# UNIVERSITY OF CALIFORNIA Santa Barbara

# Indium Gallium Nitride/Gallium Nitride Vacuum Microelectronic Cold Cathodes: Piezoelectric Surface Barrier Lowering

A dissertation submitted in partial satisfaction of the requirements for the degree of

**Doctor of Philosophy** 

in

**Electrical & Computer Engineering** 

by

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# The dissertation of Robert D. Underwood is approved

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Dedicated to my parents,
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### **PUBLICATIONS**

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# **FIELDS OF STUDY**

Major Field: Solid State

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InGaN/GaN Field Emitters and the Piezoelectric Surface Barrier Lowering Professors Umesh Mishra and Steven DenBaars

#### **ABSTRACT**

Indium Gallium Nitride/Gallium Nitride Vacuum Microelectronic Cold Cathodes:
Piezoelectric Surface Barrier Lowering

by

### Robert Douglas Underwood

Vacuum microelectronic devices are electronic devices fabricated using microelectronic processing and using vacuum as a transport medium. The electron velocity in vacuum can be larger than in solid state, which allows higher frequency operation of vacuum devices compared to solid-state devices. The effectiveness of vacuum microelectronic devices relies on the realization of an efficient source of electrons supplied to the vacuum. Cold cathodes do not rely on thermal energy for the emission of electrons into vacuum. Cold cathodes based on field emission are the most common types of vacuum microelectronic cold cathode because they have a very high efficiency and high current density electron emission. Materials used to fabricate field emitters must have the properties of high electron concentration, low surface reactivity, resistance to sputtering by ions, high thermal conductivity, and a method of fabrication of uniform arrays of field emitters. The III-V nitride semiconductors possess these material properties and uniform arrays of GaN field emitter pyramids have been produced by selective-area, self-limited metalorganic chemical vapor deposition.

The first GaN field emitter arrays were fabricated and measured. Emission currents as large as  $82~\mu A$  at 1100~V from 245,000 pyramids have been realized using an external anode, separated by 0.25~mm, to apply voltage bias. The operation voltage was reduced by the development of an integrated anode structure. The anode-cathode separation achievable with the integrated anode was in the

range of 0.5-2.4  $\mu$ m. The turn-on voltages of these devices were reduced to the range of 175-435 V.

The operation voltage of field emitter cathodes is related to the surface energy barrier, which for *n*-type semiconductors is the electron affinity. A new method to reduce the effective electron affinity using a piezoelectric dipole in an InGaN/GaN heterostructure has been proposed and tested. The piezoelectric field produced in the strained InGaN layer on a GaN pyramid produces a dipole that counteracts the surface barrier. The reduced barrier is characterized by defining an effective electron affinity. Emission results of InGaN/GaN field emitter arrays have shown a reduced electron affinity as low as 1.0 eV when compared to the electron affinity of GaN (3.5eV).

# **TABLE OF CONTENTS**

Chapter 1 I	ntroduction	1
(1.1)	Cold Cathodes	1
(1.2)	Cold Cathode Types	
(1.3)	Planar Cold Cathodes vs. Field Emitters	5
(1.4)	Field Emitter Basics	
(1.5)	Materials Issues for Field Emitters	8
(1.6)	Nitride-based Field Emitters	10
(1.7)	Vacuum Microelectronics & Applications	13
(1.8)	References	
Chapter 2 F	Field Emission	. 31
(2.1)	History and Background	
(2.2)	The Band Diagram	
(2.3)	The Supply Function	
(2.4)	The Transmission Function	
(2.5)	Image Force Correction to the Transmission Function	
(2.6)	A Fowler-Nordheim Equation for <i>n</i> -type Wide Band Gap	
, ,	Semiconductors	
(2.7)	Field Enhancement	
(2.8)	Current-Voltage Characteristic & the Fowler-Nordheim Plot	t
(2.0)		
(2.9)	Engineering Considerations and Refinements to Field Emiss	sion
(2.10)	Theory	
(2.10)	References	55
Chapter 3 C	SaN Field Emitter Development	. 66
(3.1)	Introduction	66
(3.2)	GaN Field Emitter Growth	
(3.3)	GaN FEAs with an External Anode	72
(3.4)	GaN Field Emitter Arrays with Integrated Anode	83
(3.5)	References	
Chapter 4 P	elezoelectric Surface Barrier Lowering in InGaN/GaN	1
•	ield Emitter Arrays	
(4.1)	Introduction.	
(4.2)	Surface Barrier Lowering Using Cesium	
(4.3)	Piezoelectric Effect In Nitride Semiconductors	
(4.4)		

