MONOLITHIC MULTIFINGER LATERAL NANODIAMOND ELECTRON
EMISSION DEVICES

By

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To my dearest wife,
&
To my beloved parents and sister
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ABSTRACT

Chemical-vapor-deposited (CVD) diamond is an excellent electron emission material due to its low electron affinity, robust mechanical and chemical properties, high thermal conductivity, and ability to withstand high temperature and radiation. Nanocrystalline diamond, also known as nanodiamond, is an emerging form of CVD diamond which vastly expanding its applicability in vacuum electronics. Apart from the assets of the conventional CVD diamond, it possesses certain distinct properties which include smaller grain-size, high volume density of grain-boundaries, smoother surface morphology, n-type dopant incorporation and increased \( sp^2 \)-carbon content. However, the utilization of nanodiamond in vacuum micro/nanoelectronics has been limited by the complexity associated with its process integration.

The purpose of my research is to develop a reliable process technique to fabricate efficient nanodiamond lateral electron emission devices operable at low voltage with high emission current for applications in vacuum microelectronics and integrated-circuits. To achieve this goal, first, a well-controlled process to realize useful and potential nanodiamond electron emitter structures in array configurations using electron beam lithography (EBL) and plasma etching techniques has been developed. Detail study includes optimization of processing parameters for EBL, metal-mask deposition and nanodiamond dry etching. The main part of the research includes the application of these recently developed process techniques for the design, fabrication and characterization of micro/nanopatterned nanodiamond lateral field emission devices which include sub-micron gap two-terminal and multifinger three-terminal structures. 140-fingered
nanodiamond lateral diode has been achieved for the first time with 300nm interelectrode distance. On the other hand, the three-terminal structure is composed of 140 finger-like emitters with integrated anode and gate, which also has never been reported before. The electrical characteristics of these fabricated nanodiamond vacuum lateral field emission devices demonstrated promising behavior with very low turn-on voltage with high and stable emission current. It has also been observed for the first time that three emission mechanisms dominated at different potential levels. The three-terminal structure showed anode current enhancement and suppression behavior by changing gate bias. These developments in the field of nanotechnology signify the integration of vacuum electronics with the well-established IC process techniques favorable for high-speed and high-power, IC-compatible, extreme-environment vacuum micro/nanoelectronics applications.
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CHAPTER I

INTRODUCTION

1.1 Overview of vacuum tubes and vacuum microelectronics

The invention of solid-state transistors in 1947 [1] and the development of integrated circuits in 1958 [2,3] had influenced scientists to believe that the time of using large, fragile, and inefficient vacuum tubes was over. Compared to the tiny, fast and reliable solid-state transistors, thermionic tubes required a vacuum to operate and used a cathode heated to over 1000 °C to generate the electrons which required a huge power in performing a similar electronic task. For example, the first computer, ENIAC, had about 18,000 vacuum tubes, consumed a massive 200 kW of power and weighed over 30 tons [4]. Consequently, solid-state transistors and ICs have replaced vacuum tubes in almost every application of modern microelectronics and computing.

However, the rebirth of the vacuum tube in microstructure has generated renewed interests in the exploitation of vacuum microelectronic devices (VMDs) for many new applications such as high power and/or high frequency devices, e.g. medical X-ray, RF for magnetic resonance imaging (MRI) machines, high voltage switching of computed tomography (CT) scanners, electronic warfare, radar and communication systems, industrial RF heating and welding, and radio and television broadcasting industries [5]. Unlike thermionic vacuum tubes, these VMEs devices are micro-structured vacuum devices fabricated using state of the art semiconductor microfabrication technology. These devices are sometimes referred to as cold cathode field emitters. The main feature in
VMEs devices is the ballistic electron transport in vacuum which is more efficient than the collision-dominated and mobility-limited transport in solid-state semiconductors. This fundamental difference results in no dissipation of energy, a very small electron transport time, almost independent of the ambient temperature and insensitive to radiation damage.

To generate free electrons in vacuum, the three most frequently applied mechanisms are thermionic emission, field emission and thermionic-field emission. Concisely, in thermionic electron emission process [6], the cathode is heated up to a very high temperature (>1000°C) in order to increase the internal thermal energy of electrons so that they can overcome the work function or surface potential barrier of the material to escape into vacuum. On the contrary, field emission is the process [7] of extraction of electrons from a solid by applying intense electric fields across the vacuum. In this case, electrons quantum-mechanically tunnel through the surface potential barrier into vacuum. Lastly, thermionic-field emission process [8] involves both thermal heating and application of electric field in the electron emission process. Details of electron field emission theory proposed by Fowler-Nordheim which is used in this research are discussed in Chapter III.

These “junction-free” vacuum devices also possess high-speed and long lifetime. These characteristics are favorable for employing vacuum microelectronics in many additional applications such as active elements in integrated circuits, field emitter arrays for flat panel displays, large-area electron guns for high-definition television, scanning electron microscopy and e-beam lithography [9-11]. However, the electron transport in VMDs is limited by the crystal lattice of the emitting material, placing a bar on both the miniaturization and the switching speed of active electronic devices. Table 1.1
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Table 1.1: Comparison of vacuum microelectronic & solid-state electronic devices

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<td>B</td>
</tr>
<tr>
<td>Electron energy</td>
<td>$&lt; 0.3$ eV</td>
<td>Several to 1000 eV</td>
<td>D</td>
</tr>
<tr>
<td>Cutoff frequency</td>
<td>$&lt; 20$ GHz (Si)</td>
<td>$&lt; 100$-1000 GHz</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>$&lt; 100$ GHz (GaAs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>Small</td>
<td>Large</td>
<td>B</td>
</tr>
<tr>
<td>Speed</td>
<td>Moderate</td>
<td>Very fast</td>
<td>B</td>
</tr>
<tr>
<td>Radiation hardness</td>
<td>Poor</td>
<td>Excellent</td>
<td>B</td>
</tr>
<tr>
<td>Temperature sensitivity</td>
<td>-30 to $+50$ °C</td>
<td>$&lt; 500$ °C</td>
<td>B</td>
</tr>
<tr>
<td>Reliability</td>
<td>Fair</td>
<td>Good</td>
<td>B</td>
</tr>
<tr>
<td>Lifetime</td>
<td>Medium</td>
<td>Long</td>
<td>B</td>
</tr>
<tr>
<td>Technology</td>
<td>Very well established</td>
<td>Recently developing</td>
<td>P</td>
</tr>
</tbody>
</table>

Because of the above mentioned advantages, the search for the appropriate material as electron field emitters with low operating voltage, high and stable emission current for potential applications has been the core research of vacuum microelectronics.
for last several decades. Recent works on field emission have been focused on the use of electric field enhancement on sharp microtips and low work function emitter materials.

The hunt for appropriate material for VMEs devices started in early 1960s with metal field emission diodes and triodes [13-23]. However, they have limited potential applications due to their high work functions which led to high threshold electric fields. Further, the problem of impurity adsorption on metal surfaces contributed to current instability and therefore, ultra high vacuum condition is required for stable operation. Therefore, several approaches such as thermal annealing [19] and co-adsorption of silicon (Si) and titanium (Ti) on tungsten (W) [24] have been proposed to improve the stability and emission characteristics of the metal cathode. However, these approaches increased the complexity of the fabrication process rather than significant performance improvement. Several other materials such as GaN [25-27], BN [28], ZrN [29], GaAs [30], and resist polymers [31] have also been reported as electron emission material. However, electron field emitters made of these materials did not shown promising performance for potential applications.

Next, silicon field emission devices have been studied because of well-established silicon based microfabrication technology [32-43] which makes mass production of the emitters possible. Diodes and triodes have been developed as the candidate for VME devices. The silicon cathode is usually heavily doped (n⁺) to achieve low work function (Φ ≈ 4.12 eV) and good ohmic contact with metal. The potential drop across the depletion region in the n⁺ silicon is generally very small compared to the potential drop across the vacuum gap because only small voltage is required for electrons to quantum-mechanically tunnel through the thin depletion potential barrier into the conduction band.
of n+ silicon. Thus, it is practical to assume that most of the potential drop across the vacuum gap. The electric field at the apex allows electrons in conduction band of silicon to quantum-mechanically tunnel through the silicon-vacuum potential barrier into the vacuum and finally, they are accelerated by the electric field and collected at the anode. But their field emission characteristics are relatively poor due to inadequate electrical, thermal, mechanical, and chemical properties. For example, silicon field emitters, like metal emitters, are very sensitive to impurity adsorption and thus require extremely high vacuum condition for a stable operation. In addition, poor thermal conductivity and low electric breakdown field prohibits its use in high power as well as high emission current applications. Further, emission current has been found to degrade with time and eventually the device has destroyed due to heat accumulation and atomic migration [44-45]. Therefore, despite comprehensive efforts to develop efficient cathodes, only a limited number of VME devices have moved to actual prototypes. These include silicidation by metal adsorption [46-47], surface coating with different materials such as TiN [48], and advanced emitter structures such as p+-n++ junction [49], MOSFET [50], MIS cathode [51-52], MOS cathode [53-54], porous silicon diodes [55] and hybrid integration of field emitter arrays (FEAs) with solid-state MOSFETs or JFETs [25]. Again, as before, these techniques result in complicated fabrication processes with little improvement in device performances and applicability in certain areas.

Recently, beside metal and Si cathodes, researchers working on VMEs have been searching for alternate cold cathode materials, primarily allotropes of carbon; diamond, diamond-like-carbon (DLC) and CNTs. Electron field emissions from diamond or diamond-coated surfaces have been shown experimentally to yield large currents at low
electric fields relative to that of metals or narrow band-gap semiconductors. Table 1.2 summarizes the material properties of diamond, silicon and metal for field emission applications [56]. Chapter II gives the detailed insight and advantages of the nanodiamond film used for vacuum field emission (VFE) devices to be studied in this research proposal.

Table 1.2: Material properties of diamond, silicon and metal for field emission applications

<table>
<thead>
<tr>
<th>Property</th>
<th>Diamond</th>
<th>Silicon</th>
<th>Metal</th>
<th>Advantages of diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron affinity (eV)</td>
<td>Low EA and NEA on some facets</td>
<td>4.05</td>
<td>4-6</td>
<td>Low operating voltage</td>
</tr>
<tr>
<td>Electrical breakdown field (V/cm)</td>
<td>$1 \times 10^7$</td>
<td>$2.5 \times 10^3$</td>
<td>N/A</td>
<td>High power application</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm²°C)</td>
<td>20</td>
<td>1.5</td>
<td>5-0.5</td>
<td>High emission current/current density</td>
</tr>
<tr>
<td>Electrical mobility (cm²/V.s)</td>
<td>$1.5 \times 10^3$</td>
<td>$2.0 \times 10^3$</td>
<td>$10^2-10^3$</td>
<td>High carrier saturation velocity</td>
</tr>
<tr>
<td>Surface chemical stability</td>
<td>Relatively inert to adsorption</td>
<td>Very sensitive to adsorption</td>
<td>Quiet sensitive to adsorption</td>
<td>High stability, larger emitting area</td>
</tr>
<tr>
<td>Vacuum requirement (Torr)</td>
<td>Relatively low vacuum ($10^{-5}-10^{-6}$)</td>
<td>Very high vacuum ($10^{-10}-10^{-11}$)</td>
<td>Very high vacuum ($10^{-9}-10^{-11}$)</td>
<td>Practical vacuum environment</td>
</tr>
<tr>
<td>Process Technology</td>
<td>Recently developing</td>
<td>Well established</td>
<td>Well established, but with slow progress</td>
<td>Technology rapidly advancing</td>
</tr>
</tbody>
</table>
1.2 Motivation

This work was mainly motivated by the apparent advantages of vacuum microelectronic devices over solid-state microelectronics and thermionic devices [57]:

- Electrons travel much faster in vacuum with less energy lost and dissipation than semiconductor devices. Because of optical and acoustic phonons scattering, the speed of electrons in solid-state is limited by the carrier saturation velocity of the solid (~$10^5$ m/s in silicon); whereas in vacuum, electrons’ speed is limited only by the fundamental speed of light, $\sim 3 \times 10^8$ m/s.

- Fast modulation with high electron energy is possible in VMDs devices. The operating speed is limited only by the speed of light and device capacitance.

- VMDs should hold high temperature and radiation tolerance, high reliability and long life properties than solid-state devices which are primarily dominated by electron scattering transport in semiconductors. This creates damages to the crystal structure leading to spurious signals and general performance degradation.

- Electron field emission can provide higher current density than thermionic emission.

- VMDs can operate at room temperature. Thus, eliminates the high operating temperature requirement, as in vacuum tube.

- VMDs can operate much faster than the traditional vacuum tubes because of their small size.
1.3 Objective of this research

The scope of this research is focused on developing a reliable and consistent process technique to fabricate submicron-gap diodes and multi-finger triode based on nanocrystalline diamond thin films and to study their electron field emission characteristics. The idea is to develop integrated-circuits compatible vacuum devices operable at lower voltages or electric fields with higher emission currents for applications of vacuum micro/nanoelectronics in harsh environment. This study may be classified as follows:

- Development of consistent process techniques for micropatterning diamond to realize useful microstructures using dry etching techniques and multilevel mixed lithography, viz. optical and electron beam lithography (EBL) approach.
- Implementation of fabricated micro-gap nanodiamond lateral diode for vacuum logic function realization and other applications.
- Design and fabrication of micropatterned monolithic nanodiamond field emission multifinger triodes using EBL.
- Design and fabrication of micropatterned monolithic nanodiamond field emission diodes with sub-micron gap interelectrode distance using EBL.
- Electrical characterization of the fabricated nanodiamond vacuum field emitter devices.
1.4 Organization of the dissertation

There are seven chapters in this report and they are organized in the following topics:

- *Chapter I* provides an overview of vacuum tubes and vacuum microelectronics. In addition, the motivation, objectives and organization of this research are defined.

- *Chapter II* is dedicated to introduce the material used in this research, nanocrystalline diamond, and its unique properties, with particular emphasis on its applicability to vacuum micro/nanoelectronics.

- *Chapter III* contains a theoretical background of basic electron emission in vacuum. It describes the basic electron conduction mechanisms through nanodiamond leading to electron emission. This chapter also provides an extensive survey of recent theoretical and experimental work on diamond field emission.

- *Chapter IV* explains the proposed research and the methodological approaches to be used to achieve the objectives.

- *Chapter V* describes the details of experimental, consisting of material and device processing, with the corresponding SEM images and discussion.

- *Chapter VI* presents the vacuum electrical characterization techniques and the field emission performance of all devices developed, followed with analysis and discussion of the device performance.

- *Chapter VII* summarizes the accomplishments of the proposed research and recommendations for future work.
CHAPTER II

NANOCRYSTALLINE DIAMOND

Diamond has the most extreme physical properties of any material, yet its application in science and/or engineering has been limited due its scarcity and expense. It is the high-pressure form of carbon with $sp^3$-tetrahedral bonded cubic structure. Face-centered cubic structure of the diamond crystal shown in Figure 2.1 [58], can be viewed as two interpenetrating face-centered cubic lattices shifted along the body by $(a/4, a/4, a/4)$, where ‘a’ is the dimension of cubic unit cell. With the recent development of techniques for depositing thin films of diamond on a variety of substrate materials, we have the ability to exploit its various properties in many new and exciting applications. As this research oriented towards the development of promising cold cathode material using chemical vapor deposited (CVD) nanocrystalline diamond, it would be appropriate to dedicate a chapter to explain the basic science and technology underlying of the CVD diamond thin films and its rapid advancements in various fields including vacuum nanoelectronics, NEMS, biomedicine, electrochemistry, optics, and beyond.

2.1 Introduction to CVD diamond

CVD processes offer an opportunity to exploit many desirable physical properties of diamond. As Table 2.1 [59] shows, diamond is the hardest known material with lowest coefficient of thermal expansion, is chemically inert and wear resistant, offers low friction, has high thermal conductivity, is electrically insulating and optically transparent
Figure 2.1: Face-centered cubic structure of the diamond crystal [58].

Table 2.1: Properties of CVD diamond and single-crystal diamond

<table>
<thead>
<tr>
<th>Property</th>
<th>CVD diamond</th>
<th>Single-crystal diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm⁻³)</td>
<td>2.8–3.51 [1]</td>
<td>3.515</td>
</tr>
<tr>
<td>Thermal capacity at 27 °C (J mol⁻¹ K⁻¹)</td>
<td>6.12</td>
<td>6.195</td>
</tr>
<tr>
<td>Standard entropy at 27 °C (J mol⁻¹ K⁻¹)</td>
<td></td>
<td>2.428</td>
</tr>
<tr>
<td>Standard enthalpy of formation at 27 °C (J mol⁻¹)</td>
<td></td>
<td>1.884</td>
</tr>
<tr>
<td>Effective Debye temperature at 0 – 827 °C (K)</td>
<td></td>
<td>1860 ± 10</td>
</tr>
<tr>
<td>Thermal conductivity at 25 °C K⁻¹ (W m⁻¹ K⁻¹)</td>
<td>2100</td>
<td>2200</td>
</tr>
<tr>
<td>Thermal expansion coefficient at 25–200 °C °C⁻¹ (×10⁻⁶ °C⁻¹)</td>
<td>~2.0 [2, 3]</td>
<td>0.8–1.2 [2, 3]</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>5.45</td>
<td>5.45</td>
</tr>
<tr>
<td>Electrical resistivity (Ω cm)</td>
<td>10¹²–10¹⁶</td>
<td>10¹⁶</td>
</tr>
<tr>
<td>Dielectric constant at 45 MHz – 20 GHz</td>
<td>5.6</td>
<td>5.7</td>
</tr>
<tr>
<td>Dielectric strength (V cm⁻¹)</td>
<td>10⁶</td>
<td>10⁶</td>
</tr>
<tr>
<td>Loss tangent at 45 MHz – 20 GHz</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Saturated electron velocity (×10⁷ cm s⁻¹)</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Carrier mobility (cm² V⁻¹ s⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electron (n)</td>
<td>1350–1500</td>
<td>2200</td>
</tr>
<tr>
<td>positive hole (p)</td>
<td>480</td>
<td>1600</td>
</tr>
<tr>
<td>Young’s modulus * (GPa)</td>
<td>820–900***</td>
<td>910–1250</td>
</tr>
<tr>
<td>at 0–800 °C [4]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compression strength (GPa)</td>
<td></td>
<td>8.68–16.53</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td></td>
<td>0.10–0.16</td>
</tr>
<tr>
<td>Coefficient of friction in air</td>
<td>0.035–0.3 [5]</td>
<td>0.05–0.15</td>
</tr>
<tr>
<td>Vickers hardness * (GPa) [varies with crystal orientation]</td>
<td>50–100</td>
<td>57–104</td>
</tr>
<tr>
<td>Index of refraction at 10 μm</td>
<td>2.34–2.42</td>
<td>2.40</td>
</tr>
</tbody>
</table>

* higher than any other known materials
** lower than Invar
*** Young’s modulus = 895[1–1.04×10⁻⁴(T–20)], (GPa), where T in °C
from the ultra-violet (UV) to the far infrared (IR) [60]. In most CVD methods, diamond nucleation on non-diamond surfaces without pretreatment is usually very difficult and slow. Most of the earlier studies on the low pressure CVD (LPCVD) diamond have focused on examining various deposition techniques and characterizing the deposited films which have led to a reasonable understanding of growth mechanisms and processing parameters. Figure 2.2 shows some of the common types of LPCVD reactors [61]. Extensive work [62-73] has been performed on the nucleation and early growth stages to enhance the diamond nucleation to control film morphology. Thus, technical problems associated with the nucleation of polycrystalline diamond films have been adequately addressed. A number of nucleation enhancement methods [74-81] have been developed to enable the control of nucleation density over several orders of magnitude. It has been increased from <10^5 cm^{-2} on untreated substrates to 10^{11} cm^{-2} on scratched or biased substrates. The effects of surface conditions and deposition parameters on the nucleation process have been investigated [82-85] in details to provide the guideline for the selection of optimum surface pretreatment methods and deposition parameters. Recently, advancements in experimental measurement method make it possible to directly observe the nucleation stages. Table 2.2 gives the details of surface nucleation densities of diamond after various surface pretreatments. The experimental investigations have significantly contributed to understand the nucleation mechanisms in diamond CVD process which may allow diamond to realize its potential as an electronic material in the near future.

