data for two different emitter contacts were depicted. Higher current was **detected** when emitter contact was established from the backside of the wafer. This trend is **similar** to the vertical device where type A device which has emitter contact at the **backside** of the wafer showed higher current density than type B device.



d= 9~10 μm



Figure 5.18. Measurement setup for (a) type A and (b) type B device.



Figure 5.19. I-V curve and F-N plot of diamond field emitter for type A and B device.



Figure 5.20. I-V curves of type A (inset) and type B devices for continuous and array type emitters with the same total area.



Figure 5.21. Measurement setup for lateral device from Al on top of diamond film (a) and Al on Si backside.

Current (Amp) 0.2

() 2



Figure 5.22. I-V and F-N data for lateral device two different emitter contact.

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5.7 Discussions

The results in the preceding sections raise the following questions:

- (1) Why electron emission is possible at 10^{-2} Torr? (section 5.2)
- (2) Why diamond seeded with high nucleation density shows higher current than diamond film seed with low nucleation density? (section 5.3)
- (3) Why low resistivity film exhibits higher emission current? (section 5.4)
- (4) Do different contacts to diamond affect emission current from diamond? (section 5.4 and 5.6)
- (5) Why emission from diamond is non uniform? (section 5.4 and 5.6)
- (6) Why emission current seems to be higher even at same field when anode to emitter distance is larger? (section 5.5 and 5.6)?
- (7) Why dot patterned film shows more current than continuous film? (section 5.2 and 5.6)
- (8) How does diamond film quality relate to the emission characteristics?
- (9) What is the best emitter structure for achieving high current densities needed for FED?

To address some of the questions two additional experiments were conducted as described in the following sections.

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5.7.1 Effect of diamond deposition condition

To study the role of film deposition parameters on the field emission current density, which may address the questions (2), (3), (8) and (9), three different sets of diamond films were prepared on p-type Si. Using different CH₄ concentrations in hydrogen, the samples with different sp³/sp² ratios were produced in the first set. The sp³/sp² ratio is calculated by subtracting the base line value from Raman spectrum and comparing count numbers at 1332 cm⁻¹ and 1580 cm⁻¹. In the second set, the boron doping concentration of films was varied using solid or powder sources for in-situ doping of diamond [104]. The resistivity was measured by the four-point probe method. Depending upon the relative position from either solid source or boron powder crucible, the resistivity varies. For the third set, diamond films with grain sizes in the range of ~0.3 to ~1.5 µm and film thicknesses in the range of 10^{11} and 10^8 cm⁻² [105], respectively. Table 5.1 summarizes the deposition conditions of all the films used in this study.

For the field emission measurement, a 50 μ m thick quartz plate was used as a spacer between the anode and the diamond emitter. A polished brass column was used as an anode [15].

Figure 5.23 shows I-V curves, Raman spectra and SEM pictures for samples with CH_4/H_2 ratios of 0.5, 1 and 2%. With increasing CH_4 concentration, a deterioration of sp^3/sp^2 ratio and thus the diamond quality is indicated by the decreasing height of the diamond peak in the Raman spectra. The diamond with low sp^3/sp^2 ratio exhibits low emission fields and high current densities. It is particularly interesting to note from the SEM micrographs that with an increasing CH_4 concentration the number of small grains on the diamond surface increases, resulting in a higher density of grain boundaries. A similar trend is also observed in films grown in microwave CVD [106].

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Summary
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Emission field (MVcm ⁻¹) at	lmAcm ⁻²	~0.49	~0.41	~0.29	~0.68	-0.39	~0.45	~0.38	~0.29	~0.18
	0.01 mAcm ⁻²	~0.36	~0.23	~0.15	~0.4	~0.27	£.0~	~0.33	~0.18	~0.1
Resistivity (Ωcm)		~35	~27	~10		~189	~52	~110	~3	~1.7
Doping source		B powder	B powder	B powder			B ₂ O ₃ wafer	B ₂ O ₃ wafer	B powder	B powder
Growth time (hours) undoped+ doped		6+2	6+2	6+2	8 + 0	4+0	0+8	6+2	0+8	0+2
sp ³ /sp ² ratio		~5.4	~4.1	~1.3	~6.3	~5.8	~3.7	~4.8	~3.3	~2.8
CH ₄ /H ₂		0.5%	1%	2%	1%	1%	1%	1%	1%	1%
Sample ID		#1	#2	#3	7 #	#2	9#	#7	8#	6#

Current (µA)

Intensity (Arbitrary Unit)

Figure



Figure 5.23. I-V curves, Raman spectra, and SEM pictures of samples for samples with different CH₄ concentrations.

met their This conc ł studi dope of gr durin of no evide contir presu diamo films. unders To Wafer v ^{is} the s ^{film} she found t ^{one} dep Current ^{on to}p o A higher CH_4 concentration results in lower resistivity as measured by 4-point probe method. As the density of grain boundaries is enhanced through high CH_4 concentration, their contribution to the conduction may be responsible for the observed low resistivity. This may suggest that the presence of graphitic phase may be related the enhanced conduction.

As the high doping levels affect sp^3/sp^2 ratio, grain boundaries and grain sizes [96], we studied the effect of doping on the field emission current. As seen in Figure 5.24, the doped film shows enhanced emitter current. Again, the low sp^3/sp^2 ratio and high density of grain boundaries seems to result in a low field and high current density. Although during the preparation of the undoped sample no dopant source was used, the early stage of non-continuous film shows some conductivity with resistivity larger than 1 K Ω cm as evident from the 4-point probe measurement. When it is grown longer and becomes continuous, this conducting behavior disappears probably indicating that B source, presumably from p-type Si wafer, is now completely covered by diamond film and diamond film is becoming non-conducting. During the measurements on some undoped films, arc was observed before the start of the emission, the origin of which is not well understood.

To produce samples with large differences in doping levels, boron powder or B_2O_3 wafer was used as a dopant source. As shown in Figure 5.25, although CH₄ concentration is the same, sp^3/sp^2 ratio tends to decrease with increasing B concentration. Highly doped film shows low field and high current density emission. In earlier experiments [71], it was found that a diamond film deposited directly on Si results in a lower sp^3/sp^2 ratio than the one deposited on top of an undoped diamond film. As shown in Figure 5.26, the emission current from a doped film deposited directly on Si was higher than that of a film deposited on top of undoped diamond. In all the above results, the relationship between the low

Intensity (Arbitrary Unit) Current (µA)

Figl



Figure 5.24. I-V curves, Raman spectra, and SEM pictures of samples for samples with doped and undoped film.

Intensity (Arbitrary Unit) Current (µA)

Figure



Figure 5.25. I-V curves, Raman spectra, and SEM pictures of samples for samples doped with two different doping methods.