(4.5)	InGaN/GaN Field Emitter Results115	
(4.6)	References124	
Chapter 5	Conclusion	
(5.1)	Summary of Accomplishments131	
(5.2)	Suggestions for Future Work133	
(5.3)	References136	
Appendix A	Exact Transmission Function for the Triangular	
Barri	er137	
Appendix B	Physical Constants of Wurtzite GaN and InN 143	
Appendix C	Example Process Sheet for FEA with an Integrated Anode	
Appendix D	Derivation of Piezoelectric Polarization in the c-directio for Dihexagonal Polar Crystal Class	n
Bibliography	of Field Emission and Vacuum Microelectronics Literature	
Index	293	

# LIST OF FIGURES AND TABLES

# **FIGURES**

Figure 1.1. Cross-sectional schematic of Spindt-type field emitter array in a triode-like configuration. An extraction electrode (striped) surrounds the field emitter tips (black). The field created by the voltage applied to the extraction electrode, $V_g$ , modulates the electron emission. If the anode voltage, $V_a$ , is sufficiently larger than the extraction voltage, the electrons will be accelerated toward and collected by the anode.	14
Figure 1.2. Schematic diagram of flat-panel display based on field emission arrays. The field emitters are connected to the column electrodes and the emission current is switched on and off by the row electrodes. In the simplest design, the anode-cathode separation is made small enough so that the electrons strike the phosphors above the array without the need for focusing electrodes.	16
Figure 1.3. Current state of technology for various vacuum and solid-state devices. Reprinted with permission from Figure 3 of V.L. Granatstein, R.K. Parker, and C.M. Armstrong, <i>Proceedings of the IEEE</i> , vol. 87, no. 5, pp. 702-715, 1999.	18
Figure 2.1. Schematic of field emission microscope. (a) tungsten loop with tungsten tip field emitter, (b) glass vacuum envelope, (c) phosphor screen, (d) electron trajectories from cathode to anode. The separation of the tip from the screen is x.	33
Figure 2.2. Band diagrams of (a) metallic field emitter and (b) <i>n</i> -type semiconductor field emitter. The vacuum level is shown with a field applied and the image lowering is shown by a dotted line near the apex of the barrier.	35
Figure 2.3. Schematic of a triangular barrier for calculation of transmission probability	38
Figure 2.4. Illustration of field enhancement for hemisphere on plane. The dotted lines indicate the equipotentials and the compression of the near the sphere represents the field enhancement $(F = -\nabla \Phi, \text{ where } \Phi \text{ is the potential})$ .	45
Figure 2.5. Relative current fluctuation versus the electron affinity of a field emitter. The full dependence (equation 2.31) is given by the solid line and an approximation (equation 2.30) is given by the dashed line. The approximation fails below about 2 eV	50