But the conventional CVD microcrystalline diamond is not used widely for applications in micro/nanoelectronic devices, optical devices, nanoelectromechanical
systems (NEMS) and thermal management devices. It is very important to modify this material to feed-in to suitable application. To achieve this, the processing challenges and the difficulties encountered in applying diamond in thin film and device forms can be minimized by the development of nanocrystalline diamond or “nanodiamond” which possesses a grain size in the nanometer scale between 1 nm and 100 nm. Small grain size
and massive network of grain boundaries of nanocrystalline diamond (ND)/ultrananocrystalline diamond (UNCD) offers certain unique properties while maintaining the meritorious nature of the conventional CVD microcrystalline diamond. Nanodiamond has a very smooth and uniform surface morphology, possess super-hardness and lower internal stress. Most importantly, its higher degree of $sp^2$-bonded carbon content and incorporated dopant into its small grain sized film are strong electric field enhancement factors. Further, all these properties of nanocrystalline diamond can be controlled, reproduced, and tuned over a broad range, elevating the utility of nanodiamond for vacuum micro/nanoelectronic device applications.

Table 2.2: Typical surface nucleation densities of diamond after various surface pretreatment conditions

<table>
<thead>
<tr>
<th>Pretreatment method</th>
<th>Nucleation density ($cm^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pretreatment</td>
<td>$10^3 - 10^5$</td>
</tr>
<tr>
<td>Scratching</td>
<td>$10^6 - 10^{10}$</td>
</tr>
<tr>
<td>Ultrasonic scratching</td>
<td>$10^7 - 10^{11}$</td>
</tr>
<tr>
<td>Seeding</td>
<td>$10^6 - 10^{10}$</td>
</tr>
<tr>
<td>Biasing</td>
<td>$10^8 - 10^{11}$</td>
</tr>
<tr>
<td>Covering/Coating with Fe film</td>
<td>$4.84 \times 10^5$</td>
</tr>
<tr>
<td>graphite film</td>
<td>$10^6$</td>
</tr>
<tr>
<td>graphite fiber</td>
<td>$&gt;10^9$</td>
</tr>
<tr>
<td>a-C film</td>
<td>$3 \times 10^{10}$</td>
</tr>
<tr>
<td>C$_{70}$ clusters + biasing</td>
<td>seeding effect enhancement</td>
</tr>
<tr>
<td>Y-ZrO$_2$, a-BN, SiC layer</td>
<td>enhancement</td>
</tr>
<tr>
<td>C$^+$ ion implantation on Cu</td>
<td>enhancement</td>
</tr>
<tr>
<td>As$^+$ ion implantation on Si</td>
<td>$10^5 - 10^6$</td>
</tr>
<tr>
<td>Pulsed laser irradiation + coating a-C, WC, cBN layer</td>
<td>enhancement</td>
</tr>
<tr>
<td>Carburization</td>
<td>enhancement</td>
</tr>
</tbody>
</table>
2.2 Morphology of nanocrystalline diamond

The grain size of a nanocrystalline diamond film can be typically controlled to be as small as 2 nm. Figure 2.3 shows the typical cauliflower-like morphology of nanocrystalline diamond with grain size of 15-20 nm [86]. The morphology change in the diamond film brings with a large increase in the utility of the material. While considering field emission, the nanometer range grain size results in formation of emitter tips with ultra-small radius of curvature, leading to a high geometrical field enhancement factor. Further, the increased grain boundary network can act as conduction channels, increasing the electrical conductivity and thereby allowing better electron transport through the film.

Nanocrystalline diamond films overcome most of the drawbacks of traditional microcrystalline diamond films as they are smooth, dense, pinhole free, phase-pure, and can form conformal coating on a wide variety of materials. The nanocrystalline diamond deposition technique and the effect of controlling the plasma chemistry on the morphology of the diamond film have been explored by our research group in past [86-87]. The SEM and atomic force microscopy (AFM) images in Figure 2.3 [86] confirm that nanodiamond films have a smoother surface morphology and wider latitude for materials integration than the microcrystalline microwave plasma-enhanced CVD (MPCVD) diamond films.

The surface roughness (100-400 nm) of the CVD microdiamond film is considered to be high for many applications. In order to overcome the problem of surface roughness of diamond films either post-polishing should be adopted or naturally smooth films should be grown without compromising their hardness and other useful properties. However, post-polishing is expensive and time consuming. Nanocrystalline diamond has
a very smooth and uniform surface morphology with a typical RMS surface roughness of 8-20 nm, independent of the film thickness. The smoothness of the thin film is directly related to its mechanical properties like coefficient of friction relevant to MEMS, and is also a very critical factor in several cases including micropatterning of diamond films to realize useful structures, and integration of different materials with diamond.

![Figure 2.3: SEM and AFM images of nanocrystalline and microcrystalline MPCVD diamond films [86].](image)

**2.3 sp²/sp³ composition of nanocrystalline diamond**

Nanodiamond is highly \( sp^3 \)-bonded in nature. Due to the decrease in the grain size and increase in the volume density of grain boundaries, nanodiamond films encompass increased \( sp^2 \)-bonded non-diamond carbon content, preferentially in the grain boundaries [86]. It is known that the intensity and broadening of Raman peaks are directly correlated
to the crystal size of films. A broad $sp^3$-diamond peak (1332 cm$^{-1}$) and higher $sp^2$-carbon shoulder (1560-1580 cm$^{-1}$) are typical characteristics of the Raman spectrum obtained from a nanodiamond film, as shown in Figure 2.4 (a), in comparison with that of a conventional microdiamond film (grain size: 1 µm-3 µm), featuring a sharp $sp^3$-diamond peak and a very small $sp^2$-carbon signature, Figure 2.4 (b). The visible Raman spectroscopy is mainly suitable to monitor the $sp^2$-carbon behavior and follow the evolution of $sp^2$-carbon phase. It often gives rise to an intense background photoluminescence that can mask the Raman line in nanodiamond, even in films with low amounts of $sp^2$-bonded carbon. Also, Raman scattering in visible range is about 50 times more sensitive to the $sp^2$-bonded carbon than the $sp^3$-bonded carbon [88-91].

UV–Raman spectroscopy using higher photons energy (shorter wavelength) can characterize the nature of $sp^3$-bond in the films more clearly [92]. Figure 2.5 (a) - (b) show the typical visible and UV Raman spectra of nanocrystalline diamond films respectively. The peak at 1332 cm$^{-1}$, characteristic to $sp^3$-bonding, which is not easily resolvable in visible Raman spectroscopy, is clearly observed in Figure 2.5 (b). Also, it can be seen that the ratio of the diamond (1332 cm$^{-1}$) to the nondiamond (1560 cm$^{-1}$) band intensities, is large for the film deposited without any added N$_2$ and decreases for the films deposited with the gas. One of the theories suggests that, increasing the N$_2$ in the source gas mixture causes an increase in the relative number of grain boundaries in the film, and it is at these grain boundaries that the $sp^2$-bonded carbon atoms exist [93]. The presence of $sp^2$-carbon as a strong field enhancement factor for electron emission has been discussed in Chapter III.
Figure 2.4: (a) Visible Raman spectrum of a nanocrystalline diamond film with 3-5 nm grain size; (b) Typical Raman spectrum of a microcrystalline diamond film [89-91].
Figure 2.5: (a) Visible Raman spectra of nanocrystalline diamond films deposited from 0, 2, 4, and 10% N\textsubscript{2} in CH\textsubscript{4}/Ar/N\textsubscript{2} source gas mixture; (b) UV Raman spectra of nanocrystalline diamond films deposited from 1, 5 and 10% N\textsubscript{2} in CH\textsubscript{4}/Ar/N\textsubscript{2} source gas mixture [92-93].

2.4 Nitrogen as an n-type dopant in nanocrystalline diamond

The success in fabricating diamond-based electronic devices has been limited mainly due to the difficulty in achieving the effective n-type diamond. The problem lies in the difficulty of finding a way to dope diamond so that its conductivity and carrier mobility are sufficiently high to make diamond-based devices work at room temperature. Nitrogen is among a few suitable dopants for nanocrystalline diamond. But, traditional doping with nitrogen does not work, since nitrogen atoms at substitutional sites introduce a deep donor level 1.7 eV below the conduction band, and thus is not thermally activated at room temperature [94-95]. Unlike nitrogen doped single crystal diamond or microcrystalline films, nanodiamond, due to its small grain size and thereby a high density of grain boundaries, allows for easier incorporation of nitrogen impurities [96-100]. Secondary ion mass spectroscopy (SIMS) data has shown that the content of nitrogen in the UNCD film saturates at 2x10\textsuperscript{20} atoms/cm\textsuperscript{3} (\sim 0.2 % total nitrogen content in the film), Figure 2.6 (a)-(b), when the nitrogen concentration in the plasma is 5 %
The conductivity at room temperature increases dramatically with nitrogen concentration, from 0.016 (1 % N₂) to 143 Ω⁻¹cm⁻¹ (20 % N₂), Figure 2.6 (c) [96]. Further, the nitrogen incorporation has been confirmed to be consistent through the depth of the film, shown by the profiles of the carbon and nitrogen concentrations as a function of depth for a nanocrystalline diamond film deposited from 1% CH₄/5% N₂/95% Ar, [93] Figure 2.6 (d).

Researchers, including our group have reported successful nitrogen incorporation and high electrical conductivity in nanocrystalline diamond. The high electrical conductivity of nanodiamond obtained from CH₄/H₂/N₂ plasma is attributed to the In-situ addition of nitrogen gas to the growth chemistry in the MPECVD process. Energy dispersive spectrometry X-ray microanalysis revealed the incorporation of nitrogen in the nanodiamond film, Figure 2.7 (a) which displays a real time histogram of X-ray count per channel versus energy expressed in keV [86]. The nanodiamond film profile exhibits the characteristic carbon and nitrogen elemental peaks at X-ray energies of 0.277 and 0.392 keV, respectively. Further, RBS experiments conducted [86] on the CH₄/H₂/N₂-plasma derived nanodiamond film also indicated the incorporation of nitrogen. The semi-log RBS plot, Figure 2.7 (b), displays a distinct nitrogen edge, thus confirming the presence of nitrogen in the nanodiamond. An idea of the nitrogen distribution profile can be obtained using the graph. While the edge, typically occurring at 565 keV according to the RBS calibration, shows that nitrogen is present at the surface of the film, the step-like profile is indicative of nitrogen also distributed in the nanodiamond bulk. Quantitatively, the nitrogen concentration was found to be ~ 4.5×10²¹ cm⁻³ in the near-surface region (~ 50 Å) of the nanodiamond film. The actual percentage composition was ~ 1.45 %. RBS,
being a surface-sensitive technique, could be used to accurately verify the nitrogen concentration in the near-surface region. The electrical conductivity of nanodiamond can be enhanced by increasing the percentage of nitrogen included in the growth plasma. Another effective technique to achieve nitrogen-doping in nanocrystalline diamond is to increase the microwave power and pressure at a particular nitrogen gas flow rate.

**Figure 2.6:** (a) High-resolution SIMS spectra of the UNCD film revealing the incorporation of nitrogen with a CN⁻ secondary ion peak with a mass of 26.0030 amu; (b) Total nitrogen content and room-temperature conductivity as a function of nitrogen in the plasma; (c) Arrhenius plot of conductivity data obtained in the temperature range 300–4.2 K for UNCD films synthesized using different nitrogen concentrations in the plasma; (d) Depth profiles for the atomic carbon and nitrogen concentrations in a 1 µm-thick NCD film [93,96].
Figure 2.7: (a) EDS x-ray microanalysis composition profile (X-ray count Vs Energy) of the nanodiamond film deposited by CH$_4$/H$_2$/N$_2$ MPECVD, indicating the incorporation of nitrogen impurity in the diamond film; (b) Semi-log RBS plot (backscattered ion count vs. energy) obtained from the CH$_4$/H$_2$/N$_2$-nanodiamond possessing a distinct nitrogen edge in its composition profile [86].
2.5 Effect of growth temperature

In most CVD processes, substrate temperature is set to above 700 °C to obtain high quality crystalline diamond films at reasonably high deposition rates which have greatly limited the applications of diamond films in microelectronic devices. Therefore, reducing the substrate temperature during deposition without sacrificing the quality of diamond films and deposition rates comparable to those characteristic of high-temperature growth, is of great scientific and practical significance. Researchers [101-102] have shown successful dense and continuous ND/UNCD film synthesis at temperatures as low as 400 °C using optimized ultrasonic seeding process. The nanocrystalline diamond growth process plasma chemistry exhibits much less temperature dependence than the conventional microcrystalline diamond deposition process. The temperature dependence of the UNCD deposition is reflected in the microstructural development shown in the SEM micrographs, Figure 2.8 (a)-(b). The UV-Raman spectra of the UNCD films prepared at different temperatures are shown in Figure 2.8 (c). There are three prominent peaks in this spectrum, with a clear diamond peak at 1332 cm$^{-1}$ that increases in intensity as the deposition temperature decreases. The peak labeled N$_2$ is due to nitrogen gas present along the optical path of the spectrometer. This reported development signals a suitable platform material for application to diamond-based stand alone microelectronic and/or integrated microelectronic/microelectromechanical systems (MEMS) devices. Deposition at low temperatures can enhance the feasibility of integrating diamond with other materials, and can pitchfork its application in integrated circuits and other applications, Figure 2.8 (d).
Figure 2.8: (a)-(b) SEM images of the surface morphology and corresponding cross-section of UNCD films deposited at 800 °C and 400 °C; (c) UV-Raman spectra of UNCD films deposited at various temperature; (d) Low temperature UNCD as hermetic coating for BioMEMS, showing the materials integration feasibility offered by the material [86,101-102].

So far, this chapter elucidates how the unique properties of nanocrystalline diamond can be favorable for electron field emission. Nitrogen-incorporation to nanocrystalline diamond makes it electronically active, while retaining the thermal and mechanical stabilization properties of the diamond material, making it a highly potential and reliable candidate for electron emitter. The possible electron conduction mechanisms through bulk diamond resulting in emission current have been discussed in Chapter III. Later, Chapter V describes the process techniques and exact parameters developed for growing nanodiamond film used in this research.
CHAPTER III

ELECTRON EMISSION and VFED OPERATING PRINCIPLES

This chapter reviews the theoretical aspects of electron emission in detail and the present understanding of the possible electron emission mechanisms from CVD diamond. Following that, some of the important results reported so far from diamond emitters are presented. Last but not least, the basic operating principles of VFE devices, such as diode and triode, are presented.

3.1 Basics of electron emission into vacuum

Electron emission is the process of emitting electrons from a solid surface into vacuum under external influences, viz. electric field or heat or both. The three most common processes of electron emission are thermionic emission, thermionic-field emission, and field emission. In each of these processes, energies in form of either heat or electric field or both are exerted on the solid to extract electron. The mechanisms for these processes can be explained by considering the energy band diagram [87] of a metal-vacuum system as shown in Figure 3.1.

For thermionic emission, electrons emit into vacuum at very high temperature of 1500-2500 °C depending on the metal work function. At 0 K, all the electrons in solid have energy below the Fermi level \(E_F\). With the increase in temperature, some electrons gain kinetic energy and thus, have total energy above Fermi level. At sufficient high
temperature, some electrons gain total energy higher than vacuum level \( (E_{\text{vac}}) \), \( (T) \) e\(^{-}\) in Figure 3.1, and readily emit into vacuum with no applied potential.

At moderate temperature, some electrons, \( (T-F) \) e\(^{-}\) in Figure 3.1, have total energy above \( E_F \) but below vacuum level and thus, are not readily to emit into vacuum. In order for these electrons to emit into vacuum, a moderate electric field must be applied to thin down the potential barrier as illustrated in Figure 3.1. This thermal-field activated emission process, via quantum-mechanical tunneling, is called thermionic-field emission. Depending on the metal work function, thermionic-field emission from metal can be observed at temperature range of 700-1500 °C.

![Figure 3.1: Mechanisms for thermionic (T), thermionic-field (T-F), and field emission (F) [87].](image)

Whereas, electron field emission is a unique quantum-mechanical effect of electrons, \( (F) \) e\(^{-}\) in Figure 3.1, tunneling from a condensed matter (solid or liquid) into vacuum. At low temperature, most of electrons have total energy below \( E_F \). Thus, a strong external electric field must be applied to extract the electrons. Since, electric field is the main energy source that induces electron emission; this phenomenon is called field
emission. The efficiency of this process is tens of millions of times higher than in other known emission processes. The extremely high current density and no energy consumption by the emission process afford exceptionally wide possibilities for practical application of this effect. Electron emission can also occurs by other methods such as light excitation (photoelectric electron emission), external electron energy (secondary electron emission), and internal polarization switching (ferroelectric electron emission). These interesting electron emission phenomena are beyond the scope of this research. However, the basic theoretical aspects of electron field emission as the main topic of this research are further discussed in the two following sections.