Current (µA)

Intensity (Arbitrary Unit)

Figu



only

2 µm

Figure 5.26. I-V curves, Raman spectra, and SEM pictures of samples for samples with doped only layer and doped layer over undoped layer.

еm An Lo [10 film (Ta repo of c ratic sma emis cons dens these diam emiss densi E [108] anon factors and the fields a have be emission field and (i) low sp³/sp² ratio and (ii) high grain density is consistently obvious. Another interesting feature of the results is the presence of both small and large grains. Lower quality diamond films were found to results in enhanced emission in earlier studies [102,103].

It would be interesting now to compare the emission behavior of small and large grain films. As shown in Figure 5.27, the small grain film results in the lowest emission field (Table 1). In an earlier study, current densities in the range of 10 Acm⁻², the highest reported for diamond, were reported for nanocrystalline diamond [107].

The data in the present study provides an experimental evidence for the enhancement of current density and reduction in the emission field for diamond films with low sp^3/sp^2 ratios, high doping densities, and large densities of grain boundaries (*i.e.* high densities of small grains). Field enhancement at the grain tips, surface termination, defects, number of emission sites and grain orientation may have played a role in the field emission. These considerations lead to a number of questions: Does the fine grain film result in a higher density of emission sites than a film with a combination of small and large grains? Are these emission sites related to field enhancement at the tips? Is the presence of defects in diamond necessary for field emission from p-type or undoped diamond? Is the field emission from single crystal diamond with a smooth surface [108] related to defect densities?

Electron emission from flat surface of boron-doped natural diamond has been reported [108]. In this case, defects, orientation and surface passivation of the diamond may be among the critical factors. However, in the case of polycrystalline diamond, additional factors such as grain boundaries, grain size differences, high densities of surface defects and the field enhancement at grain tips, should be taken into account. The lower threshold fields and higher current densities for polycrystalline than those of single crystal diamond have been attributed to lower sp³/sp² ratios and the related defects found in polycrystalline

Current (µA)

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Intensity (Arbitrary Unit)

Figure



Figure 5.27. I-V curves, Raman spectra, and SEM pictures of samples for samples with different grain size.

l i la pl gra a f 065 data den 4 III a sepai Type mixtu with c emitter neighb previou emissio ^{may} ind aperime films [102,103]. The role of field enhancement at the grain tips may vary for small and large grain films, and for films containing both the small and large grains. The density of emission sites in a particular film may depend on field enhancement, grain size, surface termination, and defect densities.

When both the small and large grains are present on the diamond surface, the height of large grains can lead to a larger field at their tips and, therefore, the emission may be initiated at these sites first when a field is applied. The small grains present between the large grains will have a lower field at their tips and the field emission will primarily take place from the highest tips. However, when the number of small grains between the large grains increases, the density of emission sites in the small grains area increases. Thus, for a film consisting of small grains only, a larger density of the emission sites may be observed due to similar fields at the emitting tips. This may be related to the measurement data found for discrete sample in section 5.3 where film seeded with high nucleation density exhibited larger current than low nucleation density seeded film.

As shown in Figure 5.28, films with small and large grains, categorized into types I, II, III and IV, were simulated to study the field enhancement using anode to emitter separations of 1 or 10 μ m. Type I represents small grain film. Grain size is set to 0.5 μ m. Type II represents large grain film. Grain size is set to 2 μ m. Type III denotes 50-50 mixture of small grain and large grain film. Type IV represents mostly small grain film with occasional large grain film. Figure 5.29 shows electric fields at the tips for the four emitter types. Data shows that field enhancement is larger when separation between the neighboring tips and anode to emitter distance is larger. This result is consistent with previous simulation studies of Si microtip emitters [109,110]. This may suggest that the emission is enhanced when anode to emitter distance is larger at a given field strength and may indicate that emission is predominantly coming from grain tips. To verify this effect experimentally, the same film was measured for anode to emitter separations of 1.6 μ m

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and 50 μ m. As shown in Figure 5.30, the larger separation results in higher current and lower threshold field. This may explain question (6) raised in the beginning of section 5.7. This has also been noticed at the characterization of lateral device of testchip II (section 5.5, Figure 5.16).

The adsorption of H on the surface of diamond is known to lower its electron affinity [111]. As all our samples were treated in hydrogen plasma in the HFCVD system just after the diamond film deposition, it is believed that the film surface is passivated with hydrogen for all samples. It is conceivable that the surface termination with hydrogen is more pronounced for small grain films due to a larger density of grain boundaries. Consequently, the enhanced field emission behavior of small grain films may also be due to low electron affinity.

5.7.2 Effect of Implantation

Defects can be introduced in diamond through the variation of deposition conditions [112, 102] or by ion implantation [103, 35]. Zhu *et al.* [103] studied field emission from ion-implanted diamond. In their experiment, boron, carbon and sodium ions were implanted. But only one energy level was selected for each ion source. Although we only select carbon ion for implantation, we selected two different doses and two different energy levels in an effort to study the field emission dependence on the depth of damaged layer as well as the density of damage sites.

Four 1 x 2 cm² samples consisting of B-doped polycrystalline diamond films grown on p-type Si by HFCVD system were prepared under similar deposition conditions. Half of each sample was covered with metal to block implantation so that direct comparison of emission current from both implanted and unimplanted areas can be made. The implantation doses and energies were 5×10^{16} cm⁻² and 5×10^{15} cm⁻², and 20keV and 50 keV, respectively. Samples were implanted with either C²⁺ or C⁴⁺ depending upon their



Figure 5.28. Four different structures for ANSYS simulation: (a) Type I



Figure 5.28. Continued. (b) Type II



Figure 5.28. Continued. c) Type III



Figure 5.28. Continued. (d) Type IV

Tip-Field (MV/cm)



Figure 5.29. Simulated electric fields at the tip for different types for anode to emitter distances of 1 and 10 μ m.

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Figure 5.30. Measured emission current as a function of field for anode to emitter distances of 1.6 and 50 μ m.

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doses. Implantation was done at National Superconducting Cyclotron Laboratory by Dr. T. Grimm [113]. Detailed sample preparation conditions are summarized in Table 5.2.

Sample ID	Energy (keV)	Dose (cm ⁻²)
HI-2	20	5x10 ¹⁵
HI-3	50	5x10 ¹⁵
HI-5	20	5x10 ¹⁶
HI-9	50	5x10 ¹⁶

 Table 5.2. Implantation energy and dose for four samples.