Figure 3.1. SEM picture of the first UCSB MOCVD GaN pyramids grown by selective area epitaxial regrowth. The dark gray regions are the SiO <sub>2</sub> mask and the light gray is the GaN.	68
Figure 3.2. Comparison of the overgrowth mode and self-limited growth mode of GaN FEA pyramids.	70
Figure 3.3. SEM micrograph of two GaN pyramid arrays on the same sample with different levels of completion. The array on the left side is 7.5 $\mu$ m base width pyramids on 8.5 $\mu$ m centers and the array on the right side is 5 $\mu$ m base width pyramids on 8.5 $\mu$ m centers.	73
Figure 3.4. SEM micrograph of an array of completed, self-limited GaN pyramids. The inset shows a close-up image of a pyramid top with a radius of about 70 nm.	74
Figure 3.5. Schematic of UHV sample holder. The spacers are used to vary the anode-cathode separation. Au wire bonds connect the sample contacts to the Cu pins on the holder, which are attached by wires to the system feedthroughs.	76
Figure 3.6. Schematic of electrical circuit used to measure the field emission from GaN FEAs. The resistor is used to protect the picoammeter and the arrays from vacuum arcs.	77
Figure 3.7. First GaN field emission measurements (left) and Fowler-Nordheim plot (right).	78
Figure 3.8. Field emission I-V (left) and F-N plot (right) for an array of 5 μm pyramids on 11 μm centers. The F-N plot is shown with a linear fit over several orders of magnitude indicating field emission	79
Figure 3.9.(a)-(i) Process flow of integrated anode field emission array	84
Figure 3.10. Optical microscope top-view of suite of GaN FEAs. The number of tips in the device array is indicated in parantheses. Each array has its own cathode and anode contact pads. The airbridges are connected to the anode contact pads and span the GaN FEAs	86
Figure 3.11. SEM micrograph of completed air bridge anode.	87
Figure 3.12. (a) <i>I-V</i> characteristic of the GaN FEAs listed in Table 3.3. (b) F-N plots for data given in (a) with weighted least squares fits	89
Figure 3.13. Field enhancement as a function of anode-cathode separation and fit.	90
Figure 3.14. SEM image of anode damage caused by a vacuum arc. The field emitter tip shown on the mesa finger appears undamaged	91

Figure 4.1. (a) Energy diagram of a separate metal surface and Cs atom with common vacuum level. The line on the Cs atom indicates the top-filled electron level. (b) As the Cs atom adsorbs on the metal surface, the Cs atom ionizes and the electron is transferred to the conduction band of the metal. The result is a surface dipole that counteracts the metal work function.	99
Figure 4.2. Tensors for evaluation of piezoelectric effects for crystals with 6mm symmetry.	101
Figure 4.3. Illustration of the lattice dimension changes representative of pseudomorphic growth.	102
Figure 4.4. Normalized piezoelectric charge versus polar angle simulated using ABAQUS <sup>TM</sup> finite element program	105
Figure 4.5. Schematic conduction band diagram of InGaN/GaN field emitter. Electrons travel ballistically across the InGaN layer and, thus, effectively tunnel from the maximum of the GaN conduction band edge at the GaN/InGaN interface. The vacuum level is shown for an applied bias.	106
Figure 4.6. Strain in pseudomorphic In <sub>x</sub> GaN layer as a function of In mole fraction, x.	108
Figure 4.7. Calculated band diagram of InGaN/GaN field emitters. The growth direction is to the right. The InGaN layer can identified by the downward sloping region directly in front of the vacuum region. The In concentration is 5% and the InGaN thickness is varied from 5 to 100 nm (a)-(e). In this figure, the Fermi level is at 0 eV	109
Figure 4.8. Calculated effective electron affinity of InGaN/GaN field emitters as a function of InGaN thickness with the In mole fraction as a parameter.	111
Figure 4.9. Simple estimation of the critical thickness of InGaN on GaN	112
Figure 4.10. Effect of field penetration on the conduction band of the InGaN/GaN FEAs demonstrating the limitation of the effective electron affinity model. (a) 5% In, 50 Å InGaN. (b) 5% In, 500 Å. The numbers next to the profiles indicate the applied electric field in units of V/nm.	113
Figure 4.11. Variation of the pyramid base width for samples of differing InGaN layer thickness	116
Figure 4.12. Current-voltage characteristics of In <sub>0.05</sub> GaN/GaN FEAs	117