3.2 Fowler-Nordheim (F-N) theory of field emission

The original field emission (FE) theory for cold cathodes with flat surface was first developed by Fowler and Nordheim in 1928 [103]. If an electric field is applied to the surface of a solid, the rectangular surface potential step change into a triangular shape which is shown in Figure 3.2. If the width of the surface potential barrier approaches ~2 nm, which is the tunneling distance for low energy electrons, the confined electrons will quantum-mechanically tunnel from the highest occupied states in the solid into vacuum and an emission current will be detected at the positively biased anode [7,57].

According to Fowler-Nordheim (F-N) theory, the dependence of the emission current density, \( J \) (A/cm\(^2\)), on the work function of the emitting surface, \( \Phi \) (eV) and the local electric field just above the emitter surface, \( E = V/d \) (V/cm), is exponential. The F-N equation can be written as [103-105]:

\[
J = \frac{I}{A} = k_1 \frac{E^2}{\Phi} \exp\left(-k_2 \frac{\Phi^{3/2}}{E}\right)
\]  

(3.1)
where \( I \) (A) is the emission current, \( A \) (cm\(^2\)) is the emission area, and \( k_1 \) and \( k_2 \) are universal constants given by:

\[
k_1 = \frac{e^3}{8\pi\hbar} = 1.54 \times 10^{-6} \text{AeV}^2 \quad (3.2)
\]

\[
k_2 = \frac{4(2m_e)^{1/2}}{3e\hbar} = 6.83 \times 10^7 \text{eV}^{-3/2}\text{Vcm}^{-1} \quad (3.3)
\]

where \( e \) is the elementary positive charge, \( m_e \) is the electron mass, \( \hbar \) is the Planck’s constant, and \( \hbar = \hbar/2\pi \).

**Figure 3.2:** The field emission model for a metallic emitter proposed by Fowler and Nordheim. Diagram shows the potential barrier and the triangular surface potential under an applied electric field \( E \).

The Eq. 3.1 was derived for a metal cathode with the following physical assumptions [7]:

I. The metal cathode has a free-electron band structure,

II. The electrons obey Fermi-Dirac statistics,

III. It is at 0 °K,
IV. The cathode has a smooth flat surface,

V. The cathode has a work function which is uniform across the emitting surface and independent of electric field.

VI. The electric field outside the metal surface is uniform, and

VII. The effect of image field between the emitted electrons and the surface is neglected in a first approximation.

To include the image field effect, in 1956, Murphy and Good [106] presented a full mathematical analysis of the standard physical assumptions in F-N theory. The result is the inclusion of two electric field dependent elliptical functions $v(y)$ and $r^2(y)$ in Eq. (3.1), where $y$ is the image charge lowering contribution to $\Phi$ given by,

$$y = k_3 \frac{F^{1/2}}{\Phi}$$  \hspace{1cm} (3.4)

where,

$$k_3 = \left( \frac{e^3}{4\pi \varepsilon_0} \right)^{1/2} = 3.79 \times 10^{-4} \text{ eV} \text{ V}^{-1/2} \text{ cm}^{1/2}$$  \hspace{1cm} (3.5)

and $\varepsilon_0$ is the permittivity of vacuum ($8.85 \times 10^{-14} \text{ Fcm}^{-1}$).

Further, let us consider the sharp cone structure, as shown in Figure 3.3 [107] which results in non-uniform electric field as illustrated in Figure 3.2. The electric field is highest at the tip apex and rapidly decreases outward to the anode. Thus, the F-N equation, Eq. (3.1), which is derived for planar cathode cannot be precisely applied. The precise calculation of potential distribution, electric field, and emission current for a sharp microstructure involves numerical calculation of 3-dimensional Poisson equation and Schrödinger equation for electron emission [108-110]. However, the emission current for a sharp microstructure can be obtained with a simple modification of Fowler-
Nordheim equation for a planar metal cathode by replacing the parallel electric field \((E)\) in Eq. (3.1), with electric field at the apex of the sharp microstructure \((F)\) that is

\[
F = \beta E
\]  

(3.6)

where, \(\beta\) is defined as the geometrical field enhancement factor.

So taking all into consideration, the revised F-N equation can then be expressed as [7]:

\[
\frac{J}{A} = k_i \frac{(\beta E)^2}{\Phi r^2(y)} \exp \left(-k_2 \frac{\Phi^{3/2} v(y)}{\beta E}\right)
\]  

(3.7)

**Figure 3.3:** Series of SEM images of a 25 nm diameter Si tip emitter coated with a UNCD film with incremental coating thickness. The tip on the left is uncoated and successive images represent coatings ranging from 100 nm to 2.4 µm in thickness [107].

This simple approximation implies that the emission current for a sharp microstructure, generally referred as the “Spindt cathode”, is equivalent to the emission current of a planar cathode of the same vacuum gap but the effective electric field is increased by the factor of \(\beta\). This approximation agrees very well with experimental results because the electric field of a sharp tip is strongest at the apex and reduced rapidly for the region away from the apex and hence, it can be assumed that most of emission
current arises from electron tunneling within the vicinity of this highest electric field region. Thus for FE, electrons with energies below the \( E_F \) predominates and tunneling through field dependent barrier is mainly responsible for variation in emission current at low temperature. FE can be verified by a straight line with a negative slope by plotting the one over electric field \((1/E)\) as abscissa (x-axis) and the \( \ln(J/E^2) \) as the ordinate (y-axis).

### 3.3 Theory of Thermionic-Field emission

As the field emission equation is independent of temperature term, a diversion of the experimental data from the F-N straight line has been observed at moderate or high temperature. In 1956 [106], Murphy and Good presented an elaborated calculation considering the thermal effect on field emission. In absence if any external heating, Dolan and Dyke [111] used an internal tip heating model to calculate the steady state temperature rise at the tip which is given by:

\[
\Delta T = a J^2 r^2
\]  

where \( a \) depends on the emitter cone angle and \( r \) is the tip radius. In brief, as proposed by them in 1953, there are two main sources of energy which cause heating of the tip during field emission at higher field. The first is Nottingham heating, which produces a power density input \( W_I \) (W/cm\(^2\)) at the tip surface,

\[
W_I = J \cdot \Delta E_F
\]  

where \( \Delta E_F \) is the difference between \( E_F \) and the average electron energy \( (E_{F_{avg}}) \), i.e. \( \Delta E_F = E_F - E_{F_{avg}} \). This heating occurs at or just inside the emitter tip surface and is proportional to the emission current density \((J)\). As \( J \) increases, Nottingham heating
increases which increases the tip temperature. This results an increase in average energy of the emitted electrons and become equal to the Fermi energy at the inversion temperature ($T_i$). As temperature increases further, Nottingham cooling takes place. Hence it tends to stabilize the tip temperature at a value near the inversion temperature.

The second energy input to the tip is resistive heating, which produces a power density $W_2$ (W/cm$^2$) inside the tip,

$$W_2 = \rho J^2$$  \hspace{1cm} (3.10)

where $\rho$ is the resistivity of the emitter. Thus $W_2$ is proportional to $J^2$ and increases as $\rho$ and $J$ increases with the tip temperature increment. Hence an unstable emission could be possible at higher current density and temperature.

The theoretical treatment of thermionic emission leads to Richardson’s equation modified by the Schottky dependence on the square root of the applied field \[112\]. The origin of Schottky barrier lowering comes from the image potential that an electron experience near the conducting surface. The force ($F'$) between an electron at $x$ into the vacuum from the surface and its image is given by \[113\]:

$$F' = eE = \frac{-e^2}{16\pi\varepsilon_0 x^2}$$  \hspace{1cm} (3.11)

The potential energy is found by integrating the force from $x>0$ to $\alpha$, resulting:

$$V(x)_{image} = -\int_0^{\alpha} E dx = \frac{e}{16\pi\varepsilon_0} \int_0^{\alpha} \frac{1}{x^2} dx = \frac{e}{16\pi\varepsilon_0 x}$$  \hspace{1cm} (3.12)

Now, under the applied electric field $E$:

$$V(x)_{field} = -F' x = -eEx$$  \hspace{1cm} (3.13)

Thus the sum of the potential $U(x)$ is given by:
\[ U(x) = -eEx + \frac{e}{16\pi\varepsilon_0 x} \]  

(3.14)

The maximum is obtained by differentiating the potential and setting equal to zero, i.e.

\[ \frac{d}{dx} \left[ \frac{e}{16\pi\varepsilon_0 x} - eEx \right] = 0 \]  

(3.15)

which gives,

\[ V_{\text{max}} = -e \left[ \frac{E}{16\pi\varepsilon_0} \right]^\frac{1}{2} \]  

(3.16)

Therefore, under applied field the surface potential barrier \((\Phi_{\text{eff}})\) is effectively reduced to \(\Phi - V_{\text{max}}\), as shown in Figure 3.4 (a). The emission current associated with this Schottky Barrier Lowering (SBL), namely Thermal-Field Emission (TFE), is given by [106]:

\[ J = AT^2 \exp \left[ -e \left( \Phi - \sqrt{\frac{eE}{4\pi\varepsilon_i}} \right) \right] \frac{kT}{4\pi\varepsilon_i} \]  

(3.17)

where \(A\) is effective Richardson’s constant, \(\varepsilon_i\) is the material permittivity, \(k\) is the Boltzmann constant and \(T\) is the temperature in Kelvin. TFE can be verified by a straight line with a positive slope by plotting the square root of the electric field \((E^{\frac{1}{2}})\) as abscissa (x-axis) and the \(\text{Ln}(J/T^2)\) as the ordinate (y-axis).

Under higher electric field, the dimensions of the potential barrier at the solid-vacuum interface become on the same order as interatomic distances and the radii of close-range interactions [7]. The width of the image force barrier, \(\Delta x = |\Delta x_1 - \Delta x_2|\), where \(x_1\) and \(x_2\) are the classical turning points as shown in Figure 3.4 (a), has been calculated [7] by assuming the kinetic energy of the electrons in the direction of emission is zero at the turning points, i.e.
\[
\Delta x = \frac{\phi^2 - e^3E}{eE}^{\frac{1}{2}} \\
x_m \approx \frac{1}{4} \left( \frac{e}{\pi \varepsilon_0 E} \right)^{\frac{1}{2}}
\]

where \(x_m\) is the distance from the interface of the potential maximum, as shown in Figure 3.4.

**Figure 3.4:** (a) The dependence of the barrier width on image forces; (b) the barrier width and the position of its maximum as a function of applied field; (c) the maximum height of the barrier as a function of applied field [7].

Fabrication and characterization of sharp cone structure has been reported by various research groups using either silicon or metal materials which have been mentioned in previous chapters. Several other groups have tried diamond as emitter material with Vanderbilt considered being the leading research team. **Section 3.5** presents some of the important results reported so far from diamond emitters. As nanodiamond being the emitting material in this research, it would be appropriate to discuss the theory behind the electron propagation through it leading to emission, in brief.
3.4 Electron emission from nanodiamond

Diamond is one of the main high-pressure crystalline allotropes of carbon with \( sp^3 \)-tetrahedral bonded cubic structure, as shown in Figure 3.5 [114]. When its surfaces are terminated with hydrogen atoms, the electron affinity, which is a measure of the energy barrier that electrons must overcome to escape into vacuum, can become negative. Thus, the presence of low/negative electron affinity (NEA) on hydrogen-terminated diamond surfaces, coupled with practical chemical vapor deposition (CVD) of diamond on a variety of substrates, has attracted attention of diamond’s promise as a high performance cold cathode material. Experimentally, diamond has been observed to emit electrons at relatively low electric fields and generate useful current densities [87].

3.4.1 Energy band diagram of nanodiamond

Electron field emission from diamond has been experimentally observed to yield high emission current at low applied electric field. However, the mechanisms responsible for low field emission from diamond are not clearly understood. Diamond surfaces have remarkable energy band diagrams, which are different from most of other semiconductors. A complete knowledge on energy band diagram of diamond surfaces is key information to understand electron field emission from diamond.

Diamond is an indirect wide band-gap material with \( Eg = 5.45 \text{ eV} \). So far, three distinct types of diamond surfaces have been widely studied [115-123]. Figure 3.6 (a) illustrates hydrogen-free diamond surfaces with small positive electron affinity. Partially hydrogenated (111) and (100) diamond surfaces have effective negative electron affinity (NEA), as illustrated in Figure 3.6 (b). This reduction in electron affinity, together with a
short characteristic band bending at the surface results in the effective negative electron affinity surface. Furthermore, diamond surface coated with a thin layer of metal such as Zirconium (Zr), Cobalt (Co), and Ni [124-125] also exhibit effective negative electron affinity property as illustrated in Figure 3.6 (c).

Figure 3.5 Eight allotropes of carbon (a) Diamond; (b) Graphite; (c) Lonsdaleite; (d) C60 (Buckminsterfullerence); (e) C540; (f) C70; (g) Amorphous Carbon, and (h) Single-walled carbon nanotube [114].
Further, it is believed that a true NEA surface also exists on the Cesium (Cs) or Cesium oxide (Cs$_2$O) coated diamond (100) surface [126]. The occurrence of the true NEA has not been found for conventional semiconductor materials. Assuming a diamond surface with small positive electron affinity, a complete energy band diagram for electron emission from that surface may be drawn as shown in Figure 3.7 [87]. For electron emission to occur, electrons must quantum-mechanically tunnel through the potential barrier at metal-diamond interface into diamond. Then the electrons will drift through the bulk diamond to reach a small potential barrier at diamond-vacuum interface and finally tunnel into vacuum under an electric field. Small or even negative electron affinity of diamond is believed by many to be responsible for observing low field emission because it would allow electrons from the conduction band to emit into vacuum easily with low applied electric field. However, electron in conduction band of diamond is limited due to its wide band gap. Thus, electron must be injected from metal into conduction band of diamond in order for emission to occur. This requires a high electric field since the potential barrier at metal-diamond interface would be as high as work function of silicon or metals. Thus, the basic energy band diagram as described is inadequate for the explanation of the observed low field emission from diamond.

In order to explain the field emission mechanism from diamond, a better understanding of carrier transport through diamond-metal interface and the bulk diamond film is needed. A more complete energy band structure, which includes the effect of grain boundary and defects of polycrystalline diamond, is also required to be studied. So far, several field emission mechanisms, carrier transport through the bulk and field emission enhancement models for various types of diamond emitters have been proposed. The
following section summarizes some of the important proposed theories and models. The low/negative electron affinity property of diamond surfaces may be important and can make diamond an efficient emitter but it is not adequate to explain its good field emission behavior. For field emission to occur, and sustain, there must be a continuous supply of electrons into the bulk diamond and a sustainable electron transport mechanism through it to reach the emitting surface. Moreover, the energy levels of these electrons relative to the vacuum level are critical in determining the threshold field required for emission.

**Figure 3.6:** Energy band diagrams of diamond. (a) Positive electron affinity; (b) Effective negative electron affinity; (c) True negative electron affinity [87].
Figure 3.7: (a) Diamond cathode structure; (b) Energy band diagram at thermal equilibrium; (c) Energy band diagram under forward bias [87].
3.4.2 Emission mechanisms

Simple field enhancement model

Among the various models, the simplest argument cites the classic field emission theory by considering local field enhancements on sharp morphological features protruding from the diamond surface. The electric field at a given applied potential is enhanced by these sharp microstructures [127] and thereby more electron tunnel into vacuum. Field emission from diamond-microtips exhibit significant enhancement in both total emission current and stability compared to planar diamond emitter. The geometrical field enhancement factor $\beta$ depends only on the shape of the microstructure. The figures of merit ($f$) for various shapes are estimated [12] and shown in Figure 3.8. It can be concluded that the rounded whisker shape is the closest to the “ideal” field emitter. While on the contrary, a wide-angle pyramidal shape is very poor as a field emitter even though it has excellent thermal and mechanical stability. Further, the electric field distribution at the surface of a rounded whisker, Figure 3.8(a), can be evaluated in closed form as a function of polar angle $\theta$ using elementary electrostatic theory as [12]:

$$E = \frac{V}{d} \left( \frac{h}{r} + 3 \cos \theta \right)$$  \hspace{1cm} (3.20)

$$\beta = \frac{h}{r} + 3 \cos \theta$$  \hspace{1cm} (3.21)

where $h$ is the height of the sphere from the base and $r$ is the radius of the tip. For $h \gg r$, $E \approx (h/r)(V/d)$ and $\beta \approx h/r$. Ideally, the field at the apex of a floating sphere is given by $E = (h/r)(V/d)$. However, to apply the simple field enhancement model, the microstructure must have certain geometry with a smooth surface which is not practical.
Figure 3.8: Various shapes of field emitters and their figure of merit; (a) Rounded whisker; (b) Sharpened pyramid; (c) Hemi-spheroidal; (d) Pyramid [12].

Two step field enhancement (TSFE) model

This model is the modified version of the simple field enhancement model to account for the complicated morphology of diamond surface. The emitting surface is considered to be rough and consists of a number of small protrusions act as tiny tips. The emitting tip with height $h_1$ and sharpness of radius $r_1$ is assumed to consist of a number of tiny tips with height $h_2$ and sharpness of radius $r_2$ as shown in Figure 3.9 [128]. The electric field on the blunt tip is equal to

$$E_1 = \left( \frac{h}{r_1} \right) \frac{V}{d} \quad (3.22)$$

and the field enhancement at the end of protrusions is equal to

$$E_2 = \left( \frac{h_2}{r_2} \right) E_1 = \left( \frac{h_1 h_2}{r_1 r_2} \right) \frac{V}{d} \quad (3.23)$$

Based on the TSFE model, the emission current were calculated using the F-N analysis from diamond coated silicon field emitters and found to be in good agreement with experimental data. This model has also been well applied to explain the increase in the
geometrical field enhancement of sharpened pyramidal diamond microtips [86-87]. In this case, the sharpened diamond microtip was modeled as a large conical tip with tip height of $h_1$ and tip radius curvature of $r_1$, superimposed with a sharp tiny conical tip with tip height of $h_2$ and tip radius curvature of $r_2$, as shown in Figure 3.9 (c). The electric field at the sharpened tip apex arises from a two-cascaded tip structure. In the first step, the electric field at the apex of large conical tip is enhanced by the factor of $h_1/r_1$ from the planar base, while in the second step; the electric field at the apex of the sharp tiny conical tip is enhanced by the factor of $h_2/r_2$ from the apex of large conical tip. Thus, the total geometrical field enhancement factor could be written as the product of the two field enhancement factors of the cascaded tip structure:

$$\beta_g = \left( \frac{h_1}{r_1} \right) \left( \frac{h_2}{r_2} \right)$$

(3.24)

**Figure 3.9:** Geometry of emitters; (a) The simple field enhancement approach; (b)-(c) Illustration of the TSFE approach [128].
Estimation of the geometrical field enhancement using this model was found to be in good agreement with the result obtained from F-N analysis. However, this model does not address the source of electrons in the wide-bandgap and effective electron transport to the surface of diamond.