SEM and Raman spectroscopy were done both on implanted and unimplanted areas of the samples before I-V characterization. As shown in Figure 5.31, SEM pictures reveal that implanted areas show darker image than unimplanted areas indicating secondary emission is less from implanted areas. Raman spectra show that implanted areas have shorter peak at 1332 cm⁻¹ and wider full width half maximum indicating that quality of diamond is deteriorated due to implantation. Electrical characterization was performed at two different locations, Michigan State and Varian Associates. First, I-V characterization of the samples are performed at Michigan State. Brass anode described in section 3.4.1.2 was used for measurement set-up. Figure 5.32 shows I-V curves. I-V data clearly show that threshold field is lower and current density is higher for higher doses and lower energies. The data support the fact that shallow defects can enhance the field emission since emission increases as the implant dose is increased and made shallower. It was also observed that, for all samples, larger anode to emitter separations led to higher currents. This may be due to the field enhancement found for larger anode to emitter separation [112, 35]. Parts of the samples were cut and shipped to Varian Associates for the measurements. Dr. S. Bandy led the measurement work in collaboration with Mr. L. Garbini. The area of the sample was about 25 mm² and the rectangular samples were

Fig



Figure 5.31. SEM image and Raman spectra of implanted and unimplanted area.

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Figure 5.32. I-V curves for four samples measured at Michigan State.





Figure 5.33. F-N curves for sample (a) HI-5 and (b) HI-9 measured at Varian.

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attached to a stainless steel conflat blank using indium metal. The anode was a molybdenum screen of 76.2 μ m diameter wire by 1016 μ m mesh attached to a micrometer drive for positioning above the sample surface. The I-V measurements were made with a curve tracer. An Inficon QX-2000 residual gas analyzer (RGA) was used for gas analysis and the system was pumped with an ion pump plus sublimator after being rough pumped with a turbo backed with a turbo plus diaphragm backing pump.

All samples had the same characteristics when first operated in normal mode, i.e. drawing current to the anode positioned about 50.8 µm above the emitter surface. Emission abruptly started in the 800-1000V region after arcing was first experienced at these same voltages. While arcing, the current flow had the appearance of a gas sustained discharge and no data for F-N relationship could be taken because of current instability. Samples HI-5 and HI-9 were operated drawing current from "anode electrode" to sample with a continuous power supply at up to a few mA current after testing in the standard mode. After this treatment stable current could be drawn from the sample up to about a few µA and had the characteristics of field emission per F-N curve. Figure 5.33 shows F-N plots for HI-5 and HI-9. Emission currents of up to 100 µA, which is equivalent to current density of ~0.1Acm⁻², were measured on HI-9 before onset of gas discharge destroyed the emitting site while in the process of trying to achieve higher currents levels. Severe local disruption of the diamond surface on both samples was seen by SEM after conclusion of the testing. This may indicate that emission from the surface was non-uniform and small number of sites contribute to majority of current.

After collecting data on HI-5, the Inficon QX-2000 was attached to the station for gas analysis. Analysis of sample HI-9 initially indicated nitrogen, CO, water, hydrogen, methane, argon and carbon dioxide as the components when drawing current to the anode.


Figure 5.34. Residual gases for HI-2 after 450 °C 16 hr bake out: two graphs are used for clarity.

i à Vž fro Sta whe disci 5.8 Fi resulte emple B₂O_{3 W} implante 20keV ar Based Sample HI-2 was baked at 450 °C, with the anode in contact with the sample to prevent movement above the melting point of the indium solder. The RGA charts shown in Figure 5.34 were taken after a 450 °C bake out with a three day stand. The major gas liberated from the sample was CO. All pressure increases on these charts were related to onset of current flow. Magnitude of pressure was related to voltage and anode to sample spacing in all cases. Higher voltage and greater spacing produced higher gas pressure. Sample HI-3 was given a hydrogen plasma treatment using the curve tracer as a power supply. No improvement in the emission instability was seen after this treatment. CO was again found as the major component curing emission from the diamond surface. Measurement at Varian seems to support vacuum arc discharges preceding high electron field emission from carbon films suggested by Groning *et al.* [114]. In our measurement at Michigan State, it has also been noticed that auto trip-off of power supply took place occasionally when load impedance changes abruptly. This may be related to the effect of vacuum arc discharges preceding electron field emission from carbon films.

5.8 Summary

Films with different growth conditions were prepared and careful characterization resulted in valuable data in a systematic way. Characterization was performed for the samples, with CH₄ concentration varying from 0.5% to 2%, doped with B powder and B_2O_3 wafer, seeded with nucleation density in the range of ~10⁸ cm⁻² to 10¹¹ cm⁻², and implanted with carbon at the dose of 5×10^{16} cm⁻² and 5×10^{15} cm⁻² and dose energy of 20keV and 50 keV.

Based on a large amount of field emission data collected from a variety of samples, it

\$ đ Π ar er et ex me ado fac que high that not a due progr amp edge (^{ratio} 0 type A żis edg was found that emission from diamond is enhanced when (i) sp^3/sp^2 is low, (ii) peak at 1332 cm⁻¹ is wider, (iii) grain in the film is small, (iv) film is highly doped, (v) film is damaged by ion implantation, especially density of damage is high and location of damage is shallow, (vi) grain boundary is present, and (vii) roughness film is small. These seems to suggest field emission from polycrystalline diamond is affected by (i) NEA, (ii) defects, and (iii) field enhancement effect at grain tips. These results seem to support a model proposed by Huang *et al.* [53] and Zhu *et al.* [102], which explains that electrons are transportation of electrons to the surface state through the defect states and subsequent emission from surface state. Other models by Givargizov *et al.* [37], Choi *et al.* [40], Geis *et al.* [42], and Lerner *et al.* [54], which are also mentioned in Chapter 2, may be valid to explain emission from very thin diamond film, either n-type or undoped, coated on Si or metal but may not be suitable to explain emission from thick diamond film in our case. In addition to defects, field enhancement factor in grain tips are found to be one of important factors for emission from polycrystalline diamond film.

Some unanswered questions, which were raised in the beginning of section 5.7, are questions number (1), (4), (5), and (7). Diamond's ability to emit electrons in relatively high pressure may be due to its chemical inertness. Although it was noticed in Figure 5.13 that different contact methods to diamond do change emission current, question (4) was not addressed in this study. Non-uniform emission from diamond film (question 5) may be due to non-uniform film morphology. New characterization system being built with a programmable stage of resolution 1 μ m may help answer this question by mapping whole sample with in-situ Raman or other film characterization system. For question number (7), edge effect may have played a role. For example, as shown in Figure 5.20, although area ratio of continuous film vs. dot patterned film for type A and B is 1:1, edge ratio is 2:1 for type A and 3:1 for type A. Current ratio seems to agree with this ratio but it is not clear this edge effect is sole reason for enhanced emission.

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CHAPTER 6

APPLICATIONS

6.1 Introduction

Although application area for field emitters are numerous, driving force for field emission research has been a realization of FED. In this chapter, fabrication and characterization efforts of two types of diamond FEDs in triode mode are mentioned. Fabrication technology of pressure sensor is also presented. Realization of triode FED was reported for the first time [115].