Figure 4.13. Fowler-Nordheim plots of emission data given in Figure 4.12	118
Figure 4.14. Experimental effective electron affinity of the InGaN/GaN FEAs (dashed line with hexagonal symbols) compared the theoretical effective electron affinities.	121
Figure 4.15. Experimental turn-on voltage (solid) and the theoretical turn-on voltages (dashed) calculated for 5 and 10% In composition InGaN/GaN FEAs. Also plotted on the right side, are two points calculated assuming the 5 and 10% InGaN layers are relaxed	122
Figure 4.16. Picture of curve tracer screen with highest emission current observed for InGaN/GaN FEAs with 500 Å InGaN	123
Figure 4.17. InGaN/GaN FEA lifetime test.	124
Figure 5.1. Comparison of the band diagrams of the PDBEE and the suggested piezoelectric planar electron emitter. The PDBEE band diagram is taken from [1].	135
Figure A.1. Potential energy diagram of triangular barrier for the problem of electron tunneling through vacuum between two metals.	137
Figure A.2. Plot of the exact (solid) and WKB approximation (dashed) transmission probabilities for the triangular barrier problem. $(F=10^9 \text{ V/m}, C=3.5 \text{ eV}, \phi_{ma}=4.5 \text{ eV}, d=1 \text{ mm})$	140
Figure A.3. Ratio of WKB approximation to exact solution for energies below the barrier.	141
TABLES	
Table 1.1. Survey of Cold Cathode Types	3
Table 1.2. Summary of Advantages and Disadvantages of Field Emitters and Planar Emitters.	6
Table 1.3. Some Applications of Cold Cathodes and Field Emitters	20
Table 3.1. Selective Area, Self-limited GaN Growth Parameters.	71
Table 3.2. Comparison of Plane-Parallel Turn-on Fields of GaN FEAs	81
Table 3.3. Measured Parameters of GaN FEAs with Integrated Anode	88
Table 4.1. Measured Anode-Cathode Separations and Theoretical Field Enhancement Factors (k=1.77).	119
Table 4.2. Measured and Calculated Data from InGaN/GaN FEAs	.120

Table B.2. Selected Physical Constants	143
Table B.3. Piezoelectric Constants.	143

# Chapter One

# Introduction

"...new or improved electron sources have frequently contributed to advances in both basic science and electronics, the industry in which free electrons are employed."—W.W. Dolan and W.P. Dyke, "Temperature-and-Field Emission of Electrons from Metals," *The Physical Review*, vol. 95, pp. 327-332, 1954.

### (1.1) Cold Cathodes

Electron sources of high intensity and high efficiency are desirable for a variety of applications. Cathodes with high current density and high transconductance are required for microwave power vacuum tubes. For emissive displays, highly efficient electron sources allow portable operation of displays with high brightness. The most common electron source is the thermionic cathode in which a material is heated to a high temperature. The electron population in the material is raised in energy to the point that a small fraction of electrons has sufficient energy to surmount the work function barrier. Thermionic cathodes provide stable emission currents over long lifetimes and can provide current densities that are adequate for many applications in power vacuum tubes and information displays such as the ubiquitous cathode-ray tube (CRT). Because research and development of macroscopic thermionic cathodes is for the most part mature, designers of systems in which these cathodes meet the performance specifications can reference a substantial literature base.

Thermionic cathodes do have several limitations and disadvantages that as yet have been unsolved. The disadvantages of heating the cathode are the wasted energy and the relatively large minimum separation that can be reliably achieved between the cathode and current modulating electrodes. Thus for microwave power tubes, in order to achieve high operating frequency, long drift regions that add size, weight, and focusing complexity are required. For displays, thermionic cathodes waste too much energy for portable applications, and display tubes based on a single heated cathode require substantial depth to allow scanning of the electron

beam. Finally, while thermionic cathodes provide adequate current densities for many applications, other applications, such as high-power vacuum tubes and high definition television, require higher current densities. The most advanced thermionic cathodes can produce current densities on the order of 100 A/cm² but suffer from reproducibility problems.[1] The most common thermionic cathodes generally operate in the range of 0.5 A/cm².[2] Maximum current densities from thermionic cathodes are ultimately limited by the reliability problems related to operating cathodes at temperatures where significant evaporation of the cathode material occurs.

Cold cathodes, as the name implies, do not rely on the heating of a material to emit electrons over the vacuum barrier.[3] Consequently, thermal issues are not the prime limitation on the maximum current density achievable from cold cathodes and, generally, higher current densities are theoretically possible. The lack of heating also obviates the need for complex separation of the cathode from other devices lending cold cathodes to denser integration than achievable with thermionic cathodes and also decreasing the demands on the cathode power supply. Finally, since no energy is wasted in heating the cathode, a higher efficiency is obtainable. There are several types of cold cathodes and a survey of the varieties is given in Table 1.1. Cold cathodes can be classified based on their geometry. Field emitters rely on field enhancement created by sharp points or edges to facilitate tunneling of electrons. Planar cold cathodes fall into a large variety of types but in general do not rely on field enhancement for their operation.