**Lowering of the surface work function model**

In the lowering of the surface work function model, it is assumed that the sharp microtip and the complicated surface morphology result in significant reduction of the surface work function. A significant enhancement in field emission after diamond coating on silicon tip was observed which could also be attributed to the lowering of the surface work function by diamond [128]. Although it is unclear how diamond could have sufficient amount of electrons in or near the conduction band to produce large emission currents. In addition, it has been found that the diamond surface work function can be lower by coating with a low work function material such as Cs [126]. It has been found that the diamond surface treated with O₂ plasma and Cs deposition substantially enhances the electron emission for Li-doped and N-doped diamond [129]. It has been suggested that oxygen-terminated diamond surface reacts with Cs to form an oxygen-stable diamond-O-Cs surface that lowers the surface work function of diamond. However, the lowering of work function by Cs treatment for field emission enhancement is not a practical technique because Cs is an expensive and reactive element.

Further, hydrogen treatment on diamond surfaces was found to improve field emission characteristic significantly [120-121]. The lowering of work function of diamond surfaces by hydrogen termination was believed to be the most probable explanation for the observed field emission enhancement. The termination of hydrogen
on diamond surface is known to form a positive surface dipole that could produce band bending and result in lowering of electron affinity and work function of diamond surfaces. On the other hand, oxygen treatment was found to degrade field emission characteristic of diamond surface [125,130]. The degraded emission property was believed to cause by the increasing of work function of diamond. The termination of oxygen on diamond surface is known to form a negative surface dipole to produce band bending which results in increasing of electron affinity and work function of diamond surfaces.

**Defect/impurity theory**

The defect/impurity theory suggests that structural defects and impurities can form energy states within the band gap of diamond [131-132]. When the defect density is sufficiently high, the electronic states of various defects can interact and form additional energy bands. If these bands are wide enough or closely placed, the electron hopping mechanism within the bands, similar to the Poole-Frenkel conduction mechanism or the Hill type conduction [133-135] could easily provide a steady flow of electrons to the surface and sustain a stable electron emission. The electrons can either be excited into the conduction band or unoccupied surfaces states from these defect/impurity bands to emit, or tunnel directly from the defect/impurity bands into vacuum. These defects/impurities essentially raise the Fermi level by acting as donors of electrons and thus reduce the tunneling barrier. This theory is supported by overwhelming experimental data indicating that defective or lower quality diamonds have better emission properties. It also appears to explain why emission characteristics are enhanced in many “doped” diamonds, not
necessarily because of the electrical doping effect, but rather by the creation of defects during the doping process.

**Presence \(sp^2\)-carbon content in the diamond film**

This model is based on the observation that active emission sites correspond to discrete location of defects or graphite inclusions on the diamond surface [136-139]. To sustain a continuous flow of emitting electrons, it has been assumed to be supplied to the emitting surface through conduction channels formed in diamond via an electroforming process at high electric fields [87]. Also, grain boundaries in diamond films [108] and hydrogenated diamond surfaces [109,140] have been suggested to function as conduction channels.

Wisitsorat-at [87] proposed that isolated conducting \(sp^2\) nano-particles in the diamond film form a series of cascaded MIM (metal-insulator-metal) microstructures. Such a particle could therefore enhance the electric field distribution locally across the junction where it forms a contact with the electrode surface, which enhances the electric field inside the diamond film, thereby increasing the field enhancement factor. The image effect at the diamond-\(sp^2\) interface causes band bending in the conduction band of diamond as illustrated in Figure 3.10. The enhanced electric field decreases the width of tunneling distance, \(W\), at the metal-diamond interface significantly, and thereby increases the electron tunneling probability from metal into the conduction band of diamond. The electrons in the conduction band of diamond are then accelerated toward the next floating \(sp^2\) particle under the induced electric field. Thus, the \(sp^2\) particles would enhance diamond field emission.
Field emission enhancement via doping

If the conduction band of diamond, with small or negative electron affinity, can be directly populated with electrons via donors, a very small electric field is sufficient to induce electron emission. So in theory, adding n-type donor impurities into diamond is the best approach to enhance electron emission. On the other hand, the addition of p-type acceptor impurities into diamond should degrade mission from diamond since the addition of holes in the valence band would reduce the number of electrons in the conduction band. In practice, it is not easy to introduce impurities especially donors into diamond since diamond is a wide band gap material with very tight lattice structure. The diamond film doped with various n-type dopants such as phosphorous (P) and nitrogen (N) has currently been shown to be possible [129,141-143] using ion implantation for the first time. N and P have been successfully incorporated into CVD diamond films by the addition of various dopant gases such as nitrogen (N₂), ammonia (NH₃), urea ((NH₃)₂CO), and phosphine (P₂H₅) into CH₄/H₂ plasma [86,144]. The n-type dopants...
such as N, Li and P provide donor levels within the energy gap as illustrated in Figure 3.11. The energy levels associated with Li and P dopants are still unknown, but it has been found that the substitutional nitrogen forms a donor level ~ 1.7 eV below the conduction band [87]. Assuming NEA property on diamond surface, the vacuum energy level is ~ 0.7 eV below the conduction band. Thus, the nitrogen donor level is 1 eV below the vacuum level, which means that the work function is approximately 1 eV. Therefore, a low electric field is sufficient for electron emission. Other experiments [141-146] using phosphorous and nitrogen as n-type dopants with no Cs treatment have independently confirmed that a diamond emitter with n-type dopants shows a better emission characteristic than a p-type (boron-doped) diamond emitter. In this research, n-type dopant incorporated nanodiamond film developed by Vanderbilt [86] has been used to achieve enhanced electron field emission.

**Figure 3.11** Energy band of diamond with dopants’ energy levels [87].

**Other interesting models**

Various other proposed models provide additional insight into the conduction of electron through the bulk of the diamond [87,147]. These methods include electron
injection over a Schottky barrier at the back-contact interface between a metallic substrate and diamond [148], field concentrations induced by chemical inhomogeneity (such as hydrogen termination) on the surface [149], dielectric breakdown that provides conductive channels in diamond [150] and surface arcing that results in increment in surface roughness providing additional geometric field enhancement [151]. However, it is important to remember that all these mechanisms are not necessarily mutually exclusive, because each addresses a particular part of a overall complex field emission process that includes the critical steps of supplying electrons to diamond, transporting them through the bulk to the surface, and emitting them into vacuum.

3.5 Electron conduction through bulk-nanodiamond

The electron emission mechanism from the nanodiamond surface could be modeled by F-N or TFE, as discussed earlier in this chapter. However, at higher forward bias region the electron conduction through the bulk may experience space-charge limited (SCLC) effect, which restricts the electron emission into vacuum [152-154]. This mechanism is strictly dominated by the bulk properties and the thickness of the insulative or low mobility semiconductive film, which forms traps in the film. These traps control the current conduction of the majority carriers through the material. The ideal SCLC conduction is characterized by square law dependence of current on voltage and is given by [154]:

\[ J = \left( \frac{9\varepsilon_0 \mu V^2}{8d^3} \right) \]  

(3.25)

where, \( \mu \) is the majority charge carrier mobility and \( d \) is the thickness of the insulative layer. For an n-type material electrons are the majority carrier and trap energy levels are
located below the Fermi level for shallow traps and above the Fermi level for deep traps, 

**Figure 3.12.** The voltage at which the traps are filled is called the Trap Filled Limited voltage, $V_{TFL}$, and defined as:

$$V_{TFL} = \left( \frac{e n_0 d^2}{\epsilon \epsilon_0} \right)$$

(3.26)

where $n_0$ is the electron occupancy of traps in the region of conduction.

**Figure 3.12:** Energy band diagrams explain the (a) shallow trap and (b) deep trap energy levels in an n-type material [154].

### 3.6 Reported emission characteristics from nanodiamond structures

The NEA property of diamond was first reported by Himpsel et al. [116] in 1979, but the investigations of its field emission properties did not start until when diamond film coating with controlled quality on many different substrates became widely available due to the emergence of low pressure CVD techniques in the early 1990s. Many published reports claimed that diamond and diamond-like-carbon (DLC) materials are good field emitters, with low turn-on fields and useful emission current densities. Electron emission has been observed from many different types of diamond materials,
vapor-deposited islands and films with varying surface morphologies, crystallite sizes and nanocrystalline coatings [86-102,116-132].

Few of the early reports on diamond field emission include Wang et al. [136] who reported low-field (< 3 V/µm) electron emission from undoped CVD polycrystalline diamond films, Geis et al. [128] who measured emission currents from a diamond diode structure consisting of a p-type & carbon ion implanted diamond surface, and Djubua et al. [15] who showed that arrays of diamond-like carbon cones formed by plasma polymerization required the lowest operating voltage for emission when compared to arrays of Mo and Hf tips. Outstanding emission properties are discovered in both ultrafine diamond powders containing 1- 20 nm crystallites produced by explosive synthesis and nanocrystalline or ultra-nanocrystalline diamond films (composed of ~1-100 nm crystallites) [144,155-158]. Emission has been found to originate from sites that are associated with defect structures in diamond rather than sharp features on the surface [136, 158-161]. Compared with conventional Si or metal microtip emitters, diamond emitters show lower threshold fields, improved emission stability, and robustness in low/medium vacuum environments. Attempts have also been made to apply diamond coatings on tips of silicon or metal-emitter arrays to further enhance the emission characteristics [128, 151].

Nanocrystalline diamond, a strongly emerging form of CVD diamond as an engineering material, has dominated research in vacuum micro/nanoelectronics in recent years. Over the last few years Vanderbilt Diamond Group has become one of the leading research groups in this area and reported emission characteristics from various structures. A uniquely engineered mold transfer process has been developed for the fabrication of
micro-patterned pyramidal diamond emitters with uniform microtip structures. In addition, methods to improve the diamond field emission behavior have been systematically studied which include the incorporation of sp$^2$ into diamond tips/bulk, vacuum-thermal-electric (VTE) treatment, p-type doping, and tip sharpening. Figure 3.13 (a)-(b) shows the SEM micrograph of a high density sharpened diamond tips array and corresponding field emission behavior [87]. Also, triode and transistor structures were fabricated and their emission characteristics were studied as a function of the device parameters of anode-cathode spacing, diamond doping, and array sizes. Figure 3.13 (c)-(d) shows a typical nanodiamond vertical transistor structure and corresponding electrical behavior.

Further, optical lithography-controlled finger-like emitter geometry and small interelectrode spacing in a versatile, low capacitance structure with a built-in gate, anode and insulator, achieved using a simple fabrication method are attributes of the lateral field emitter array (FEA) device [86]. Diode structures have been achieved with different interelectrode spacing. Figure 3.14 shows three diode structures with different numbers of finger-like emitter and corresponding emission behavior showing that the current enhancement obtained by increasing the emitter area. Furthermore, vacuum triode and transistor have also been demonstrated successfully in a completely integrated planar lateral emitter configuration, as shown in Figure 3.15. Importantly, this had led to the development of the first vacuum microelectronic technology with operational temperature immunity (upto 200 °C) as well as radiation hardness; tested upto 15 MRad total doses and 4.4(10$^{13}$) neutrons/cm$^2$ level of radiation exposure.
However, there are couples of limitations which are preventing the application of nanodiamond lateral FEDs into microelectronic circuits. Maximum current limit is one of them. The lateral vacuum triodes and transistors, as mentioned above, demonstrated an emission current in the range of ~1 μA which is quite low compared to its solid state counterparts. The current enhancement in the diode structures has been achieved by increasing the number of emission sights/tips. But it has increased the device area footprint as well as fabrication complications leading to lesser yield. Further, emission current has been increased by reducing the interelectrode gap [86]. However, lithography limitation and other fabrication techniques used in the process put on hold on further miniaturization.
Figure 3.13: (a) SEM micrograph of a high density sharpened diamond tips array, inset shows the high magnification image; (b) I-V and F-N plots (inset) for different growth recipes; (c) a typical nanodiamond vertical transistor structure; (d) corresponding dc characteristics [87].
Figure 3.14: SEM micrographs of the nanodiamond lateral devices. (a) A 6-fingered emitter, showing the intentionally undercut silicon layer beneath the nanodiamond; (b) a section of a 125-fingered emitter; (c) a 2000-fingered comb array device; (d) Field emission characteristics (I-E) of the ND lateral devices [86].
Figure 3.15: (a) SEM micrograph of a completely integrated nanodiamond lateral field emission triode; (b) corresponding triode characteristics ($I_a$-$V_a$-$V_g$) of the one-finger nanodiamond lateral field emitter device, inset shows F–N plot; (c) monolithic diamond lateral vacuum transistor; (d) corresponding DC transistor characteristics [86].
3.7 Operating principles of VFE devices

3.7.1 Vacuum field emission diode

VFE diode is the most fundamental form of vacuum devices with only two electrical terminals or electrodes, viz. anode and cathode as shown in Figure 3.16 (a) [162]. The cathode is an electron source where electrons are emitted under the influence of an electric field. The anode is separated from the cathode by means of insulating material such as spacer or vacuum gap, and is positively biased to collect the emitted electrons, resulting in the flow of current from cathode to anode. When, they strike the anode, they give up most of their energy to the anode in form of heat. To allow emission occurring at a low electric field, the cathode is normally made of low work function material and/or with a sharp structure. The cathode-anode gap is usually on the order of few microns to several hundreds of microns. Figure 3.16 (b) shows circuit symbol of a VFE diode. Under reverse bias where a negative voltage is applied to the anode with respect to the cathode, electrons may tunnel from anode into vacuum. However, the electron emission from anode into vacuum only occurs at a very high electric field because the anode is normally made of a high work function metal with planar structure, which does not allow emission to occur at low electric field. Therefore, field emission diode has a rectifying I-V characteristic. The reverse breakdown field and voltage depend on the anode-cathode spacing, type of anode, and condition of anode surface. A typical [87] current-voltage (I-V) characteristic of a VFE diode is shown in Figure 3.13 (b). All the I-V curves show a rectifying behavior with an exponential increase in the emission current with increasing positive anode voltage and zero current in reverse bias. The corresponding F-N plot of Ln(I/V^2) vs. 1/V as shown in Figure 3.13 (b) inset is almost
linear with a negative slope. No deviation due to image and space charge effect can be observed because the current density is not sufficiently high.

3.7.2 Vacuum field emission triode

Field emission vacuum triode is a three-electrode electronic device, as shown in Figure 3.16 (c)-(d) [162]. The first two electrodes are cathode and anode as described for the field emission diode. The third electrode is called grid or gate which is placed between the cathode and anode in the form of a suitable mesh, screen or circular flat structure. The emission current flowing from the cathode to the anode must pass through the gate. Due to the proximity of the gate electrode to the electron-emitting cathode, a small gate voltage is sufficient to cause a high electric field on the emitter for the extraction of electrons into vacuum. The gate is, therefore, in a strategic position, and can largely control the anode current flow. Also, it helps to reduce space charge when operating in vacuum diode configuration. If the gate is grounded to the cathode, the field emission behavior of a triode is the same as that of a diode because the gate contributes no effect on the electric field between anode and cathode. If the gate is made slightly positive with respect to the cathode, the gate significantly increases the electric field at the cathode, thus permitting the anode to draw a larger emission current. On the other hand, if the gate is made negative with respect to the cathode, the negative electric field of the gate significantly reduces the electric field at the cathode, which results in a smaller emission current.

A standard thermionic field emission triode normally operates with the gate voltage made negative with respect to cathode. In this way, cathode-anode current is controlled by repelling electrons from the gate. On the other hand, the field emission
triode normally operates in the opposite regime as the thermionic field emission triode. If the gate were biased more negative than the cathode, there would be a possibility of having electron emission from the gate that would create an undesired gate-anode leakage current. By operating the gate with positive bias, there will be no reverse field emission from the gate. Under reverse bias where a negative voltage is applied to anode with respect to cathode at a given gate voltage, there will be no emission current between anode and cathode until the reverse breakdown voltage is reached where reverse electron tunneling from anode occurs. Normally, field emission triodes do not operate under these conditions.