6.2 Diamond Field Emitter Display

The growing need for developing low cost and high performance flat panel displays has spurred a strong research effort in FED technology. Prototype 6" diagonal color FED [116] was demonstrated using Spindt type [2] microtip metal field emitters. For this type of FED, it is necessary to fabricate micron sized micro-tips and grids over large area panels, which results in higher cost. In addition, even though the lifetime of metal microtips has been demonstrated, use of sulfide based color phosphors is a potential problem due to contamination of metal tip from loose phosphor powder particles.

A prototype black and white 1" diagonal diamond FED based on diode configuration has been demonstrated [12] using amorphous diamond films. The major drawback of

F P di re tri 6.2 alon disp emin 4.7. 7 throug is dep Th of eithe 15 x 15 of dots. 6.1(a) ai diamond The p diode structure is relatively high switching voltage. To address this problem, triode type diamond FED technology has been developed at Michigan State.

6.2.1 Diamond Field Emitter Display with Bridge Shaped Grid

In this section, first diamond field emission triode display cells using p-type polycrystalline diamond field emitter [15] is described. Using a 4-mask lithographic process, display cells are fabricated on oxidized Si wafer. Initial measurements of these display cells in diode configuration show field emission at a gate field of 0.1-0.2 MV/cm resulting in gate switching voltage as low as 50 volts. When tested with phosphor anode in triode configuration, successful operation of display cells was confirmed.

6.2.1.1 Fabrication

As briefly described in Chapter 4, triode display cells are fabricated in test chip III along with other structures. An overview of the test chip containing a six by six array display has already been shown in Figure 4.7. Fabrication process of a diamond field emitter triode display cell is almost identical to that of type B device described in section 4.7. The only difference is that grid structure has many holes in it to pass emitted electrons through them. Although only unique points in FED will be discussed here, whole process is depicted in Figure 6.1.

The emitter (p-type diamond) area shown in Figure 6.1(a) forms one pixel and consists of either a continuous film or an array of diamond dots. The array size varies from 2 x 2 to 15 x 15. The SEM micrographs shown in Figure 6.1 are for pixels with different number of dots. For example, pixels consisting of array of 8 x 8 and 5 x 5 dots are shown in Figure 6.1(a) and 6.1(b) while the one for Figure 6.1(c) shows a pixel consisting of a continuous diamond film.

The patterned (Figure 6.1e) Al layer has a 15 by 15 array of $4x4 \ \mu m^2$ holes to permit



Figure 6.1. FED cell fabrication process; cross sectional views and SEM micrographs.



Figure 6.1. continued.

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electron supply to the anode. The sacrificial photoresist layer is removed (Figure 6.1f) to produce gap between gate and emitter.

After removing the sacrificial layer, the separation between Al and diamond, computed by taking into account the thicknesses of the sacrificial photoresist layer and the diamond film, is in the range of $2 \sim 3 \mu m$ (Figure 6.1f). Al is also evaporated on the part of Cr pattern to serve as a cathode contact. Completed samples are annealed at 400 °C in N₂ ambient for 30 min using a rapid thermal processor. SEM picture of a completed cell of diamond field emitter is shown in Figure 6.1(f) and a magnified view of the gap between gate and cathode is shown in Figure 6.2. Note that even though sacrificial layer was quite thick, step coverage by Al is still acceptable.

6.2.1.2 Testing

• I-V Data

Fabricated samples are first characterized by current versus voltage (I-V) measurement in a diode configuration to confirm the field emission from diamond FED cells. Figure 6.3 shows the measurement setup (a) and the I-V data (b) measured at 10^{-6} Torr. The emission starts at approximately 20 V leading to an emission field in the range of 0.07 - 0.1 MVcm⁻¹. As evident from the inset of Figure 6.3 (b), the I/V² versus 1/V plot is a straight line showing a typical F-N field emission behavior. The current density measured at 0.2 MVcm⁻¹ is approximately 0.1 A/cm² as compared to reported values in the range of 0.1~10 Acm⁻². As compared to the switching voltage of several hundred volts used in the prototype diamond diode FED [12], a gate voltage in the range of 50 - 100 volts was enough to control the field emission in our triode FED structure described in the next section.



Figure 6.2. A magnified view of a display cell showing vacuum gap between gate and emitter.



Figure 6.3. (a) Experimental setup for I-V measurement and (b) I-V curve and F-N plot of a display cell when tested in a diode configuration.

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Triode Cell Testing

Phosphor anode described in Chapter 3 was used as an anode to test the triode FED cells. A quartz spacer with a thickness of 0.1 or 1 mm was used between the phosphor anode and the diamond emitter structure. Figure 6.4 shows such an experimental setup to inspect light emission from one pixel. The grid and anode potentials are in the ranges of 100 and 500 volts, respectively. The grid or anode currents were not monitored in this experiment which focussed only on light emission pattern depicted in Figure 6.4. The pattern was recorded in a vacuum chamber with a pressure of 10^{-6} Torr.

Figure 6.5 shows experimental setup for light emission from a triode FED with an array of 1 x 4 pixels and its emission pattern recorded by a camera. It may be pointed out that the actual number of holes in the Al grid for every pixel is 225. However, in Figures 6.4 and 6.5, only 4 holes were shown for clarity.

Although the triode diamond FED cells have been demonstrated successfully for the first time, some problems were encountered during the fabrication process. As shown in the SEM micrography of Figure 6.1(b), (d), and (f), there are a number of stray diamond particles in areas where they should not appear. They result from the diamond particles which could not be washed away completely during the development process of photoresist mixed with diamond particles. They can affect the yield if they form a continuous film and if their size becomes too large. Figure 6.6 shows a failed cell due to clustered diamond particles. Due to these problems, only a fraction of the FED devices were found to function properly. For later samples shown in Figure 6.1(a) and (c), double layer patterning technique described in Chapter 4 was applied. It shows reduced number of stray particles.

6.2.2 Diamond Field Emitter Display with Self-Aligned Gate

Although the first diamond FED in triode mode is demonstrated in the previous



Figure 6.4. Setup for emission image from a triode display cell and its corresponding image.



Figure 6.5. Setup for measuring emission image from four triode display cell array and its corresponding image



Figure 6.6. A failed display cell due to a cluster of diamond particles.

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section, it had low yield and high gate current. It also requires μ m range lithography to define small gate halls and accurate alignment. In this section, diamond FED in triode mode with more relaxed and self-aligned gate structure is developed and demonstrated.

6.2.2.1 Fabrication

Detailed fabrication process is shown in Figure 6.7. Four transparency masks with minimum feature size of ~50 were used. First layer defines diamond pattern, second layer emitter contact, third layer gate hole, and fourth layer metal. Oxidized four inch wafer was used as a substrate. One wafer consists of two display chips.