# (1.2) Cold Cathode Types

The most common type of microelectronic cold cathode is the field emitter. Field emitters operate by tunneling of electrons from a material into vacuum as the result of an impressed electric field.[4] The high electric field serves to thin the vacuum barrier and allow electrons to tunnel. As the field emission process is dependent on a high electric field at the surface, a sharp, tip-like geometry is

Table 1.1. Survey of Cold Cathode Types.

Type of Cold Cathode	Operating Principle	Common Materials	Cesium Required
Field Emitter	Enhancement of electric field allows tunneling.	Mo, W, Si, diamond	No
Metal-Insulator-Metal (MIM) Tunnel Emitter	Electrons tunnel through insulator into vacuum level of top metal.	Insulator: SiO <sub>2</sub> and Al <sub>2</sub> O <sub>3</sub>	Yes
Negative Electron Affinity (NEA)	Vacuum level is below the bulk conduction band edge.	diamond, AlN	GaAs, Silicon: Yes diamond: No
Photocathodes	Photons excite electrons above the vacuum barrier. In an optoelectronic cold cathode, the photon source is integrated with the cathode.	LaB <sub>6</sub> AlGaAs	No
Planar-Doped Barrier Electron Emitter	Hot electrons are emitted over triangular barrier and gain energy to overcome surface barrier.	AlGaAs/GaAs	Yes
Schottky Barrier Emitter	Forward biased n-type Schottky diode with metal work function lower than the Schottky barrier height.	ZnS:Pd	Yes
• Forward-biased <i>p-n</i> Junction	Vacuum acts as collector of <i>npn</i> transistor and requires the <i>p</i> -type surface to have NEA.	Si, GaAs	Yes
<ul> <li>Reversed-biased p-n     Junction     (includes Avalanche     Electron Emitter)</li> </ul>	Hot electrons created in depletion region accelerated to energy above the vacuum level.	SiC, Si	Yes
Ferroelectric     Cathodes	Rapidly changing electric field is applied to ferroelectric ceramic.	PLZT (lead- lathanum-zirconium- titanate)	No
Secondary emission	Malter-effect or RF electron trajectories create self-sustaining discharge.	MgO	No

necessary. Field emission wastes no energy in the emission process and thus can approach 100% efficiency.

There are many other types of cold cathodes; most have a planar emitting surface and use a variety of principles for electron emission. A full discussion of these cathodes is outside the scope of this work but a list of the major types and a simple description of their operating principles is given for completeness. First, the negative electron affinity emitter, can emit electrons at very low electric fields because the surface vacuum level is below the bulk conduction band edge and, consequently, there is no barrier for electron emission and no need for field enhancement.[5],[6] The externally applied field penetrates the material and accelerates the electrons to the surface for emission. Another type of planar cold cathode is the tunnel emitter based on a metal-insulator-metal structure.[7-11] When the top metal is positively biased, electrons can tunnel from the bottom metal through the thin insulator and into the vacuum level of the top metal. Next, a subset of the planar cold cathodes, including planar-doped barrier electron emitter[12] and reverse-biased p-n junction cathodes[13-16], emit hot electrons. Conduction band electrons gain kinetic energy in the high field regions of the cathode and a fraction of those electrons acquire energies higher than the surface barrier. Another type of planar cathode is the forward-biased junction emitters (Schottky and p-n junction) in which electrons are injected into a surface region that has a very low surface barrier.[17-19] Photocathodes use photonic energy to impart electrons with enough energy to be emitted into vacuum;[20-22] optoelectronic cathodes are photocathodes that have the photon source integrated with the cathode.[23, 24] Ferroelectric cathodes rely on the application of alternating fields on a film of ferroelectric ceramic, which produces an electron emission from one face of the ceramic.[25] The final common type of cold cathode is based on secondary electron emission. In fact, the most common type of cold cathode currently in use in vacuum tube technology is the secondary electron emitter.[26] Materials with secondary electron yield greater than one can exhibit an amplification of electron emission (known as the Malter effect)[27] or radio frequency electron trajectories

in vacuum tubes such as klystrons can be used to create large secondary emission currents.