Figure 3.16: (a)-(b) Field emission vacuum diode structure and symbol respectively; (c)-(d) Field emission vacuum triode structure and symbol respectively [162].
Three characteristic coefficients of a vacuum triode

The performance characteristics of a vacuum triode are determined by three important parameters [87], viz. amplification factor ($\mu$), gate-anode transconductance ($g_m$), and anode resistance ($r_a$). These three coefficients are particularly useful for ac equivalent circuit modeling of vacuum triode. First, $\mu$ is a measure of the effectiveness of gate voltage ($V_g$) in controlling the anode current ($I_a$). In other words, the amplification factor is the ratio of a change in anode voltage ($V_a$) to a change in gate voltage at constant anode current. It is also called static gain. This parameter determines the voltage gain ($A_v$) of the amplifier for signal amplification applications. Mathematically, it can be defined as,

$$\mu = \left. \frac{\partial V_a}{\partial V_g} \right|_{I_a=\text{const}}$$

(3.27)

Next, $g_m$ indicates the current driving capability, the voltage gain and high frequency response of a triode amplifier. It is defined as the change in the anode current due to a change in the gate voltage at a given anode voltage. It is also called mutual conductance or simply, transconductance. Mathematically,

$$g_m = \left. \frac{\partial I_a}{\partial V_g} \right|_{V_a=\text{const}}$$

(3.28)

Last, $r_a$ measures the effectiveness of anode voltage in controlling anode current at a certain gate voltage and can be expressed as:

$$r_a = \left. \frac{\partial V_a}{\partial I_a} \right|_{V_g=\text{constant}}$$

(3.29)
The values of $\mu$, $g_m$ and $r_a$ are not constant, in the strict sense, because these values vary with the operating conditions. For a given set of conditions, however, a useful relation exists among these coefficients.

\[
    r_a g_m = \frac{\partial V_a}{\partial I_a} \cdot \frac{\partial I_a}{\partial V_g} = \frac{\partial V_a}{\partial V_g} = \mu
\]  

(3.30)
CHAPTER IV

PROPOSED RESEARCH AND APPROACH

4.1 Overview

The purpose of this research is to develop a reliable fabrication process to achieve efficient monolithic multifinger nanodiamond lateral field emission devices operable at low voltage with high emission current for vacuum micro/nanoelectronics and IC-compatible applications. To achieve this goal, the research is classified into two main sections. First part deals with the study, processing and optimization of the processing parameters for multilevel electron beam lithography (EBL) and dry etching methods used in this research to develop well-controlled, highly selective and reproducible processes for micropatterning of nanodiamond films using thin metal film as masking layer. The Raith eLiNE EBL tool, Figure 4.1 [163-164], has been used throughout the research for precise lithography. The following part of the research includes the application of these developed processes for designing, fabrication and characterization of micro/nanopatterned nanodiamond lateral field emission devices. Various multi-mask level fabrication schemes, involving RIE-enabled batch-processing have been successfully employed to yield nanodiamond lateral field emitter cathodes in sub-micron gap two-terminal and multifinger three-terminal configurations. The specific device design, fabrication details, characterization techniques, device behaviors and experimental results achieved are presented and discussed in chapter V and VI. The following sections summarize the significance of this research and the adopted approach.
4.2 Development of nanodiamond micropatterning technique

As discussed in the previous chapters, nitrogen-incorporated nanocrystalline diamond is a very promising form of CVD diamond. The nanodiamond growth plasma chemistry can be effectively controlled to define the grain size, $sp^2$-carbon content, and the nitrogen n-type conductivity in the thin film. A suitable process technique involving CH$_4$/H$_2$/N$_2$ microwave plasma-enhanced chemical vapor deposition (MPCVD) to grow nitrogen-incorporated nanodiamond on silicon-on-insulator (SOI) has been identified. This nanodiamond film would be utilized for vacuum field emission in different geometry. Detail growth technique is mentioned in the next chapter.
The fabrication method adopted in this research is a subtractive process. Each additional step that requires selective removal of unwanted materials potentially widens the pattern. The amount of widening is dependent on the masking material thickness. Thus, the development of robust micropatterning technique for nanodiamond is essential to utilize its unique properties and realize useful device structures. Non-uniformity in diamond emitter microstructures can result in uncontrolled randomly scattered emission sites, inconsistent emission behavior and no long-term stability. Nanodiamond lateral devices with micron-range anode-cathode spacing have been reported earlier using optical lithography [86]. However, minimizing the gap is necessary for achieving sub-volt turn-on. EBL has been introduced to overcome the conventional photolithography limitations and to achieve sub-micron gap design requirements. Incorporation of EBL into the process sequence would make it more complicated and thus, require developing a new series of recipes which involve the identification of proper photoresist with right thickness, optimum EBL exposure parameters and appropriate metal masking layer thickness. Further, nanodiamond etch recipe for the sub-micron gap pattern will be developed using inductively coupled plasma-reactive ion etch technique (ICP-RIE) in pure oxygen plasma with good selectivity, etch rate and reproducibility. Experimental trials involve different etchant gas chemistries, power and pressure, which would ultimately lead to establish a complete nanodiamond micropatterning process for fabricating advanced nanodiamond lateral diode and triodes.
4.3 Development of monolithic nanodiamond lateral vacuum diodes

The basic design of the sub-micron multifinger nanodiamond lateral field emission diode is presented in Figure 4.2. The nanodiamond cathode is equipped with an array of 140 uniformly spaced high aspect-ratio finger-like emitters laterally tapering to end in sharp apexes. The anode has a straight edge structure. The EBL-delineated interelectrode gaps are separated by a distance as small as 300 nm. The active silicon layer supports the electrode structures on an insulating substrate of 4 µm thick silicon dioxide (SiO$_2$), which serves as the isolation material. The SiO$_2$ layer is supported on 525 µm thick Si substrate. The entire arsenal of deposition, micropatterning and other processing techniques developed would be applied to fabricate these devices for the first time. A mixed lithography approach which combines conventional optical lithography with EBL has been used for the complete device delineation. Further, the scope and applicability of the designed and fabricated diodes and its subsequent electron emission characteristics would be measured and analyzed.

Figure 4.2: Basic design of a sub-micron gap multifinger nanodiamond lateral field emission diode.
4.4 Development of monolithic nanodiamond lateral vacuum triodes

Lateral configuration is one of the best approaches to achieve 3-terminal field emission devices, as those can be fabricated in monolithic configuration. An important parameter for vacuum triode design is the emission current modulation by gate voltage. For most practical applications, the modulating voltage is desired to be small. Similarly for the diamond vacuum triode, the gate voltage relays on the turn-on electric field of diamond cathode, the gate-cathode spacing and the number of emission sites. Figure 4.3 represents the multifinger nanodiamond lateral triode design which has never been realized earlier. The structure is a monolithic field emission device, with 140 efficient nanodiamond finger-like emitter array as cathode with integrated anode and gate. SOI wafer has been used as the basic substrate. As expected, the fabrication complicacy has gone higher with more EBL steps and further etching/lift-off processes. A majority of this research would be focused on the development of these multifinger nanodiamond lateral field emission 3-terminal structures owing to its immense potential as a microelectronic device. To realize the structure, Figure 4.3, a selective portion of the SOI oxide(SiO$_2$) has to be etched away from under the nanodiamond finger to expose them to the underneath handling Si. Selection of proper masking material for etching the 4 µm SiO$_2$ has proved to be a challenging task. Next chapter elaborates the fabrication challenges encountered and their solutions. Later, the electrical performance of the fabricated devices has to be studied.
Figure 4.3 Basic design of a nanodiamond lateral multifinger field emission triode.
CHAPTER V

DEVICE FABRICATION, RESULTS and DISCUSSION

A nanodiamond field emission device developed in lateral configuration can result in efficient low-voltage and high-frequency electronic performance. A lithography-controlled emitter geometry and small interelectrode separation in a versatile, low capacitance structure including a built-in anode and insulator are salient attributes of a lateral field emitter device. By process integration of nitrogen-incorporated nanodiamond film deposition with the controlled diamond micropatterning technique, multiple lateral nanodiamond field emitter arrays have been batch-fabricated on SOI wafers, creating a useful approach to realize potential vacuum electron devices for applications. This chapter describes the process techniques developed for the nanodiamond material, and the fabrication schemes for the development of monolithic nanodiamond lateral field emitter devices, along with experimental results.

5.1 Deposition of nanocrystalline diamond thin-film

In this research, nanocrystalline diamond films were deposited in an ASTeX® MPCVD system with a 1.5 kW generator, operating at 2.45 GHz. The schematic of a typical MPCVD system is shown in Figure 5.1 (a). The substrate temperature was set using an induction heater independent of the plasma. The growth system was coupled with a controlled gas handling system, allowing precise control of the process gas flow rates. Since silicon-on-insulator (SOI) wafers (2 μm active Si on 4 μm buried oxide on a
Figure 5.1: (a) Schematic diagram of a typical ASTeX® MPCVD system [86]; (b) snapshot of the CH₄/H₂/N₂ plasma during nanodiamond deposition.

525 μm Si substrate) were used as the main substrate throughout the research, the same substrate has been used to verify the nanodiamond growth rate and surface morphology before further implementing in this work. The substrates were pretreated by mechanically polishing the surface using a 2.5-μm diamond powder, and ultrasonicating with 5-20 nm nanodiamond powder in acetone solution to augment diamond nucleation. A two-step growth process began with the samples being transferred to the CVD chamber and the chamber evacuated to a base pressure of 10⁻² Torr. At the first stage, all the samples were heated to 800°C, followed by introducing a gas mixture of CH₄/H₂/N₂ to initiate plasma for nitrogen-incorporated nanodiamond growth. Figure 5.1 (b) shows typical CH₄/H₂/N₂ plasma during nanodiamond deposition. The gas flow rates of 15/135/15 sccm (CH₄/H₂/N₂) were maintained at a pressure of 13 Torr and microwave power of 550 W. This low-power low-pressure stage, called “nucleation stage” was continued for 1 hour. During this process, diminishing the microwave power reduces the energy of the plasma, and decreasing the reactant pressure spreads out the microwave plasma in the CVD
growth chamber. Thus the reaction process is starved. Hence, the two events, diamond nucleation and growth compete against each other for the limited amount of energy available. In this condition, the nucleation density will increase and the grain size diminishes [86]. Thus, a high density of nano-sized, fine diamond grains conglomerate on the substrate to initiate the nanocrystalline diamond film. This growth rate control process methodology facilitates the synthesis of a very thin, continuous and smooth layer of CVD nanodiamond. In the next step, viz. ‘growth stage’, to conduct a set of comprehensive trials, the growth temperature and pressure were varied while the same gas flow rate and temperature were maintained. Microwave power was increased to 1000 W from 550 W for faster growth rate. This process was continued for another 3 hours. 

**Table 5.1** summerizes the process parameter variation associated with respective samples. The morphology of the CVD diamond films were examined using a scanning electron microscope (SEM), while the average grain size was determined by scanning across the surface of the film. **Figure 5.2** shows the set of CVD diamond films that was synthesized in order to identify a smooth and conductive diamond film for this study. The images revel that the “Sample d” has the lowest surface roughness compared to the others and that is why it has been selected for further processing. **Figure 5.3** shows the high magnification and cross-sectional images of the corresponding sample, which clearly shows the small grain size of 5-10 nm and a thickness of 1-1.2 µm on SOI wafer.
Table 5.1: Summery of the process parameter variation associated with respective samples

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Pressure (Torr)</th>
<th>Temperature (°C)</th>
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<td>a</td>
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<tr>
<td>c</td>
<td>28</td>
<td>850</td>
</tr>
<tr>
<td>d</td>
<td>28</td>
<td>800</td>
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</tbody>
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Figure 5.2: SEM micrographs of deposited nanocrystalline diamond film grown by CH₄/H₂/N₂ MPECVD process technique at different conditions as shown in Table 5.1.
Figure 5.3: (a) The high magnification SEM of the nanodiamond film to be used in this research with average grain size of 5-10 nm deposited by CH$_4$/H$_2$/N$_2$ microwave plasma CVD process; (b) Corresponding cross-sectional view shows the thickness of the film.

The film growth rate was found to be \(-0.25 \, \mu m/hr\). The low surface roughness is extremely important to minimize the photon/electron scattering during lithography; otherwise it would result into wider device structure. A common method of scratch test which was used to evaluate the adhesion strength of the nanodiamond film onto the substrate showed that film has an excellent adhesion to its base. Further, electrical resistance measurements were performed using a multimeter, probed on identical-sized gold (Au) circular electrodes on the surface of nanodiamond film. Direct measurement of the electrical conductivity at room temperature showed that the “Sample d” has a resistance of 1-10 k\(\Omega\). The high electrical conductivity of nanodiamond obtained from CH$_4$/H$_2$/N$_2$ MPCVD is attributed to the incorporation of nitrogen. Also, the nitrogen concentration should be uniform throughout the diamond layer because the incorporation technique is homogeneous throughout thin film deposition. The Increase in electrical conductivity clearly indicates a decrease in the work function; experimental techniques to estimate this reduction in the work function of the material form a subject of further study. The continuity, conductivity and uniformity of this thin film over a 1-inch wafer
area were found to be highly suitable for integration into device forms based on previous studies discussed elsewhere[86]. The grain size has been assumed to be the same throughout the depth of the diamond film.

5.2 Micropatterning of the nanocrystalline diamond film

One of the reasons for CVD diamond being less utilized as a field emitter is that it is difficult to pattern diamond films due to the scarcity of appropriate wet or dry etching techniques. Diamond, being the hardest material, requires a well-controlled etch process to be patterned uniformly to realize useful structures for varied applications. Lithography on microcrystalline diamond substrates is also a concern, due to its surface roughness. With the nanodiamond films developed in this research, having a small grain size and smooth surface morphology and uniformly controllable thickness, it is possible to overcome many lithography problems. The Vanderbilt Diamond Laboratory has previously created a mold transfer and diamond micropatterning technique to generate topologically managed diamond vacuum field emitters in both lateral and vertical geometry [86-87]. In this research, first, a reactive ion etch (RIE) nanodiamond micropatterning process technique is developed using a Trion Phantom II RIE tool, which has been utilized later in this study in the fabrication of a variety of diamond-based devices. Next the development of lateral sub-micron gap diode and multifinger triode has been discussed using EBL.
5.2.1 Nanodiamond RIE process development

Reactive ion etching of diamond has been attempted by different research groups with moderate success. Low etch rate, non-uniform etching, and inadequate mask-defined selectivity for device-level micropatterning have been some of the issues encountered during the etching. This research overcomes these concerns to develop a consistent and well-controlled micropatterning technique and realize potential electron field emitter structures. Experimentation involving different plasma technology sources, etchant gas chemistries, power and pressure conditions, and masking materials of varied thicknesses led to the establishment of the nanodiamond micropatterning process. The utilization of an ICP-RIE system, based on the inductively-coupled plasma technology combining a high conductance, high vacuum compatible process chamber with an ICP source to produce very high ion density at controlled low pressures. Metal used as an etching mask would protect un-exposed areas on the diamond from being removed. Since aluminum (Al) did adhere well to the diamond substrate, it was tested as masking material. As thickness is a critical parameter, for subsequent lateral field emission device processing, the Al mask thickness was optimized according to diamond film thickness and ND RIE process parameters as shown in Figure 5.4. Al masking layer of 400 nm thick was found to offer good selectivity, allowing the micropatterned nanodiamond structures to retain the beneficial properties of the material. Based on the results, several other modifications in the fabrication process have been done to avoid problems in future. First, an additional ultrasonic cleaning in acetone was introduced after ND growth to remove any unwanted particle or carbon flex from the surface enhancing the smoothness of the ND surface. These carbon flexes were believed to deposit on the surface from the inside wall of the
MPCVD chamber during or after the synthesis. Next, the substrate heating during RIE of ND has been addressed. Since the RIE tool, Trion Phantom II, does not provide any substrate holder cooling mechanism, the total etch time has been divided into several small etching steps and a cooling gas has been introduced into the chamber in between. Thus each modified ND RIE cycle consists of two steps; Oxygen (O\textsubscript{2}) plasma etching followed by surface cooling using carbon tetrafluoride (CF\textsubscript{4}) without any plasma. CF\textsubscript{4} has been used because of its high thermal conductivity and compatibility with material used in this process. In wafer-scale fabrication, the developed process scheme can also improve the processing yield to achieve monolithic emitter devices. The results are demonstrated in the successive sections with detail process parameters.

**Figure 5.4:** Cross-sectional SEM of nanodiamond film coated with Al as masking material; (a) Al thickness during the trial run; (b) Al thickness used throughout this research.
5.2.2 Multifinger micron-gap nanodiamond lateral diodes fabrication

Nitrogen-incorporated nanodiamond films grown by the CH$_4$/H$_2$/N$_2$ MPCVD, described earlier in this chapter were applied in the fabrication of lateral nanodiamond array cathodes in four different diode configurations. The physical and electrical characteristics of the diamond devices have been explored by Subramanian at Vanderbilt [86]. Although the focus of this research is on submicron-gap diode and multifinger triode, the micron-gap diode structure obtained by several modifications and its field emission properties can be evaluated before application in advanced monolithic device configurations.

The micron-gap nanodiamond lateral field emitter devices were physically realized using an uncomplicated single-mask fabrication technique using optical lithography, paralleling conventional IC processing technology. The process schema is shown in Figure 5.5. The fabrication begins with the growth of a 1-1.2-μm thick nitrogen-incorporated nanodiamond film on a SOI wafer by CH$_4$/H$_2$/N$_2$ MPECVD. Then the substrate is ultrasonically cleaned in acetone bath to remove any unwanted particle from the surface resulting smoother surface. Next, an aluminum metal layer of 400nm thick is deposited on the nanodiamond by e-beam evaporation. The Al layer is then patterned with the lateral device structures using optical photolithography, the exposed aluminum being etched away at room temperature by a commercially available wet chemical, PAE (80% phosphoric acid-based etchant) and the photoresist removed. With this aluminum serving as a mask, micropatterning of the nanodiamond film is carried out. R.F.-assisted pure oxygen plasma chemistry was identified to be a very efficient diamond etchant. As mentioned earlier, the patterning of ND film using ICP-RIE consists of two
steps; etching and subsequent cooling. The beginning of each cycle starts with the ‘etch step’ which includes a coil R.F. power of 800 W, platen R.F. power of 150 W, oxygen flow rate of 30 sccm, at a pressure of 10 mTorr. Then, at ‘cooling step’, the gas flow was stitched to CF$_4$ with flow rate of 100 sccm at a pressure of 300 mTorr. No coil and platen power was applied during the second step. The etch conditions of high R.F. power and low pressure helped achieve good anisotropy, the high energy reactive ions with minimum ion scattering giving a moderate diamond etch rate of $\sim 0.2$ μm/min and directionality. The selective etching ratio of diamond against aluminum was found to be suitably high for device pattern formation. The etching was examined to be uniform over

Figure 5.5: Single-mask fabrication process for the micron-gap nanodiamond lateral field emission diodes.
a reasonably large area, leaving a smooth substrate surface with no residue at the end of the RIE process, facilitating high-yield batch-fabrication of devices applying nanodiamond. Finally, a silicon etch step was performed to expose the underlying SiO$_2$ layer of the SOI substrate, which serves as the isolating material. This process step is performed by using HF:HNO$_3$ solution at room temperature in 1:30 ratio. The wet etching of active Si layer ensures no plasma damage of the exposed SiO$_2$ surface layer, which enhance the device performance and life by minimizing possible surface electron conduction during device operation. Also, this Si layer has intentionally been over-etched to facilitate electron emission only from the nanodiamond tips. Post-fabrication, the nanodiamond lateral devices are subjected to RCA chemical cleaning procedure, followed in the silicon wafer industry standard process technology, to remove any contaminants present on the emitter surface. Lateral field emission diodes, fabricated using this nanodiamond micropattern process technique are presented in Figure 5.6-5.7. The emitters of 125-fingered diodes are designed in a straight line, while 650-, 2000- and 9000-fingered diodes are composed of arrays in comb shape configurations, with each comb composed of 65 fingers, as shown in Figure 5.8 (b)-(d), with uniform anode-cathode spacing. The 650-fingered lateral device is composed of two isolated anodes, 325-fingers associated with each, and a common cathode. The large contact pads aid visual electrical probing. The field emission characteristics of the nanodiamond microtip array cathodes are reported in the next chapter.