One chip consists of twelve 2.5mm wide and 35mm long diamond resistors, doped with B powder and grown on 4" oxidized Si wafer using HFCVD system. Separation between each resistor is 0.5mm. Resistance of diamond cathode is $20 \sim 32 \text{ k}\Omega$ Assuming average film thickness of 2 µm, resistivity is in the range of 2.86 ~ 4.57 Ωcm. This value is approximately in accordance with the resistivity value measured by four point probe system. Patterned diamond film is shown in Figure 6.7 (a).

Due to the limitation of low temperature oxidation facility and the simplicity of spinon-glass (SOG) process, SOG was selected for an insulating layer. First SOG used was Filmtronics' SOG (Model No. GF511F). GF511F is an alcohol solution which is applied to a semiconductor surface to yield a pure SiO₂ film similar in characteristics to a pyrolitic oxide. SOG yields a pyrolytic oxide essentially free of sodium ions or other undesirable elements deleterious to semiconductor devices. Films may be formed on a wide variety of flat surfaces by spinning, spraying or dipping. For precise control of flatness and greatest uniformity from wafer, spinning is the recommended procedure for applying SOG film.

After spinning, the film remaining on the surface of the wafer must be hardened or densified by heat treatment. The heat treatment is carried out at temperatures from 200 °C to temperatures in excess of 800 or 900 °C in air, oxygen or nitrogen. The extent of the



Figure 6.7(a). Design vew, cross sectional view, and wafer photography after diamond deposition.

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densification of the film is indicated by the etch rate in dilute HF solutions. A film densified by heat treatment at 200 °C for 15 minutes will exhibit an etch rate 1000 times faster than a thermal oxide. A similar heat treatment at 900 °C will yield a film whose etch rate is two to three times faster than a thermal oxide. In addition to the reduction in rate of etching by HF, heat treatment also affects the hardness of the film, as evidenced by its resistance to scratching with a steel stylus. Heat treatment at 800 °C will yield a film which will exhibit scratch resistance comparable to a thermal oxide. The thickness of SiO₂ film formed from Silicafilm is determined by the spin speed when the material is spun on. At 3000 rpm, a film thickness of 2000 Å is obtained after heat treatment at 200 °C. The film thickness decreases as spin speed is increased. FIIms up to 8000 Å thick may be obtained by successive applications of material applied while the wafer is spinning and allowing 5 or 10 seconds between successive application. The dielectric and optical characteristics of films formed from SOG are quite similar to the characteristics of pure SiO₂ formed by the oxidation of silicon at high temperature.

In this experiment, SOG was spin-coated three times at 3000 rpm to get at least 8000 Å. Sample is baked in convection oven at 200 °C. When sample is cooled down rapidly, some cracks in SOG film are found due to rough nature of diamond film and thermal expansion coefficient mismatch between diamond and SOG film. To assure crack free SOG film, slow ramping down heat cycle of less than 3 °C/min is required. Although great care has been taken, crack problem hindered further process development. Cracks are shown in Figure 6.8 (a).

Emulsitone's silicafilm 10,000 was used to get crack free film instead of Filmtronics' SOG. Silicafilm 10,000 is similar to Filmtronics' SOG GF511F with the exception that a thickener has been added to the solution. When applied by spinning a thick glassy layer will form, which must be heated to remove the thickener. After spinning at 3000 rpm the

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film should be heated at 200 °C for 15 minutes in air to densify the film. The heat treatment is followed by heating at 450-500 °C for one hour in air to remove the thickener by oxidation. Silicafilm 10,000 etches more rapidly than more conventional SiO_2 films. For example, a typical etch rate in 5% HF solution at 25 °C is 150 Å/second for a film heated at 500 °C. Silica 10000 was spin-coated three times at 3000 rpm to get 3 μ m thick film. Sample is baked in convection oven at 200 °C and baked in furnace at 500 °C for one hour. Crack problem has dramatically reduced. A sample without crack is shown in Figure 6.8 (b). Occasional crack was still observed if heat cycle is not properly controlled.

At the two ends of each resistor area SOG is etched to make emitter contacts. Cr is thermally evaporated on top of diamond where SOG is etched as well as on top of SOG in most area. This step is shown in Figure 6.7 (b). Cr is patterned to create gate holes. Through open Cr area, SOG is etched and it is intentionally overetched to create undercut. Two different gate structures were used to create either one by one 200 μ m wide hole in diameter or two by two 100 μ m wide hole to check emission properties from different structures. Half of gate mask has one by one 200 μ m wide gate holes and another half has two by two 100 μ m wide holes as shown in Figure 6.7 (c). Since gate hole size is very large compared to SOG thickness, it is not expected to have emission current contribution from the center of the gate hole. Majority of current is expected to initiated near the gate hole edges.

Cr is etch once again to separate each six row and twelve columns. Finished sample is shown in Figure 6.7 (d).

6.2.2.2 Testing

Figure 6.9 shows measurement setup for the sample. Gate voltage was varied from 40 to 80 Volts. Anode voltage was varied from 100 to 500 Volts. While emission pattern is



Figure 6.7(b). Design view, cross sectional view, and wafer photography after emitter contact etch followed by Cr evaporation.



Figure 6.7(c). Design view, optical microscopy picture and cross sectional view of the sample after gate definition.





Figure 6.7(d). Design view and finished wafer. Two different gate structures are also shown.



(a)



(b)

Figure 6.8. Samples with (a) cracks and (b) no crack.









Figure 6.10. Anode current I_a and gate current I_g as a function of anode voltage V_a and gate voltage V_g

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Figure 6.11. Emission pattern of the FED chip in triode configuration

recorded in the camera, gate current and anode current were monitored. Figure 6.10 (a) shows the anode current characteristics for gate voltage of 40, 60, and 80 Volts and Figure 6.10 (b) shows the corresponding gate current characteristics. These are typical I-V characteristics for triode structure [117]. I_a/I_g ratio of ~10 is found. This value is in the better end of reported value of 0.1 - 10 [42]. Figure 6.11 shows emitted pattern. Although it was successful to have two pixels working, not all the pixel emitted. Further process and design improvement is needed to address these problems. However, the purpose of this experiment was to demonstrate the possibility of new self-aligned process.

In Chapter 5, it was revealed that films grown with high nucleation density resulted in higher current density and lower turn-on voltage. Another advantage to use films with high nucleation density in this experiment is smoothness of high nucleation density film. It would reduce crack problem encountered in this experiment with low nucleation density film.