A perusal of Table 1.1 indicates that most of the planar cold cathodes require an emission surface treated with cesium or cesium and oxygen in order to operate at reasonable efficiencies or provide reasonable current densities. Cesium affects these devices by creating a dipole at the surface of the material, which lowers the surface energy barrier.[5] The effect can be quite significant, lowering the energy barrier to less than 1 eV in some cases. There are several problems associated with the use of cesium in vacuum devices.[28] First, cesium will react with the residual gases in vacuum conditions above 10<sup>-11</sup> Torr and will lose its work function-lowering properties with time. Secondly, even in applications that can support such ultra-high vacuum (UHV) requirements, the fields at the surface of the device are large enough to cause the electromigration of the highly mobile cesium atoms. If there is no system to replenish the cesium, the emission area will be left bare and the efficiency of the device will drop. Finally, cesium moving about a vacuum device may compromise the voltage-standoff capability of the insulators separating the device components. In conclusion, long lifetime, stable vacuum device operation may require a cathode devoid of cesium.

# (1.3) Planar Cold Cathodes vs. Field Emitters

Planar cathodes and field emitters both have strengths and weaknesses as cold cathodes. Some of the weaknesses are inherent to the structures while others may be overcome with improved technology or advanced materials. Planar cold cathodes have the advantage of producing a uniform current density emission and the methods of fabricating them are similar to standard integrated circuit processing. The disadvantages of planar cold cathodes are that most require cesiation to achieve an acceptable efficiency as discussed in the previous section and the devices must be operated in an UHV environment. The advantages of field emitters are that they operate at high efficiency and without the need for cesiation.

Another advantage of field emitters are that many of them can be put in parallel (the current record is  $2.5 \times 10^9$  cm<sup>-2</sup>)[29] thus increasing the maximum current available. Field emitters are not as affected by ionizing radiation as planar emitters making them suitable for use in hostile environments such as space or nuclear power plants. Weaknesses of field emitters are that they inherently produce a conical beam because of the radial direction of the electric field surrounding the emitter and the typically poor uniformity of arrays of field emitters produces non-uniform current density. Other significant problems with field emitters are the short lifetime, and poor reliability, and non-standard fabrication steps; however, most of these issues have been resolved with advances in materials, packaging, and proper design of field emission cathodes. Ultimately, the potential for high current density and high efficiency has made field emitters the most widely researched cold cathode.

Table 1.2. Summary of Advantages and Disadvantages of Field Emitters and Planar Emitters.

	Field Emitters	Planar Emitters
Advantages	<ul> <li>High efficiency (near 100%)</li> <li>High current density (1-2 kA/cm²)</li> <li>No cesium</li> </ul>	<ul> <li>Compatible with IC processing</li> <li>High current density (8 kA/cm²)</li> <li>Uniform current density beam</li> </ul>
		• Low bias voltage (<10 V)
Disadvantages	High bias voltage (>10 V)	Cesium necessary
	Non-uniform beam	Sensitive to vacuum quality (if cesiated)
	Uniformity over array poor	Low efficiency
	Lifetime sensitive to vacuum quality	(~1.5%)

### (1.4) Field Emitter Basics

A field emitter, in its most basic form, consists of a sharp, point-like structure. When the field emitter is sufficiently negatively biased with respect to another electrode separated from the emitter by vacuum, a current flows through the space. The charge is emitted from the cathode into vacuum because the normal potential barrier that exists at the surface of a material has been thinned by the application of the electric field. The thinning of the barrier allows electrons to tunnel from the material into vacuum although the electrons do not have sufficient energy to go over the barrier. Tunneling behavior can not be described by classical mechanics and one must turn to quantum mechanics for a description of the physical process.[4]

Some details of field emission theory will be covered in Chapter 2, but as an introduction, there are three important parameters describing a field emitter: the field enhancement factor, the emission area, and the work function or electron affinity. The field enhancement factor describes the factor by which the geometry of the emitter has increased the field at the surface of the emitter over that which would be produced by a plane-parallel geometry. The field enhancement can be increased by reducing the radius of curvature and increasing the height-to-width ratio (commonly called the aspect ratio) of the emitter. Field emitters with tips having single or few atoms have been produced. A high field enhancement will lower the applied voltage necessary for emission. The second factor, the emission area, is determined by the geometry, and in general, the emission area decreases as field enhancement is increased. This means that an optimum radius of curvature may not be the sharpest possible emitter but involves a trade-off of emission area and field enhancement. One method to increase emission area without taking a large field enhancement penalty is to produce an array of field emitters. The current from each pyramid will add in parallel. Since the presence of neighboring emitters will decrease the field enhancement, an optimization procedure is required here as well.