This ensuing section put forward the basic fabrication process schemes developed for monolithically integrated nanodiamond lateral submicron-gap diode and multifinger triode with some advancement and alteration in the processing sequences.
Figure 5.6: SEM micrograph of four different devices. (a) 125 finger diode; (b) 650 finger diode; (c) 2000 finger diode; and (d) 9000 finger diode.
Figure 5.7: High magnification SEM micrograph of the fabricated devices. (a) 125 finger diode; (b)-(c) comb shape configurations; and (d) higher magnification of a comb.
5.3 Fabrication of multifinger monolithic nanodiamond lateral triode

Nanodiamond lateral triode has also been fabricated using almost the same process scheme with few additional steps at the end. The monolithic lateral vacuum microtriode comprises of 140 nanodiamond finger-like structures as emitter with straight edge nanodiamond pad as 2\textsuperscript{nd} electrode, and the precisely exposed substrate Si as 3\textsuperscript{rd} electrode, all on the same substrate. The structure was achieved by control of lithography and the subsequent subtractive processes. For better understanding, the fabrication process can be divided into two parts. In the first part, a nanodiamond diode structure has been obtained with the nanodiamond electrodes sitting on active Si layer, and in the next part; EBL has been introduced to realize the third electrode.

The first part could have been achieved by optical lithography to accommodate batch fabrication. The process is performed as mentioned in section 5.2.2, until the active Si layer etch step, “Step 7” in Figure 5.5. The fabrication schematic for the nanodiamond triode structures are shown in Figure 5.8. Additionally, up to the diode configuration, the structure could have been achieved using EBL which is going to be discussed thoroughly in the next section. The Si layer has been used as a hard mask for the next processing part. In the following processing steps, after ND etching, e-Resist ZEP 520A is coated on the surface and a line of dimension 1\mu m x 1.6mm is drawn along the emitter tips on the ZEP coated Si layer using e-beam lithography. After developing, the resist is used as mask to etch the exposed Si. Figure 5.9 shows the SEM images of the device structure after controlled e-beam writing and selective Si etching. The etching is performed using the RIE tool as mentioned earlier in this chapter. ZEP 520A has been chosen over PMMA for its better compatibility for dry etching. Next, the resist is striped-off and oxide etching
is performed using the patterned Si as mask. Finally, the device Si layer is removed to achieve the electrode isolation and standard RCA cleaning procedure is performed to remove any contaminations. **Figure 5.10** shows the final device structure.

**Figure 5.8:** Mixed lithography fabrication approach schematic for the multifinger nanodiamond lateral field emission triodes.

Compatibility of diamond films for integration with many other different materials (semiconductors, metals, oxides) is a requisite for realizing active diamond-based devices. The development of the planar nanodiamond lateral field emission device
using metal and polymer mask, and an insulating spacer adds veracity to the fact that the many potential performance and reliability advantages of diamond can be successfully realized in device configurations. The electrical performances of the fabricated device are mentioned in the next chapter.

**Figure 5.9:** (a) SEM micrographs show the controlled e-beam exposure along the tip area. (b) The substrate Si layer has been etched selectively to expose the box SiO$_2$ in desired places.
Figure 5.10: (a) SEM micrographs show the controlled etching has been achieved using device Si layer of SOI wafer as hard mask. (b) The substrate Si layer has been exposed in selective places.
5.4 Fabrication of multifinger submicron-gap nanodiamond lateral diode

Decreasing the interelectrode distance is one of the most effective ways to reduce the turn-on voltage/field of FEDs. Due to the optical lithography resolution, much of the early research on lateral vacuum FEDs was limited to inter-electrode spacing in the micron range. Sub-micron spacing would essentially offer high field strength without the use of high voltage and can be achieved using EBL as proposed in this section. Basically, E-beam lithography consists of shooting a narrow, concentrated beam of electrons onto an e-beam sensitive resist coated substrate. This lithography technology is sequential, which means it write pattern after pattern in a sequence. A combination of self-organized designs guided by highly sophisticated software is transferred over the surface of a substrate by scanning the surface using a tightly focused high resolution electron beam. When the e-beam hits the surface, high energy electron bombardment causes bond breakage in the resist polymer which then can be used for pattern transfer. Further, software driven EBL design editor and a pattern generator make the mask design versatile.

Several important EBL process parameters have been considered for attaining submicron-gap dimension which include incident beam voltage, dosage, resist thickness and pattern development time [165]. Higher resolution can be achieved in EBL by using a very thin resist and a thinner nanodiamond film combination. Thinner films are preferred since the scattering volume of incident energetic electrons is limited in the thinner film; scattering effects are reduced as compared with a thicker film. There is also a delicate balance between the accelerating voltage that would yield a sufficient bore-through power and result in a tolerable forward and back scattering. A higher
accelerating voltage (e.g., 20-40 kV) would give a higher resolution for densely packed patterns such as the diode structure used in this work. However, back scattered electron would expose unintended areas, and as a result of the electron scattering from the proximity effect, the lines in densely patterned areas gets wider than designed. In contrast, a lower accelerating voltage would offer less scattering, however the beam resolution deteriorates and designs would be compromised. Another EBL parameter that requires attention for attaining a sub-micron emission gap is the exposure dose. As a general rule, the exposure dose increases for decreasing feature sizes. Insufficient dosage results in shorted devices while over dosage result in wide emission gaps. It can also induce cross-linking, forming a negative resist. As a result, there will be photoresist residue on the substrate, while the surrounding area that was exposed positively will wash away. The EBL written structure is also highly sensitive to development time. E-beam exposure breaks the e-resist into fragments that are dissolved preferentially by a developer. Taking all these possible variations into consideration the EBL parameters have been selected [166] to get the desired structure, which has been discussed next.

The e-beam delineated lateral vacuum diodes comprised of an array of uniformly spaced, high aspect ratio, 140 finger-like cathode emitters separated by nanometer distance. The straight-edged integrated anode is isolated by a thick oxide (SiO$_2$) layer from the emitter giving it the rectifying geometrical field enhancement factor. The fabrication process mentioned here is based on mixed lithography approach, i.e. using both optical and e-beam lithography in sequence. The complete fabrication schematic is presented in Figure 5.10. Upto Al deposition, the approach is same as micron-gap structure. Then a single-mask conventional lithography is used to delineate the contact
pads for both the anode and cathode structures on the AZ 5214E photoresist coated metal layer. The exposed Al is etched away at room temperature by a wet chemical, PAE and the photoresist removed. Next, to introduce EBL, a high performance positive e-beam resist is coated on the substrate surface. ZEP 520A has been chosen due to its high resolution, high sensitivity and extremely good dry etch resistance. EBL is then used to delineate the device structure on the e-resist coated Al mask. After developing the

![Figure 5.11](image)

*Figure 5.11:* Mixed lithography fabrication approach schematic for the multifinger submicron-gap nanodiamond lateral field emission diodes.
pattern, Al dry etch is performed to get an improved etch profile using a gas mixture of chlorine (Cl₂) and boron trichloride (BCl₃) in a Trion RIE tool. Then nanodiamond etching is performed followed by mask material removal and active Si layer etching to get the final device structure. The nanodiamond and Si etch recipe are the same as used before in this research. Finally, the fabricated nanodiamond lateral device, as shown in Figure 5.11, is subjected to RCA chemical cleaning procedure to remove any contaminants present on the emitter surface. The electrical performances of the fabricated device are mentioned in the next chapter.

Figure 5.12: (a)-(d) SEM micrographs of a 140-finger lateral nanodiamond field emission diode with 300 nm interelectrode distance.
CHAPTER VI

DEVICE CHARACTERIZATION, RESULTS and DISCUSSION

This chapter outlines the electrical characterization methods employed for the fabricated nanodiamond devices, viz. diodes and triodes. It also presents and discusses the electrical performance of these nanodiamond structures under vacuum.

6.1 Device Characterization Techniques

6.1.1 Electron emission characterization of lateral diodes

The electrical performance of lateral diode in vacuum was characterized using the test set-up shown in Figure 6.1. The fabricated device was maintained in a vacuum environment of \( \sim 10^{-7} \) Torr. Flat gold (Au) dots were placed on the contact pads of the cathode and anode of the lateral device, and were electrically connected to the circuit via metal probes. The emission current from the nanodiamond fingered emitter cathode was measured as a function of the applied anode voltage. A continuous power supply, capable of incrementing the applied voltage in very small intervals was used for low-voltage characterization of the lateral diodes. Prior to emission characterization, the nanodiamond lateral device was subjected to in-situ vacuum tip conditioning by means of thermal desorption to get rid of water vapor or other residual adsorbates on the surface of the nanodiamond accumulated at the terminus of the emitter device processing or by exposure to ambient. With the device seated on a heated stage, heat treatment was performed at 350°C for several hours inside the vacuum chamber. The temperature was
measured and controlled by means of a thermocouple feedback at close proximity of the device. The device was then cooled down slowly to room temperature. Then, without the application of an external heat source, the nanodiamond lateral emitters were maintained at a particular emission current, \(~10 \, \mu\text{A}\) for an hour or more during normal vacuum diode operation by adjusting the anode voltage, where the extracted field emission current was used to execute more localized cleaning of the nanodiamond emitter fingertip. The tip conditioning treatment was terminated when a stable current was obtained for a period of time. Such post-fabrication conditioning/processing techniques are also common in conventional silicon IC fabrication technology, such as the rapid thermal annealing (RTA) treatment performed following an ion implantation step to repair the primary crystalline damage in the silicon. After the tip conditioning, the I-V characterization of the nanodiamond lateral diode was performed.

Figure 6.1: Schematic test set-up of the vacuum field emission lateral diode.
6.1.2 Field emission characterization of nanodiamond lateral triodes

The testing circuit for emission characteristic of the monolithic lateral vacuum triode, in a common emitter configuration, is shown in Figure 6.2. Taking the advantage of the device structure, the device can be operated in two modes of operation by interchanging the anode and gate. Depending on the mode of operation, a load resistor $R_a$ in the anode circuit was used to limit the current in the case of short circuit. A resistor $R_g$ was also used to limit the gate leakage current in the case of short circuit. The anode emission current was then measured as a function of gate and anode voltages in a vacuum environment of $\sim10^{-7}$ Torr. The procedures for triode testing were as follows. Initially, the anode voltage was increased to extract electrons from the cathode, with no gate bias applied, until a significant anode emission current was perceived. Next, the gate voltage was altered from zero to apply positive and negative bias and the subsequent anode current modulation was measured.

![Figure 6.2: Schematic test set-up for of the vacuum field emission lateral triode.](image)
The anode emission currents versus time were taken by a computer data acquisition system. For each set of emission current (Ia) measurement, the anode voltage was scanned manually while keeping the gate voltage constant. The gate voltage was then changed to a new value and the same emission measurement was repeated until a complete data set for all gate voltages in the range of interest were attained. The emission characteristics of triodes were obtained by plotting the anode emission current versus gate and anode voltages.

6.2 Electrical performance of nanodiamond vacuum electron emitters

6.2.1 Multifinger micron-gap nanodiamond lateral diodes

Each of the nanodiamond lateral devices fabricated in section 5.2.2 were tested individually in a vacuum chamber, as described earlier, up to an emission current of 60-50 μA to study the current vs voltage behavior. The 9000-fingered lateral emitters showed the lowest threshold electric field of ~0.5 V/μm and ~60 μA of emission current at an electric field of ~3 V/μm or at 12 V. Next, the 2000-fingered lateral emitter was tested for electrical characterization, which showed threshold electric field of ~1.1 V/μm and ~58 μA of emission current at an electric field of ~5.5 V/μm or at 22 V. The testing was followed by the 325-fingered lateral emitter which exhibited a higher threshold field of ~1.4 V/μm and required ~57 V or an electric field of 14.25 V/μm to generate an emission current of ~50 μA. Whereas the threshold field of the lateral diodes with 125-fingered was as high as ~1.5 V/μm and the emission current of ~50 μA was observed at ~19.5 V/μm or at 78 V. The emission current value at the threshold electric field was set to 10 nA per finger. The current-voltage/field characteristics of these four different
Figure 6.3: (a) Field emission characteristics of the nanodiamond lateral diodes in discussion, showing the current enhancement obtained by increasing the emitter area. (b) Corresponding Fowler-Nordheim behaviors indicates field emission.
devices were shown in Figure 6.3 (a) and the field emission tunneling behaviors were confirmed by the corresponding linear Fowler-Nordheim plots, Figure 6.3 (b). The F-N plots of the diodes have almost equal negative slopes, indicating that the work function (\(\Phi\)) and field enhancement factor (\(\beta\)) are essentially same for all the four lateral structures. The slope can be found by taking natural logarithm of Eq. (3.7) and comparing it with the equation of a straight line, \(y=mx+c\). The observed turn-on electric field of the nanodiamond lateral emitter is significantly lower than that of comparable silicon lateral field emitters utilizing an ultra-sharp tip apex, which is typically > 100 V/\(\mu\)m [156-157,167-170]. This is attributed to the superior material properties of nitrogen-incorporated nanocrystalline diamond offering the diamond emitter diode a higher effective field enhancement factor or a lower work function than a silicon field emitter diode. The reported results from silicon lateral field emitters also confirm that for the electric fields at which the nanodiamond lateral diode operates, there can be no emission from the silicon layer beneath the nanodiamond fingers. Moreover, the lateral device processing has been optimized to overetch the Si layer intentionally, as shown in Figure 5.8 (b), which leaves the silicon having a wider gap distance from the anode and also with a larger radius of curvature pattern. Further, the active silicon layer of the SOI substrate was chosen to have a relatively low dopant concentration. All these factors clearly prove that the emission characteristics of the lateral diode are contributed solely by nanodiamond.
**Realizing Logic OR function**

Vacuum field emission logic gates have been proposed and simulated before [171-172], but practical application wasn’t possible because of their design complexity and high turn-on field. After characterizing individually, three of the four structures, 125-, 2000- and 9000-fingered diodes, were connected to their identical pair using diode-resister logic, Figure 6.4 (c), to perform the logical operations [173]. Whereas, utilizing the structural advantage, only one 650-fingered device was used to realize the same logic. The 650-fingered lateral device is composed of two identical 325-fingers diodes on a common cathode with two separately addressable anodes. A square wave from a function generator was used as the input signal. The input logic low is defined as 0 V and input logic high is defined separately with a peak to peak amplitude of 18, 10, 7 and 2.2 V for 125-, 325-, 2000 and 9000-fingered lateral structures respectively, in order to maintain the same output logic high of 1-2 V, and low of 0 V. When the input high was applied to the anode terminals, A and B, of each pair of similar devices without any time delay, the output followed the input signal. Next, whenever either of the inputs was set to logic high, output followed the input. Finally, logic zero was observed at the outputs of each configuration when both the inputs were set to zero. Oscilloscope images of the Logic OR behavior under different input configuration for each of the nanodiamond structures are shown in Figures 6.5-6.8.
Figure 6.4: (a) The standard symbol for a two-input OR gate and its Boolean expression; (b) Corresponding truth table; (c) A diode OR circuit for positive diode-resistor logic, where V(1), V(0) and V(R) corresponds to logic high, logic low and reference voltage respectively.
Figure 6.5: Oscilloscope images of Logic OR behavior for nanodiamond 125-finger lateral diodes with 4 μm anode–cathode gap connected in circuit.

Figure 6.6: Oscilloscope images of Logic OR behavior for nanodiamond 325-finger lateral diodes with 4 μm anode–cathode gap connected in circuit.
Figure 6.7: Oscilloscope images of Logic OR behavior for nanodiamond 2000-finger lateral diodes with 4 μm anode–cathode gap connected in circuit.

Figure 6.8: Oscilloscope images of Logic OR behavior for nanodiamond 9000-finger lateral diodes with 4 μm anode–cathode gap connected in circuit.
Clearly, if and only if both the inputs are logic zero, only then the output goes to zero, otherwise logic one. Hence, these gates correctly perform a logical OR function. However, while operating in OR configuration, a difference between the input-output logic highs was observed. Ideally, diodes do not introduce any losses into the circuit which is not really valid for vacuum diodes and has been explained by theory of field emission under vacuum at chapter III. It can clearly be noticed that the emission current may be increased in five different physical ways [86]:

1. Increasing the emission area;
2. Increasing the potential;
3. Field enhancement by tip sharpening;
4. Lowering the emitter work function by doping;
5. Reducing inter-electrode spacing.

Earlier in this study we have mentioned the decrease in work function of the nanodiamond film by incorporating nitrogen in the methane-hydrogen mix during MPCVD. It is also important to note that the lateral diodes were batch fabricated, ensuring same work function (Φ), field enhancement factor (β) and inter-electrode spacing. The F-N plots in Figure 6.3 (b) have almost the same slope values, reconfirms the above statement. Thus the argumentation of overall emission current capability of the multi-fingered lateral diodes is attributed to the increase in the emitter area and there by the number of potential emission sites in the cathode. This clearly explains the current-field characteristics of the different diodes, Figure 6.3 (a), and hence the mismatch in input-output logic-high levels for different pairs of structures, Figure 6.9.
Conductivity measurements of the lateral devices in an open-air environment before and after emission testing were conducted to examine the quality of the silicon dioxide layer. If the measured current is a leakage current or hopping conduction current via SiO$_2$, it must remain unchanged in open air as well as in vacuum environments because leakage and hopping are conduction currents in solid-state devices. However, no current is observed in open air environment. Therefore, it is sufficient to conclude from these experimental measurements that the measured current from the micron-gap
nanodiamond lateral diodes is indeed the field emission current from nanodiamond fingers into vacuum.

**Half-wave rectification and envelope detection**

Further, vacuum microelectronic half-wave rectifier and envelope detector using a single 2000-fingered nanodiamond lateral field emitter diode with 4 μm interelectrode spacing have been studied. The diode was connected in a simple diode-resistor circuit [173], Figure 6.10 (a), to realize the half-wave rectification. In this configuration, current is allowed to flow only when the diode is forward biased, outputting the positive half of the signal. The rectification behavior was verified by the oscilloscope images across a load resistor (R), Figure 6.10 (b). But this pulsating nature of the output voltage makes it unsuitable as a dc supply for electronic circuit. The simplest way to reduce the variation is to place a capacitor (C) across the R, Figure 6.10 (c).