6.3 Field Emitter Pressure Sensor

Commercially available piezoresistive and capacitive pressure sensors are subject to limitations of temperature and sensitivity, respectively. Due to their temperature independence and radiation hardness, the use of field emitter devices for pressure or displacement sensors has been proposed [4,118]. Although simulation of field emitter pressure sensors shows high sensitivity [118], nobody has produced pressure sensor based on field emission yet. Using the fabrication technology developed, we demonstrate the design and fabrication of a pressure sensor for the first time [119]. Main technique used is self-vacuum-sealing process [120]. The field emission behavior was confirmed in vacuum chamber.
6.3.1 Simulation

To study the displacement of diaphragm depending upon geometries and materials of devices, ANSYS finite element analysis was performed. Actual geometric and material data are fed into the simulator. Input variables to the simulation are geometric parameters of devices such as thickness, width, and length of diaphragm. Also material properties such as Young's modulus, Poisson's ratio and shear modulus are used as input parameters. Applied pressure to the diaphragm is used as a boundary condition to the problem. Constructed model was then meshed, solved and resulted in displacement. Figure 6.12 depicts a sample contour plot of displacement while Figure 6.13 shows displacement plot. Having known displacement value, assuming uniform field emission from whole cathode area, total current from a device is calculated from F-N equation as follows. We can calculate the current for each element by approximating diaphragm as a collection of flat squares of same size with different distance to the emitter. Summation of all the squares with different distance d resulted in total current. This concept is shown in Figure 6.14. It was found that 4 μ m thick Al diaphragm, which was diaphragm thickness of fabricated sample, can yield curve an order of magnitude change in anode current per applied pressure of 40 dyne/cm².

6.3.2 Fabrication

Pressure sensors were also fabricated in test chip III. The complete fabrication process for diamond field emitter pressure sensor is shown in Figure 6.15. Fabrication process is identical to type A devices described in Chapter 4 up to first Al deposition. Explanation for the fabrication process is omitted up to this point. Minor modification to type A device is incorporated to achieve self vacuum sealing. Al is patterned to form holes and part of sacrificial photoresist is now exposed to be removed (Figure 6.15c). The sacrificial layer underneath Al is removed using either acetone or remover. Wafer is then cleaned with de-







Figure 6.13. Displacement value of diaphram along A-A' of Figure 6.12. Unit is in μm .

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Figure 6.14. Approximation of pressure sensor to calculate total current.













Figure 6.15. Cross-sectional views of a pressure sensor at each process step and the corresponding pictures of top view.



Figure 6.15. Continued.

ionized (DI) water numerous times to ensure cleaning of hollow inside. Al is evaporated once again at grazing incidence angle to seal the sensor and patterned appropriately. SEM pictures in Figure 6.15 (d) shows holes just before its complete closure. Sealing evaporation has to be done three to four times in Al evaporator. In general, with maximum Al clip loading, one time Al evaporation resulted in 1 μ m thick film. It was necessary to repeat this procedure to completely seal the device. Al is then etch to separate each devices. Completed structure is shown in Figure 6.15 (e). The fabricated device is intended to be self-vacuum sealed and can be operational at the atmosphere if successful vacuum sealing is achieved. The anode is processed as a diaphragm that can be displaced by applying pressure, which will eventually change the field emission current. Al is also evaporated on the backside of wafer to serve as a cathode electrode (Figure 6.15e).

Completed samples are annealed at 400 °C in N_2 ambient for 30 min. The current voltage (I-V) data is taken by placing the wafer inside a vacuum chamber with a pressure of 10^{-6} Torr first to make sure emitter itself is functioning its successful field emission behavior.

6.3.3 Testing

The I-V characteristic of one pressure sensor as a field emitter itself is shown in Figure 6.16(b), the corresponding F-N plot is shown in the inset. This data is taken for a pressure sensor with 40 x 40 μ m² diamond emitter inside high vacuum chamber. The exponential I-V curve and the straight-line F-N plot indicate that measured current is indeed field emission current. The current density measured at 0.2MV/cm is approximately 0.5A/cm² as compared to reported values in the range of 0.1~10A/cm². Field emission behavior is continued even though absolute value of current density is decreased as



Figure 6.16. (a) Measurement setup and (b) I-V curve and F-N plot of a diamond pressure sensor when measured at a pressure of 10⁻⁶ Torr and 10⁻³ Torr.



Figure 6.17. Measurement setup for a pressure sensor at atmosphere.

the pressure inside vacuum chamber is raised up to 10^{-3} Torr range. This is due to effective work function change of emitter surface. As we have reported earlier, diamond field emitter operates at relatively higher pressure than field emitter devices made of materials other than diamond.

True pressure sensor operation is not achieved at this time. Applied external force, preferably pressurized air or N_2 blow to anode membrane could bend anode membrane since anode is very thin diaphragm. This bending decreases the distance between anode and cathode and subsequently increases the electric field affecting the field emission current. Simulation study showed that ~40 dyne/cm² force can change the emission current by one order of magnitude. In our case, when tested in atmospheric pressure with setup shown in Figure 6.17, pressure sensor didn't show measurable emission current. When this non working sensor was put inside the vacuum chamber back, reproducible emission current was again measured. This implies that vacuum sealing is not properly performed at this moment. One of the possible reasons for inadequate vacuum sealing may be due to porous Al anode diaphragm. Depending on Al evaporation condition, porous Al films have been witnessed [121].

6.4 Summary

In this chapter, the design, fabrication and characterization of two kinds of triode type diamond FEDs and the pressure sensor were described. The main purpose of these works was to demonstrate the possibility of these applications. Light emission pattern is recorded for a 1 x 4 pixel triode FED for the first time.

CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH

7.1 Summary and Conclusions

• Development of IC compatible fabrication process for diamond FED in triode

Using a testchip, IC compatible fabrication process for diamond FED in triode mode was developed for the first time. As a result, a unique testchip was designed and fabricated. Operation of diamond FED in triode mode was reported first time. Key technology developed was constructing a built-in anode to the structure. Self-aligned process technology was also successful.

• Design and execution of experiments to collect emission data from wide variety of diamond samples

Films with different growth conditions were prepared and careful characterization resulted in valuable data in a systematic way. Characterization was performed for the samples, with CH_4 concentration varying from 0.5% to 2%, doped with B powder and B_2O_3 wafer, seeded with low and high nucleation density, and implanted with carbon at the dose of 5×10^{16} cm⁻² and 5×10^{15} cm⁻² and dose energy of 20keV and 50 keV.

• Identifying best diamond for field emission and explanation of results

Based on a large amount of field emission data collected from a variety of samples, it was found that emission from diamond is enhanced when (i) sp^3/sp^2 is low, (ii) peak at 1332 cm⁻¹ is wider, (iii) grain size in the film is small and roughness of film is small, (iv) film is highly doped, (v) film is damaged by ion implantation, especially density of damage is high and location of damage is shallow, and (vi) grain boundary is present. These seems to suggest field emission from polycrystalline diamond is affected by (i) defects and (ii) field enhancement effect at grain tips in addition to NEA of diamond.

7.2 Future Research

Although in the present research, realization of triode mode diamond FEDs were first accomplished, there is a need in the following areas for introduction of the diamond FED in the near future.