The final parameter listed above, the height of the barrier that the electrons must tunnel through, contributes to determining the operating voltage of the field emitter. In metals, this barrier is the metallic work function which is defined as the amount of energy necessary to remove an electron from the Fermi level in the metal and move it to a position infinitely far from the metal (the vacuum level). In an *n*-type semiconductor, this barrier is the electron affinity, which is defined as the energy difference from the conduction band minimum to the vacuum level. For a *p*-type semiconductor, where the electrons are emitted from the valence band, the barrier would be the energy band gap plus the electron affinity. The emitter material determines these energy barriers. Using cesium can lower the surface barrier but the use of cesium involves many disadvantages as discussed above.

# (1.5) Materials Issues for Field Emitters

The ideal material for a field emitter would have high electron concentration, high thermal conductivity, and would be hard and non-reactive in the vacuum environment. High electron concentration is necessary for high emission current and most field emission research has focussed on metal as the emitter material for this very reason. A secondary concern for achieving high current density is the thermal conductivity of the emitter material. The current densities in the microscopic tips can become so high that melting or fracturing of the emitter is possible. A material with a high thermal conductivity can source more current with less temperature rise because the heat generated can dissipate into the bulk from the tip. Finally, lifetime of field emitters is determined by the reactivity and mechanical strength of the emitter material. Reaction of the surface of the emitter with the residual gas in the vacuum environment generally tends to increase the work function of the emitter with time. Emitters made from reactive materials also suffer from increased noise as residual gas atoms adsorb and

chemisorb on the surface and momentarily perturb the surface work function. In addition, operation of the cathode will cause the production of positive ions from collisions of electrons with the residual gas. These ions are accelerated toward the cathode and a fraction of them will impinge on the field emitter. Some of the ions will have sufficient energy to cause sputter erosion of the tip. This may tend to blunt or sharpen the tip, but both actions are detrimental to the reliability and lifetime of the tips. The blunting action will decrease the field enhancement and will decrease current. On the other hand, sharpening of the emitter may continue to a point where the current increases and the emitter fails from thermal destruction. Attempts to avoid this problem by ensuring a negligible residual gas presence require use of an UHV environment of 10<sup>-11</sup> Torr or better; this vacuum level is not acceptable for most applications and, in any case, is difficult and expensive to maintain. The threat of sputter damage can be significantly reduced by lowering the emission voltage. The most effective way to reduce the emitter voltage is to sharpen the emitter and decrease the separation of the emitter from the extraction electrode. Efforts to miniaturize the field emitter helped lead to the development of vacuum microelectronics, which will be discussed in section (1.7).

Nearly every metal on the periodic table has been tested for field emission. Refractory metals have received the most attention due to their high melting points. Early field emitters were fabricated from the ends of drawn wires of tungsten.[30-34] The high melting point of tungsten allowed the emitters to be heated to very high temperature which facilitated vacuum desorption of contaminants for cleaning of the emitters. In addition, field-enhanced vacuum evaporation was used to sharpen the wire ends and thereby lower the emission voltage. Metals can provide a large electron supply for emission but suffer from high reactivity with residual gases in the vacuum and the malleable nature of metals presents a poor resistance to sputter damage and deformation.

A large variety of non-metals has been proposed as candidates for field emitters. Materials such as carbon (as graphite, amorphous carbon, nanotubes and diamond) and metallic carbides have been considered for their low reactivity and high hardness.[35-38] Semiconductors are another important class of field emission materials. Although possessing much fewer conduction electrons than metals, semiconductors have the advantage of possible integration and the leveraging of microelectronic semiconductor processing methods to the fabrication of smaller emitter structures. Of course, silicon has received the most attention as a field emitter cathode due to the economies of scale and advanced fabrication technologies that exist for silicon-based electronics.[39-44] Processing involving thermal oxidation of silicon field emitters has allowed the production of emitters of extremely small points.[45] The most recent class of semiconductors to receive attention for field emission research has been the wide band gap semiconductors. Materials like diamond and III-V compound semiconductors have some potentially advantageous properties for field emission that will be introduced next.