Thus, the envelope fading behavior was observed by placing a 1 μF capacitor at the output in parallel with the 1 MΩ load resistor, Fig 3b. As the rectified output is fed to the filter circuit; the capacitor charges to the peak of the diode output. Then it discharges through the load resistor R for almost the entire cycle, until the raising rectified wave exceeds the capacitor voltage. Then the diode turns on again to charge the capacitor up to the peak as before and the process repeats by itself. The time constant value, R*C, is chosen to be much greater than discharge interval to prevent the output voltage decrease too much during discharge cycle. A 15 V peak-to-peak sine wave from a function generator was used as an input signal. However, while operating in both the
configurations, a difference of ~5.75 V between the input and output highs were observed which has been explained in the previous section.

**Figure 6.10:** (a) A basic half-wave rectifier circuit; (b) Oscilloscope images verify the half-wave rectification; (c) A linear envelope demodulator circuit; (d) Oscilloscope images verify the envelope detection.
6.2.2 Multifinger monolithic nanodiamond lateral triode

Field emitter triodes are important building blocks in the development of high-speed, temperature- and radiation-immune vacuum microelectronics. Having examined nanodiamond as a vacuum diode, the research was extended to examine a nanodiamond triode in lateral configuration. Lateral triodes were developed, utilizing the same microfabrication tools applied for the lateral diodes as mentioned in the previous chapter. Then the 3-terminal lateral configurations were tested under vacuum to investigate the triode characteristics. It was identified that the position of the gates and anode with respect to the cathode in the device design plays a significant role in determining its characteristics.

The 140-finger nanodiamond lateral triode with 10 μm spacing between the nanodiamond electrodes and 8 μm spacing between the nanodiamond finger emitter and exposed handling Si was characterized for field emission in a common emitter configuration in a vacuum condition of ~10^{-7} Torr. The device structure is shown in Figure 5.9. The circuit schematic of the test setup is shown in Figure 6.2. The device was operated similar to classical thermionic triode, where the anode was used to turn-on the cathode which incorporates multiple nanodiamond fingered emitter, while the gates were employed to modulate the emission from the cathode to the anode. The only difference in this case is the gate voltage modulates the electric field at the emitter tip and hence the tunneling probability, whereas in the thermionic triode, the gate controls the space charge near the emitter. Taking the advantage of the device structure, the triode was operated in two modes of operation by interchanging the anode and gate.
In the first mode of characterization the handling Si was used as anode and the other nanodiamond electrode as gate. Figure 6.11 (a) displays the triode I-V characteristics of the nanodiamond lateral vacuum device at room temperature, indicating that the anode current is effectively controlled with a gate bias; higher applied positive gate voltages give higher emission current, whereas negative gate voltages suppress the emission behavior. For each set of emission current ($I_a$) measurement, the anode voltage ($V_a$) was scanned manually while keeping the gate voltage ($V_g$) constant. The gate voltage was then changed to a new value and the same emission measurement was repeated until a complete data set for all gate voltages in the range of interest were attained. For example, a large anode current ($I_a$) of ~27 μA was obtained at an Anode voltage ($V_a$) of ~60 V, when the gate bias ($V_g$) was 10 V. On the other hand, when negative 10 V was applied at the gate, $I_a$ suppressed to ~12 μA at same $V_a$. During this 3-terminal operation, the resultant potential field at the cathode consists of two components. They are the potential field produced by the gate and the field provided by the anode. Thus the total voltage at the cathode ($V_t$) is given by [86]:

$$V_t = V_g + \gamma V_a$$  \hspace{1cm} (6.1)

where $\gamma$ is is a constant determined by gate construction. It also weakly depends on the gate and anode voltages. However, the characteristics of the field emission triodes depend upon many other factors such as gate-cathode spacing, gate-anode spacing, size and geometry of gate. The total emission current from the cathode is therefore obtained by putting $V_t$ into the F-N equation, Eq. (3.7), in the place of anode-cathode voltage ($V$). The device characteristics were consistent with the modified F-N relationship, Figure 6.11 (b), which confirms that the emission current is due to tunneling mechanism under
different applied electric fields. $\gamma$ has been calculated by finding the amplification factor ($\mu$), Eq. (3.27), from the $I$-$V$ curves. By performing partial differentiation according to the definition in Eq. (3.7), $\mu$ of a field emission triode can be shown equal to $\gamma^2$. Further, the transconductance parameter ($g_m$), Eq. (3.28), was determined to be $\sim$0.75 $\mu$S at $V_a = 60$ V.

In the second mode of operation the handling Si was used as gate and the other nanodiamond electrode as anode, while keeping the cathode fixed. Figure 6.12 (a) displays the triode $I$-$V$ characteristics of the nanodiamond lateral vacuum device at room temperature, indicating that the anode current was effectively controlled by gate bias. A larger anode current ($I_a$) of $\sim$40 $\mu$A was obtained at an Anode voltage ($V_a$) of $\sim$60 V, when the gate bias ($V_g$) was 10 V. Whereas, negative 10 V at the gate, suppressed $I_a$ to $\sim$20 $\mu$A at same $V_a$. It is believed that the higher current attributes to the position of the gate which is 2 $\mu$m closer than the previous case. The total cathode voltage ($V_t$) was calculated as earlier case and the device characteristics were also found to follow the accordingly modified F-N relationship, Figure 6.12 (b), confirming that the measured anode current is due to the field emission mechanism. Further, the transconductance parameter ($g_m$) was calculated to be $\sim$0.85, which is one of the highest reported for lateral device, especially with cathode-gate separation in microns. It is also important to mention here that the gate-intercepted current must be small relative to the anode current for optimum performance of the device as triode. As observed in both the cases, the gate current ($I_g$) for this lateral triode was below 1$\mu$A at the moderate positive gate voltage ($V_g$). Furthermore, the emission behavior of the lateral triode was found to be very stable, e.g. at 45 V, around 13 $\mu$A, of current was measured with 2% of fluctuations,
Figure 6.11: (a) Triode emission characteristics of the nanodiamond lateral device operating in mode-1 (handling Si as anode); (b) Corresponding F-N plots are calculated by taking $V_t$ into consideration.
Figure 6.12: (a) Triode emission characteristics of the nanodiamond lateral device operating in mode-2 (handling Si as gate); (b) Corresponding F-N plots are calculated by taking $V_i$ into consideration.
as shown in Figure 6.13. A total of $18 \times 10^3$ data points were collected over the time period of 10 hours at an equal time interval. While collecting the data, the diode configuration was achieved by shorting both the interchangeable electrodes and used as a single anode.

![Graph](image)

**Figure 6.13**: The emission behavior of the lateral triode was found to be very stable. For example, at 45V, applied to both anode and gate, $I_a$ was found to be 13 μA over a time period of 10 hours’ time with 2% fluctuation.
6.2.3 Multifinger submicron-gap nanodiamond lateral diode

The lateral construct provides latitude for further reduction of the device operating voltage by realizing sub-micron interelectrode spacing with advanced e-beam lithography. In this section, the electrical characteristics of the fabricated 140-finger vacuum diode with 300 nm anode-cathode spacing have been reported. Other than SEM observation, the isolation between the electrodes, as shown in Figure 5.11, has been verified by electrical resistance measurement using a multimeter on two nanodiamond contact pads. It was found to be open (> 500 MΩ). The circuit schematic of the test setup is shown in Figure 6.1. Prior to emission characterization, the nanodiamond lateral device was subjected to in-situ tip conditioning, as mentioned in section 6.1.1. At room temperature (27°C) the lateral emitter showed the lowest threshold voltage of ~1 V and 0.95 mA of emission current at ~29 V (97 V/μm). Next, the substrate temperature has increased subsequently to get different sets of $I$-$V$ characteristics. It has been observed that the emission currents have increased to 0.98 mA at 100°C and 1 mA at 200°C at equivalent electric field. Figure 6.14 (a) shows the corresponding $I$-$V$ characteristics. The effective voltage has been obtained by subtracting voltage drop across $R_a$ from the applied voltage ($V_a$). The emission current from the structure was allowed to stabilize over a period at different electric fields. Figure 6.14 (b) shows the stable emission current of 5, 10 and 15 μA with little fluctuation at 8.31 V/μm, 9.86 V/μm and 11.21 V/μm respectively; a total of 3600 data points were collected by a computerized data acquisition system for every current value at every second.
Figure 6.14: (a) $I$-$V$ characteristics of the fabricated 140-finger diode with 300 nm anode-cathode distance at different temperature; (b) Stable emission current of 5, 10 and 15 µA with little fluctuation at 8.31 V/µm, 9.86 V/µm and 11.21 V/µm respectively.
Previously we have observed that the field emission from micron-gap ND lateral structures, Figures 5.6-5.7, is governed by F-N equation, Figure 6.3. However, the submicron gap structure showed a significant divergence from the F-N plot at higher field region (> ~20 V/μm), as shown in Figure 6.15 (a). So it has become extremely important to study other possible conduction mechanisms for the 300 nm gap structure. The expected $I-V$ relations for some of these conduction models are given in Table 6.1, indicating that a straight line can be obtained by plotting the appropriate mathematical form of these relations as abscissa and ordinate. The coefficient of determination ($r^2$) gives a direct measure of how well each model fits the experimental data [174]; provided the direction and value of the slope has been satisfied. As seen in the F-N plot at room temperature, Figure 6.15 (a); it can be divided in three distinct regions. In other words, each region of operation is dominated by different emission mechanisms. Data fitting into six different mathematical models suggest that at lower field ($E < 20$ V/μm), electron emission follows F-N equation which is then followed by space-charge limited conduction (SCLC) [175-176] at moderate field (20 V/μm < $E <$ 40 V/μm) and finally at higher field ($E > 40$ V/μm) thermal-field emission (TFE) [106] dominates. Figure 6.15 clearly represents those three different areas. Figure 6.16-6.18 shows the data fitting into each of the emission models mentioned in Table 1. Table 6.2 summaries the coefficient of determination ($r^2$) value of the analysis at different temperature and over the entire applied electric field.
Figure 6.15: Three different mechanisms dominate the electron emission. At lower field (E < 20 V/μm), it follows F-N equation which is then followed by space-charge limited conduction (SCLC) at moderate field (20 V/μm < E < 40 V/μm) and finally at higher field (E > 40 V/μm) thermal-field emission (TFE) model dominates.

Table 6.1: The most common mechanisms of electron conduction, their expected current-voltage relations and mathematical relations required for a straight line plot [106, 175-176].

<table>
<thead>
<tr>
<th>Type of conduction</th>
<th>Current-Voltage relation</th>
<th>Ordinate</th>
<th>Abscissa</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fowler-Nordheim (F-N)</td>
<td>$I \propto V^2 \exp(-a/V)$</td>
<td>$\ln(I/V^2)$</td>
<td>$1/V$</td>
<td>(-)ve</td>
</tr>
<tr>
<td>Space-charge Limited Current (SCLC)</td>
<td>$I \propto V^2$</td>
<td>$\ln(l)$</td>
<td>$\ln(V)$</td>
<td>(+)ve*</td>
</tr>
<tr>
<td>Thermal Field Emission (TFE)</td>
<td>$I \propto T^2 \exp[(bV^{1/2}-e\Phi_0)/kT]$</td>
<td>$\ln(l/t^2)$</td>
<td>$V^{1/2}$</td>
<td>(+)ve</td>
</tr>
<tr>
<td>Transition Region (TR)</td>
<td>$I \propto cV \exp[c'V^2-\Phi_1/kT]$</td>
<td>$\ln(l/V)$</td>
<td>$V^2$</td>
<td>(+)ve</td>
</tr>
<tr>
<td>Frenkel-Poole conduction (FP)</td>
<td>$I \propto V \sinh(bV^{1/2}/kT)$</td>
<td>$\sinh^{-1}(l/V)$</td>
<td>$V^{1/2}$</td>
<td>(+)ve</td>
</tr>
<tr>
<td>SCLC with FP effect</td>
<td>$I \propto V^2 \exp(b'V^{1/2}/kT)$</td>
<td>$\ln(l/V^2)$</td>
<td>$V^{1/2}$</td>
<td>(+)ve</td>
</tr>
</tbody>
</table>

where, $a = k_2 \Phi \pi^2d/\beta$ ; $k_2 = \text{constant}$; $b = (e/4\pi\varepsilon_0)^{1/2}$ ; $c = (kT/8\pi^3)^{1/2}$ ; $c' = \Theta/24(kT)^3$ ; $\Theta = 3t^2-2vt^3$ ; $t \& v = \text{parabolic function}$; $b' = 0.89e^{3/2}/(\pi\varepsilon_0)^{1/2}$

*Theoretical slope value = 2
Figure 6.16: Fitting the obtained data, upto 20 V/µm, in different mathematical models as mentioned in Table 6.1. (a) Field Emission, best $r^2$ value with negative slope; (b) Space-Charge Limited Conduction, slope value > 2; (c) Thermal Field Emission, poorer $r^2$ value; (d) Transition Region, not a straight line fit; (e) Frenkel-Poole conduction, not a straight line fit; (f) Space-Charge Limited Conduction with Frenkel-Poole effect, worst $r^2$ value.
Figure 6.17: Fitting the obtained data, from 20 V/µm to 40 V/µm, in different mathematical models as mentioned in Table 6.1. (a) Field Emission, mismatch in slope direction; (b) Space-Charge Limited Conduction, best $r^2$ value with slope ~2; (c) Thermal Field Emission, poorer $r^2$ value; (d) Transition Region, not a straight line fit; (e) Frenkel-Poole conduction, not a straight line fit; (f) Space-Charge Limited Conduction with Frenkel-Poole effect, mismatch in slope direction.
Figure 6.18: Fitting the obtained data, beyond 40 V/µm, in different mathematical models as mentioned in Table 6.1. (a) Field Emission, mismatch in slope direction; (b) Space-Charge Limited Conduction, slope value < 2; (c) Thermal Field Emission, best $r^2$ value; (d) Transition Region, not a straight line fit; (e) Frenkel-Poole conduction, mismatch in slope direction; (f) Space-Charge Limited Conduction with Frenkel-Poole effect, mismatch in slope direction.
Table 6.2 The coefficient of determination ($r^2$) for the straight lines of best fit for different data plots given at Table 1. (BOLD digits indicate best fit)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>FN</th>
<th>SCLC</th>
<th>TFE</th>
<th>TR</th>
<th>FP</th>
<th>SCLC+FP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 V/μm &lt; E &lt; 20V/μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
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<td>0.9927</td>
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<td>0.7645</td>
<td>0.6545</td>
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</tr>
<tr>
<td>200</td>
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<td>0.9598</td>
<td>0.7236</td>
<td>0.7099</td>
<td>0.9037</td>
</tr>
<tr>
<td>20 V/μm &lt; E &lt; 40V/μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
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<td>0.9657</td>
<td>0.9791</td>
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<td>0.9971</td>
<td>0.9673</td>
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<tr>
<td>200</td>
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<td>0.9975</td>
<td>0.9626</td>
<td>0.9843</td>
<td>0.991</td>
</tr>
<tr>
<td>E &gt; 40 V/μm</td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>27</td>
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<tr>
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<td>0.992</td>
<td>0.8961</td>
<td>0.9559</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

A possible explanation for the above observation can be made using a cascaded Metal-Insulator-Metal (MIM) energy band diagram for the n-type nanocrystalline diamond film [177-178] with localized shallow trap level lying below the conduction band, as shown in Figure 6.19. For simplicity, the figure has been drawn by assuming equal grain size throughout the film. It has also been assumed that the trap density ($N_t$) is quite uniformly distributed throughout the film and initially, the trap levels remain partially occupied [154] under thermal equilibrium without external biasing or any other forms of stimulation. At lower field, neglecting the effect of image charge, the cascaded MIM (metal sp$^2$ - insulator sp$^3$ - metal sp$^2$) structure, Figure 6.19 (a), forms a conduction
channel consists of sp² floating particles allowing electrons to tunnel through sp³-diamond [135,179-180]. A voltage drop, $\Delta V$ appears across each grain or sp³ particle. In this forward bias region, since the amount of excess majority carrier (electron) concentration in the conduction band is less, the trap level remains partially occupied which causes negligible effect on the tunneling electrons. Thus, the emission behavior obeys F-N model with negative slope, given by Eq. (3.17).

As the bias increases, the trap in the insulative layer (sp³) will capture more and thereby, immobilize most of the injected electrons [103]. The rate at which this capture process occurs is proportional to the density of electrons in the conduction band ($n$), the density of empty localized state, the probability that an electron passes near a state and is captured by the state [181]. Thus, the capture rate ($r$) can be written as:

$$r = n[N_s[1 - f(E)]]v_{th}\sigma_n$$  \hspace{1cm} (6.1)

where $f(E)$ is the probability that the traps are occupied. The product of electron thermal velocity ($v_{th}$) and capture cross section ($\sigma_n$) gives the probability that an electron is captured by a localized trap. Thus, during this period of forward bias, the data points start to divert from the F-N plot and a square law dependence is observed, which is also known as SCLC conduction [175-176,182-183]. At this point the trap level is completely filled with electrons. The MIM energy band diagram of this region of the forward bias is shown in Figure 6.19 (b). The voltage drop across each grain is higher than the previous case, i.e. $\Delta V' > \Delta V$. If the localized trap charge is an appreciable fraction of the total charge in the material, it applies a considerable repulsive force on the tunneling electrons. This lowers the drift mobility and further reduces the free carrier concentration in conduction band near the surface [154]. Thus the electron emission is limited by the
availability of the majority carriers at the surface. The SCLC expression is described in Eq. (3.25). Further, the theoretical slope of SCLC model is found to be ‘two’ by taking natural logarithm on both sides of the governing equation and comparing it with an equation of a straight line. In this region, the calculated slope value based on mathematical analysis of the experimental data justifies the physical phenomenon, Figure 6.15 (b). Also, it is believed that the image charge effect can be observed in this region of operation [7], which results in a small barrier height reduction ($\Delta \Phi_{B1}$). The barrier height can be calculated as mentioned earlier in Section 3.3.