- (i) The better understanding and prediction of electron emission mechanisms of semiconducting CVD diamonds is important to optimize the performance of diamond FED.
- (ii) It is important to establish a technology to grow diamond on a large glass substrate to compete with LCD market. Low temperature diamond deposition system with uniformity over large area is essential.
- (iii) Efforts should be made to increase emission site density to achieve high current density.

APPENDEX A.

A simplified schematic diagram of this system is shown in Figure A.1. Based upon the operational function, a RFCVD reactor can be categorized into the following seven major subsystems.

- (1) Chamber
- (2) **RF** power system
- (3) Pressure and flow controls
- (4) Vacuum system
- (5) Temperature readout and control
- (6) **Process sequencers**

• Chamber

The main chamber and fixture assembly are constructed of aluminum which provides RF shielding and grounding. The substrate electrode contains a coiled resistance heater that provides uniform high temperature control. The aluminum fixtures, for the most part, are not attacked by reactive gasses typically used in deposition applications and are easily cleaned in a hot reactive gas plasma. Fixture surfaces are smooth to minimize plasma arcing and to facilitate cleaning. The lift assembly is designed to raise the top plate and electrode, allowing complete access to the substrate surface. The air design allows smooth movement and high weight capacities.

• RF power system

The RF generator is 13.56 MHz crystal controlled with 3 KW output. Automatic power control is used in conjunction with the RF generator and allows precise regulation of output power. Multiple preset power levels provide control. Automatic tuning allows for constant impedance matching which enables a predetermined Watt density to be maintained within the plasma. The results are exact process control and a virtual "hands-off" operation. The electrode voltage potentials have a direct relationship to process conditions within the reactor.

• Pressure and flow controls

The mass flow control allows precise metering of process gasses. The system controller is activated by manual or automated means and attains preset conditions through closed circuit monitoring. Total, individual, or ratio flow values are digitally displayed. Rotometers are provided for use during the process purging cycle where precise flow monitoring is not required. Solenoids activate gas flow and are manually or automatically activated. Chamber pressure is automatically adjusted by a valve, driven in a closed loop, capable of maintaining a preset level regardless of varying conditions. The valve controller can be operated in either the manual or automatic modes.

• Vacuum system

The gas control system accepts multiple gasses and is constructed of stainless steel. This component is an integral part of the vacuum system and is subsequently vacuum tight. Flushing of the process channels with an inert gas is easily accomplished during the cleaning cycle of the reactor. The vacuum system allows pump down of the reaction chamber to a low pressure, thus eliminating background gasses that may contaminate the process. Pressure and flow requirements are met through the use of an automated throttling type process valve. A pressure controller drives the throttle valve

• Temperature readout and control

The temperature controller and readout displays and regulates the temperature of the substrate. This controller monitors temperature through two independent control loops using separate sensors. An over-temperature condition is prevented by the use of a sensor located on the substrate. The temperature of this substrate is precisely controlled by a resistance heater which is capable of rapid cycling for heating, independent of plasma power.

Process sequencer

The manual processing sequencer is a central switching network that allows manual sequencing from a single panel. The optional automatic process sequencer controls the total deposition process and can be programmed for "one button" operation. The sequencer is microprocessor-based, and is capable of storing four programs, a total of 204 steps. Each step can make a decision based on 8 inputs and provide up to 16 outputs in a standard configuration. Also included is a count-down timer that is programmable from .1 second to 99.99 hours.

Operation procedure

The operation sequence of RFCVD system is carefully laid out to operate machine in different condition than original design without damaging the system.

Starting the system:

- (1) Turn on the cooling water.
- (2) Turn on the power switches: located on the system front panel.
- (3) Turn on the nitrogen flow: use the lever in the backroom.

- (4) Turn on the methane flow switches: located in the backroom. Ar flow switches are always on.
- (5) Vent the system: turn up the vent switch. Wait for 3 minutes.
- (6) Open the system: Turn the hoist switch up. Push the two white knobs in to open the system.
- (7) Clean the system. Load the sample.
- (8) Close the system: Turn the hoist switch down. Push the two white knobs in to close the system.
- (9) Turn the vent switch down. Turn the roughing switch up to evacuate the system.
- (10) Wait until the pressure is near 40 mTorr. Turn the heat exchange on.
- (11) Set the total pressure in the chamber to the desired value. For example: 1.0 at 10, 1 and 0.1 Volts means 1, 0.1 and .01 Torr, respectively. Rotate the control switch from "open" mode to "automatic" mode.
- (12) Turn up the process switch and the Ar flow switch on the front panel.
- (13) Increase the Ar flow using the Ar flow meter (meter #3). Wait until the pressure stabilizes at the desired value.
- (14) Turn up the methane flow switch on the front panel.
- (15) Increase the methane flow using the methane flow meter (meter #2).
- (16) Turn on the RF Generator. Wait 1 minute until the "RF OFF" switch turns on.

- (17) Push "RF ON" switch. Increase the power using the power knob. Watch the incident and reflected powers. Use the automatic mode of Tuning and Load to reduce the reflected power.
- (18) Watch the substrate temperature and the upper stage temperature during deposition.

Shut down procedures:

- Turn RF plasma off. Decrease the power knob back to zero. Let the cooling fan run for 3 minutes. Turn off RF generator power.
- (2) Turn Ar and methane flow switches down. Reduce the flow meters reading back to zero.
- (3) Rotate the control switch from "automatic" mode to "open" mode. Wait until system cools down. Turn cooling water off.
- (4) Turn the roughing valve down (i.e. No pumping down).
- (5) Vent the system: Turn the vent valve up. Wait for 3 minutes.
- (6) Open the system: Turn the hoist switch up. Push the two white knobs in to open the system.
- (7) Take your sample(s) out.
- (8) Close the system: Turn the hoist switch down. Push the two white knobs in to close the system.
- (9) Turn the vent switch down. Turn the roughing switch up to evacuate the system.

- (10) Wait until the pressure is near 40 mTorr.
- (11) Turn the roughing valve down.
- (12) Turn off the power switches: located on the system front panel.
- (13) Turn off the methane flow switches: located in the backroom.



Figure A.1. Schematic of RFCVD system.