As the bias has increased further, more electrons tunnel into vacuum from the emitting diamond surface. It is believed that, this high volume of electrons’ extraction from very small cathode tip area causes localized tip heating and has been explained earlier, in Section 3.3. Thus, by absorbing the available additional heat energy, the electrons tunnel into vacuum from higher energy state ($E_c + \Delta E$), as shown in Figure 6.19 (c). The emission current associated with this phenomenon is called Thermal-Field Emission (TFE), which is given by Eq. (3.19). The data fitting to the TFE model strongly support the physical explanation, as shown in Figure 6.15 (c) [184-185]. However, in the bulk, the electron transport is still limited by the space-charge and the voltage drop across each grain is higher than the previous two cases, i.e. $\Delta V'' > \Delta V' > \Delta V$. Also at this high field forward bias region, due to the increased image charge density, the barrier height reduces further ($\Delta \Phi_{B2}$), i.e. $\Delta \Phi_{B2} > \Delta \Phi_{B1}$. Furthermore, at high field region, an increase in substrate temperature by an external heater alters the total amount of charge in the conduction band of nanodiamond [186]. The additional thermal energy provides the trapped electrons the energy required to make a transition to the conduction band. This
explains the overall higher current observed with higher substrate temperature. Since the data points are normalized against applied temperature, the best fit lines almost coincide with each other, as shown in Figure 6.15 (c). However, the trapped electron concentration in the bulk doesn’t change due to continuous high volume of electron injection.
Figure 6.19: Energy band diagrams explain the three different emission mechanisms. With the higher applied field the Fermi level moves up, i.e. $qV < qV' < qV''$ and the voltage drops inside the film increases, i.e. $\Delta V < \Delta V' < \Delta V''$. Also, the barrier height lowering due to image charge at higher field is more, i.e. $\Delta \Phi_2 > \Delta \Phi_1$. (a) Electron emission governed by F-N at low field; (b) SCLC mechanism at moderate field; and (c) TFE at higher field; the additional energy $\Delta E$ is provided by internal tip heating.
Lateral 3-terminal array devices for performance enhancement – preliminary investigation for future work

An advance lateral emitter triode array can be developed in future to improve the performance of the existing triode leading to the transistor structure. It has been shown earlier in this research that the position of the electrodes play a critical role in determining the characteristics of the devices. The current scaling behavior of the nanodiamond lateral field emitters has been demonstrated by other researchers [86-87]. Increasing the cathode area and decreasing the interelectrode gap with uniformly micropatterned arrays of fingers will lower the operating electric field and voltage and enhance the current, resulting in increased transconductance suitable for achieving high signal gain from the triode device, when operated as an amplifier. Since, in the present structure the gate-cathode gap is in microns, a structural change in the lateral triode design is required to achieve an enhanced device characteristic.

Figure 6.20 shows the proposed change in the design of the electrodes. The monolithic structure is composed of an array of nanodiamond lateral finger-like emitters with metal gate pads at the same plane of the cathode and placed in between the fingers. All the gate pads are connected by a metal line placed on top of the box oxide. The device can be fabricated using the multilevel mixed lithography processes developed in this research. The nanodiamond cathode and anode can be micropatterned by optical lithography and reactive ion-etch. The gate electrode design can then be transferred onto the structure by electron-beam lithography followed by gate metal evaporation. During this research the process flow has been tried but the structure has not been successfully realized due to various factors. Figure 6.21 shows some of the SEM images captured
during processing. Figure 6.21 (c)-(d) shows the desired defect free area of the structure. However, strategically placed gate formation and metal line melting/peel-off were the two major concerns at that time. By fine tuning the process parameters and using more advanced dry etching process and tools, the realization the structure is highly possible. The distance between the anode and cathode can easily be varied by using proper mask, while the design and separation of the gate can be controlled by e-beam lithography. It is believed that, for anode-cathode distance (d) greater than 100 µm, transistor responses can be observed [86]. Further, to improve the electrical behavior, the metal lines in front of the emitting tips can be coated by insulating films which will reduce gate intercepted current.

![Figure 6.20: Proposed microstructure for the nanodiamond vacuum lateral emitter array three-terminal devices with 3-D gate.](image)

Another advance design can be proposed to achieve the transistor performance. The structure can be built from the current triode structure, as shown in Figure 6.22(b). The fabrication steps are very similar to the current structure, except an additional deep Si etching has to be performed to remove handling Si from the exposed trenches underneath the nanodiamond finger tips. This will allow moving the anode further away
from the cathode and a monolithic integration is possible. An effort has been made earlier in this research to etch the handling Si by ~80 µm using different methods, however due to various reasons the structure has not been achieved. 

**Figure 6.23** shows some of the SEM images of that effort. During the handling Si removal process, the active Si layer has also been removed, resulting cracks and bends in the diamond film. However, it is believed that by fine tuning the process parameters and using more advanced wet/dry etching processes and tools the realization of the structure is highly possible.

These nanodiamond lateral emitter device holds promise for future high-speed, high-frequency devices, switching systems and integrated circuits.
Figure 6.21: Few SEM images of the nanodiamond lateral emitter array vacuum three-terminal devices with 3-D gate. (a) After pattern transfer on nanodiamond and development; (b) Al coating to form metal lines (before ZEP520A lift-off); (c) Top view of a defect free area; (d) High-magnification inclined view; (e)-(f) Discontinuous metal line.
Figure 6.22: (a) Present design of a nanodiamond lateral multifinger field emission transistor; (b) Proposed microstructure for the nanodiamond lateral emitter array vacuum three-terminal devices with deeper anode.

Figure 6.23: SEM images of the nanodiamond lateral emitter array vacuum three-terminal devices shows that un-optimized handling Si etching resulted in cracks and bending in the diamond film.
CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

In this dissertation, nanocrystalline diamond has been developed as an applicable microelectronic material. Thin film fabrication processes have been identified for nitrogen-incorporated nanodiamond and integrated for device fabrication for utilization in vacuum field emission microelectronics (VFEM). The central idea of this development is to build and characterize monolithic submicron gap nanodiamond diode and multifinger triode devices in lateral emitter configuration, demonstrating enhanced electron emission characteristics at low turn-on voltage and electric field, high and stable emission current, operational temperature and radiation tolerance, making them potential candidates for realizing IC-compatible high-speed, high-power, extreme environment electronics, sensors, and nanoelectromechanical systems (NEMS). In this chapter, the findings from the experimental works are summarized followed by recommendations for future studies on lateral vacuum field emission device technology.

7.1 Nanodiamond thin film deposition for lateral device application

Before arriving to the actual device fabrication step, a controlled and consistent process techniques have been developed to deposit and micropattern nanocrystalline diamond thin films with properties favorable for vacuum field emission. Factors contributing to electron field emission from diamond were identified and a suitable form of the material offering these field enhancement factors realized. An effective growth-rate
control method has been obtained and implemented to deposit nanodiamond films with grain size less than 20 nm and lower surface roughness. Throughout the process CH₄/H₂/N₂ gas combination was used in a microwave plasma-enhanced chemical vapor deposition (MPCVD) system. Nitrogen, a suitable n-type dopant in nanocrystalline diamond films, has been incorporated successfully to realize high electrical conductivity at room temperature and thereby enhanced electron transport and electron emission properties. To apply nanodiamond as an efficient electron emitter, a micropatterning process was developed to derive geometrical field enhancement. The difficulty in patterning diamond films to build micron/submicron scale devices, has been resolved by the development of a highly selective and uniform nanodiamond etch process using an oxygen plasma reactive ion etch (RIE) technique. A high diamond etch rate of ~0.2 µm/min was achieved, and various electron field emitter micro/nanostructures of nanodiamond realized. Further, a process flow, compatible with conventional semiconductor integrated circuit (IC) process technology and integration, has been developed to fabricate nanodiamond lateral field emitter devices on a SOI wafer.

7.2 Nanodiamond lateral Micron-gap diode fabrication and characterization

Monolithic lateral micron gap diodes in chip-type architecture were consistently batch-processed on silicon-on-insulator (SOI) wafers using a single mask. The deposition and micropatterning techniques developed for nanodiamond were applied with precise lithography processing to yield this lateral device features. High aspect-ratio finger-like nanodiamond lateral emitters as cathode, with a nanodiamond edge structure as anode was achieved. These lateral diodes were designed with different numbers of emitters,
viz., 125, 325, 2000 and 9000, and with equal anode–cathode spacing, ranging from 4-10 µm by design. The emitters of 125-fingered diodes were put in a straight line, while 650-, 2340- and 9360-fingered diodes were composed of arrays in comb shape configurations, with each comb composed of 65 fingers. Upon completion of the fabrication step, several aspects of the field emission behavior of the nanodiamond lateral micron-gap diodes were investigated. A low turn-on voltage of 2.2 V had been achieved from the highest number of emitter structure. Further, a vacuum logic OR gate had been realized successfully for the first time using these lateral nanodiamond field emission diodes. The current scaling phenomenon had been proven to occur from the increase in emission area, i.e. the increase in number of potential emission sites in the cathode which directly affects the amplitude of the input signal required to maintain the same output logic for different pairs of logic OR gates. Furthermore, half-wave rectifier and envelope detector had been realized using one of the lateral nanodiamond field emission diodes which incorporate uniformly micropatterned nanodiamond lateral fingers in a comb-array structure at the cathode geometry. The approach demonstrates a new way of developing temperature- and radiation-tolerant logic circuits for integrated vacuum microelectronics.

7.3 Nanodiamond lateral multifinger triode fabrication and characterization

The same nanodiamond film was applied to build monolithic lateral vacuum triodes, with the lateral cathode, gate, and anode integrated on the same substrate. Advanced micropatterning techniques had been developed with precise lithography processing to yield this multifinger three-terminal structure for the first time. The anode can induce the electron emission and result in gate-modulated triode characteristics.
Taking the advantage of the device structure, the triode was operated in two modes of operation by interchanging the anode and gate. A large anode current ($I_a$) in the range of $27-40 \mu A$ was obtained with the transconductance parameter ($g_m$) calculated to be $\sim0.85 \mu S$, which is one of the highest reported for lateral device, especially with cathode-gate separation in microns. However, it was identified that the behavior of the lateral emitter device can be varied by altering the distances between the 3-terminals. Further, negligible gate leakage current attributes for reliable applications.

7.4 Nanodiamond lateral Submicron-gap diode fabrication and characterization

Reducing the inter-electrode spacing to the sub-micron range offers whole new and exciting opportunities for nanodiamond lateral device applications, such as lower operating voltage. After identifying a conductive nanodiamond film with smooth surface, work was conducted to incorporate electron beam lithography in the fabrication process and development of sub-micron gap nanodiamond lateral device technology. The micron gap lateral devices were limited by the resolution capability of traditional optical lithography. In this part of the work, 140-finger nanodiamond lateral vacuum diode with 300 nm anode-cathode distances was fabricated for the first time using multilevel-mixed-lithography, which includes optical and electron beam (EBL) lithography. Lower turn-on with higher stable emission current had been noticed. Further, the possible electron emission mechanism models were identified and verified by fitting the data to different emission models. It was observed that the diode’s region of operation is dominated by three different emission mechanisms. Data fitting into six different mathematical models suggest that at lower field, electron emission follows Fowler-Nordheim (F-N) equation.
which is then followed by space-charge limited conduction (SCLC) at moderate field and finally at higher field, thermal-field emission (TFE) dominates. The coefficient of determination ($r^2$) of the line of best fit, direction of the slope and its magnitude provided a direct measure of how well each model fits the experimental data. The behaviors have been successfully explained using electron energy band diagram.

The emission characteristics of the nanodiamond lateral devices were observed to be stable and repeatable over time. Low current fluctuations of less than 2% were observed in the $\mu$A emission current regime, which increased slightly at high currents (mA regime), operating in a vacuum condition of $\sim$10$^{-7}$ Torr. Further improvement in the current stability behavior of the diamond lateral emitters can be expected at very low pressure levels of 10$^{-9}$-10$^{-11}$ Torr. Nevertheless, the ability of the diamond emitter to function with good stability even at medium pressure levels was noticed. Overall, nanocrystalline diamond is a favorable material for electron field emission, with its properties well suited for use in a broad range of applications. With the emergence of nanodiamond, the utility of CVD diamond can now be vastly expanded to perpetuate the development of robust devices and products from the material. One such application is explored in this research in the form of lateral vacuum field emission microelectronics. The nanodiamond lateral emitter device represents a new category of diamond-based electronics, made possible from the development of a consistent microfabrication process capable of achieving desirable micro/nanostructures from the material. The potential demonstrated by the developed monolithic nanodiamond lateral field emitter diode and triode devices signify an efficient approach to accomplish rugged integrated circuits (ICs)
and electronic systems for terrestrial as well as space-based applications, offering much higher operational limits, in the near future.
7.5 Recommendations for future work

Advanced future research works on the nanodiamond lateral vacuum microelectronic devices, can be summarized in the form of following investigations:

(i) Design, simulate, fabricate, and characterize a nanodiamond lateral field emitter array triode with smaller cathode-gate distance and examine its transconductance and gain performance for high frequency amplifiers.

(ii) Design, simulate, fabricate, and characterize a nanodiamond lateral field emitter array transistor and examine its transconductance and gain performance for high frequency amplifiers.

(iii) Apply the diamond lateral field emitter diode and triode devices monolithically in integrated circuits (ICs) and build different digital logic gates, differential amplifiers, and complex electronic systems.

(iv) Develop a <100 nm interelectrode-gap diamond lateral field emission diode employing e-beam lithography patterning process and demonstrate ultra-low voltage device turn-on and operation.

(v) Pursue the reliability and high current potential shown by the nanodiamond lateral comb array emitter diode on high-k substrates for high power applications.

(vi) Develop an advanced package for the lateral device with high vacuum sealing for portable and commercial utilization of the device and technology.

(vii) Extend the temperature insensitivity and radiation hardness potential of the diamond lateral vacuum device into a packaged device and for custom applications such as space communication electronics and sensors.
(viii) Study the field emission response of the lateral vacuum device at very low (freezing) temperatures for cryogenic electronic circuits.

(ix) EBL writing is very time consuming; so further reduce the electrode area to allow for efficient use of EBL to pattern monolithic designs.
7.6 List of publications (to date)

The results of this proposed and related research have been published in journals and conferences as listed below.

Peer-reviewed journal articles:

   **N. Ghosh**, W.P. Kang, Y.M. Wong, and J.L. Davidson

   **N. Ghosh**, W. P. Kang, J. L. Davidson, and S. Raina

   **N. Ghosh**, W. P. Kang, and J. L. Davidson

4. “Nanodiamond Lateral Field Emission Vacuum Logic OR Gate”
   **N. Ghosh**, W. P. Kang, and J. L. Davidson
   Electronics letters 47 16 (2011) 926

5. “A Review of Recent Results on Diamond Vacuum Lateral Field Emission Device Operation in Radiation Environments”
   Microelectronic Engineering 88 (2011) 2924–2929

   **N. Ghosh**, W. P. Kang, and J. L. Davidson
   Electronics letters 47 21 (2011) 1187-1189

7. “Fabrication and Implementation of Nanodiamond Lateral Field Emission Diode for Logic OR Function”
   **N. Ghosh**, W. P. Kang, and J. L. Davidson
   Diamond and Related Materials 23 (2012) 120–124

8. “Nanostructure TEM Analysis of Diamond Cold Cathode Field Emitters”
   Diamond & Related Materials 22 (2012) 29–32
   N. Ghosh, W. P. Kang, J. L. Davidson, and S. Raina
   Journal of Vacuum Science and Technology B 30 (2012) 012201

Conference papers:

1. “Nano-Diamond Ridge Structure Emission Arrays Capped on Micropatterned Silicon Pillars”
   N. Ghosh, W. P. Kang, S. Raina, and J. L. Davidson

2. “Diamond Field Emission Arrays (DFEAs) for High-Power Free Electron Lasers”
   Technical Digest of the 22nd International Vacuum Nanoelectronics Conference (IVNC2009), pp. 203-204, July 20-24, 2009, Hamamatsu, Japan

3. “Fabrication and Implementation of Nanodiamond Lateral Field Emission Diode for Logic OR Function”
   N. Ghosh, W. P. Kang and J. L. Davidson
   4th International Conference on New Diamond and Nano Carbons (NDNC2010), May 16th-20th, 2010, Suzhou, China

4. “Carbon-derived Cold Cathodes for Vacuum Electronic Applications”
   Nanotech 2010 Conference and Expo, June 21-24, 2010, Anaheim, CA

5. “The effect of ballast resistor and field screening on electron emission of nanodiamond emitters fabricated on micropatterned silicon pillar arrays”
   N. Ghosh, W.P. Kang, S. Raina, and J. Davidson

6. “Resonant Tunneling and Extreme Brightness from Diamond Field Emitters and Carbon Nanotubes”
   - J.D. Jarvis, N. Ghosh, B.L. Ivanov, B.L. Kohler, J.L. Davidson, and C.A. Brau

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7. "Enhanced Supercapacitor Using 3-D CNT/MnO₂ Webs Hanging on Silicon Micro-Pillars"
   S. Raina, N. Ghosh, W. Kang, and J. Davidson
   220th ECS Meeting & Electrochemical Energy Summit, October 9-14, 2011, Boston, Massachusetts

8. “Devalopment of a miniaturized Smith-Purcell free-electron laser”
   J.D. Jarvis, N. Ghosh, B. Ivanov, J. Kohler, W.P. Kang, J.L. Davidson, and C.A. Brau
   23rd International Vacuum Nanoelectronics Conference (IVNC2010), 26-30 July 2010, Palo Alto, CA

   N. Ghosh, W. P. Kang, and J. L. Davidson
   21th European Conf. on Diamond, Diamond-like Materials, Carbon Nanotubes, and Nitrides, (Diamond 2010), P1.114, Sept 5-9, 2010, Budapest, Hungary

10. “Nanostructure Analysis of Diamond Cold-Cathode Field Emitter”
    EN-ThP17, 58th Annual American Vacuum Society Symposium, October 2011, Nashville, TN, USA

11. “Nanodiamond Vacuum Field Emission Integrated Devices”
    W.P. Kang, S.H. Hsu, N. Ghosh, J.L. Davidson, J.H. Huang, and D.V. Kerns
    25th International Vacuum Nanoelectronics Conference (IVNC), 9-13 July 2012, Jeju, South Korea

12. “Nanodiamond Microelectrode Array with Mesa Structure Fabricated for Bio-Analytical Applications”
    S. Raina, N. Ghosh, and W.P. Kang
    Pacific Rim Meeting (PRiME) on Electrochemical and Solid-state Science, 7-12 October 2012, Honolulu, Hawaii, USA
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