APPENDIX B.

```
5 'Copyright Hewlett-Packard 1984, 1985
10 '
15 ' Set up program for MS-DOS HP-IB I/O Library
20 ' For use independent of the PC instrument bus system
25 '
30 DEF SEG
35 CLEAR .&HFE00
40 I=&HFE00
45 '
50 ' PCIB.DIR$ represents the directory where the library files
55 ' are located
60 ' PCIB is an environment variable which should be set from MS-DOS
65 ' i.e. A:> SET PCIB=A:\LIB
70 '
75 ' If there is insufficient environment space a direct assignment
80 '
      can be made here, i.e
85 '
         PCIB.DIR$ = "A:\LIB"
90 '
      Using the environment variable is the preferred method
95 '
100 PCIB.DIR$ = ENVIRON$("PCIB")
105 I$ = PCIB.DIR$ + "\PCIBILC.BLD"
110 BLOAD I$,&HFE00
115 CALL I(PCIB.DIR$, 1%, J%)
120 PCIB.SEG = I\%
125 IF J%=0 THEN GOTO 160
130 PRINT "Unable to load.";
135 PRINT " (Error #";J%;")"
140 STOP
145 '
150 ' Define entry points for setup routines
155 '
160 DEF SEG = PCIB.SEG
165 O.S = 5
170 \text{ C.S} = 10
175 I.V = 15
180 \text{ I.C} = 20
185 \text{ L.P} = 25
190 LD.FILE = 30
195 GET.MEM = 35
200 \text{ L.S} = 40
205 \text{ PANELS} = 45
210 '
215 ' Establish error variables and ON ERROR branching
220 '
```

225 DEF.ERR = 50230 PCIB.ERR\$ = STRING\$(64,32)235 PCIB.NAME = STRING(16,32) 240 CALL DEF.ERR(PCIB.ERR,PCIB.ERR\$,PCIB.NAME\$,PCIB.GLBERR) 245 PCIB.BASERR = 255250 ON ERROR GOTO 410 255 ' 260 J=-1 265 I\$=PCIB.DIR\$+"\HPIB.SYN" 270 CALL O.S(I\$) 275 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 280 ' 285 ' Determine entry points for HP-IB Library routines 290 ' 295 I=0 300 CALL I.V(I,IOABORT,IOCLEAR,IOCONTROL,IOENTER) 305 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 310 CALL I.V(I,IOENTERA,IOENTERS,IOEOI,IOEOL) 315 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 320 CALL I.V(I,IOGETTERM,IOLLOCKOUT,IOLOCAL,IOMATCH) 325 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 330 CALL I.V(I,IOOUTPUT,IOOUTPUTA,IOOUTPUTS,IOPPOLL) 335 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 340 CALL I.V(I,IOPPOLLC,IOPPOLLU,IOREMOTE,IORESET) 345 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 350 CALL I.V(I,IOSEND,IOSPOLL,IOSTATUS,IOTIMEOUT) 355 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 360 CALL I.V(I,IOTRIGGER,IODMA,J,J) 365 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 370 CALL C.S 375 I\$=PCIB.DIR\$+"\HPIB.PLD" 380 CALL L.P(I\$) 385 IF PCIB.ERR <> 0 THEN ERROR PCIB.BASERR 390 GOTO 475 395 ' 400 ' Error handling routine 405 ' 410 IF ERR=PCIB.BASERR THEN GOTO 425 415 PRINT "BASIC error #";ERR;" occurred in line ";ERL 420 STOP 425 TMPERR = PCIB.ERR 430 IF TMPERR = 0 THEN TMPERR = PCIB.GLBERR 435 PRINT "PC Instrument error #";TMPERR;" detected at line ";ERL 440 PRINT "Error: ";PCIB.ERR\$ 445 STOP 450 '

455 ' COMMON declarations are needed if your program is going to chain 460 ' to other programs. When chaining, be sure to call DEF.ERR as 465 ' well upon entering the chained-to program 470 ' 475 COMMON PCIB.DIR\$,PCIB.SEG 480 COMMON LD.FILE, GET.MEM, PANELS, DEF.ERR 485 COMMON PCIB.BASERR,PCIB.ERR,PCIB.ERR\$,PCIB.NAME\$,PCIB.GLBERR 490 COMMON IOABORT, IOCLEAR, IOCONTROL, IOENTER, IOENTERA, IOENTERS, IOEOI, IOEO L,IOGETTERM,IOLLOCKOUT,IOLOCAL,IOMATCH,IOOUTPUT,IOOUTPUTA,IO OUTPUTS, IOPPOLL, IOPPOLLC, IOPPOLLU, IOREMOTE, IORESET, IOSEND, IOSPO LL.IOSTATUS.IOTIMEOUT.IOTRIGGER.IODMA 495 ' 500 FALSE = 0505 TRUE = NOT FALSE510 NOERR = 0515 EUNKNOWN = 100001! 520 ESEL = 100002!525 ERANGE = 100003! 530 ETIME = 100004! 535 ECTRL = 100005!540 EPASS = 100006!545 ENUM = 100007!550 EADDR = 100008! 555 COMMON FALSE, TRUE, NOERR, EUNKNOWN, ESEL, ERANGE, ETIME, ECTRL, EPASS, ENUM, EADDR 560 ' 565 'End Program Set-up 570 'User program can begin anywhere past this point 578 'open "hongdat" for output as #1 590 K20=712 : MPS50=709 : DVM=705 592 CSM=719 : HPDVM=722 595 KEY OFF 1005 CLS 1010 PRINT "" 1015 PRINT "" 1020 PRINT " INPUT YOUR CHOICE OF THE FOLLOWING:" 1. I FOR IV MEASUREMENTS " 1025 PRINT " 2. R TO RETURN TO MAIN MENU " 1030 PRINT " 1035 PRINT "" 1040 INPUT " COMMAND "; A\$ 1045 IF A\$ = "I" OR A\$ = "i" THEN GOTO 1059 1050 IF A\$ = "R" OR A\$ = "r" THEN GOTO 605 1055 GOTO 1040

```
1059 PRINT " TURN ON HP3457A, set the voltage"
1060 input "Name of file to save this measurement data1"; n1$
1061 input "Name of file to save this measurement data2"; n2$
1065 open n1$ for output as #1 : open n2$ for output as #2
1066 input "input Voltage ";inv
1067 write #1, inv : for r=1 to 10000 : next r
1070 'for s=1 to 10
1075 C$="RESET" : DEV=HPDVM : GOSUB 3600 'initialize voltmeter
1100 'FOR T=1 TO 2000 : NEXT T ' WAIT TILL CURRENT IS SET
1120 C$="DVC" : DEV=HPDVM : GOSUB 3600
                                             'READ VOLTS
1125 V=VAL(info$) : PRINT inv;V
1130 write #1, V : write #2, inv, v
1135 'next s
1145 INPUT " set another voltage (Y/N)";TMP$
1150 IF TMP$="Y" OR TMP$="y" THEN GOTO 1066
1155 close #1: close #2
1160 GOTO 1010
3600 LENGTH=LEN(C$)
3605 CALL IOOUTPUTS(DEV,C$,LENGTH)
3610 \text{ MAX}.\text{LENGTH} = 30
3615 \text{ ACTUAL.LENGTH} = 0
3620 INFO$ = SPACE$(MAX.LENGTH)
3625 CALL IOENTERS(DEV,INFO$,MAX.LENGTH,ACTUAL.LENGTH)
3630 INFO=VAL(INFO$)
3635 RETURN
7600 END
```

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