#### (1.6) Nitride-based Field Emitters

Paths to improving field emitter performance have followed improvements in fabrication methods and materials. Lowered voltages of operation have been achieved by increasing the sharpness of emitters and shrinking the distances between the extraction electrodes and emitters. The operating voltage can also been reduced by using materials with smaller surface barriers. In particular, a very large effort over the past decade has targeted diamond and diamond-like carbon as a material for field emission cathodes.[46-51] The initial reason for pursuing diamond was that researchers discovered that certain surfaces of diamond exhibited a negative electron affinity.[52] This means that the bulk conduction level of diamond is above the vacuum level and, consequently, no barrier for electron emission from the conduction band exists. This promised the potential for high emission currents at low voltage. Diamond also has other advantages, like low

reactivity, high hardness, and high thermal conductivity, which make it attractive for possible use in field emitter cathodes.

The primary drawback of diamond is that it is an insulator. Thus, while electrons in the conduction band see a very small barrier to emission, there are not enough electrons in the conduction band for large emission currents. Attempts to dope diamond with electron donors have met with limited success.[53] There are divers theories trying to explain observed field emission from diamond.[54] theory contends that field emission from diamond is controlled mainly by the interface of the diamond with the substrate it is deposited on or on the material quality of the diamond itself. In other words, the electrons are field emitted from the substrate into the conduction band of the diamond, are accelerated through the diamond film by the penetrating electric field, and are emitted over the small surface barrier of the diamond. Since some fraction of the electrons will be scattered while passing through the diamond film, the final emission results for diamond cathodes may not be much better than the emission from the bare substrate. Efforts to dope diamond or provide a better contact to supply electrons to the conduction band of diamond are continuing. If they should prove successful, the low electron affinity, low reactivity with residual gases, and sputter-resistant surface, may propel diamond to become the dominant material for field emitters. Even with a lack of electron donor, some encouraging results for diamond based field emitters have been obtained although the mechanisms for achieving these results are not yet fully understood.[55, 56]

The nitride-based semiconductors, GaN, AlN, and InN have much in common with diamond. They have large energy gap, low reactivity, and high surface hardness. In addition, GaN, and alloys of AlGaN and InGaN have shown the ability to be doped both *n*-type and *p*-type. AlN, with the largest band gap of the nitride semiconductors, even shows a negative electron affinity similar to diamond. Over the past decade, with the improvement in the epitaxial growth of

nitrides, a large effort to develop nitride-based electronics and optoelectronics has grown.[57, 58] Short-wavelength light-emitting diodes and lasers (from the blue to the UV regions) have been demonstrated and improved.[59-62] High power and high temperature electronics based on nitride transistors are also under development and are setting records for solid-state, single-device microwave power capability.[63, 64]

For field emission cathodes, the important properties of the nitride semiconductors are the low reactivity, high surface hardness, high electron concentration, and relatively low electron affinity. The low reactivity and high hardness should contribute to lower noise and longer device lifetime. The electron concentration achievable is similar to that found in other semiconductors used for field emission, such as silicon, but all semiconductors will suffer in comparison to metals with respect to electron concentration. The work functions of tungsten and molybdenum, which are the most commonly used metals for field emitters, are about 4.5 eV. Metals with lower work functions have shown lower operating voltages but also much reduced lifetime due to a generally higher reactivity with the residual gases in the vacuum. GaN has an electron affinity reported between 2.9 and 4.5 eV. While this is somewhat lower than the commonly used metals and semiconductors, it is not, by itself, a significant factor for lowering the operating voltage of nitride-based emitters with respect to the other materials.

Another important property of the III-nitride semiconductors is that they possess large piezoelectric constants.[65] The piezoelectric effect describes the production of an electric field caused by an applied mechanical stress and, conversely, the mechanical stress produced by an applied electric field. Epitaxial growth of a thin InGaN layer on GaN layer results in the InGaN being strained. This built-in strain produces an electric field in the growth direction. This electric field modifies the energy band profile in the semiconductor. For the case of InGaN grown on top of GaN, this modification results in a lower effective electron affinity

of the combined semiconductor layers. The bulk of this dissertation will describe the development of GaN-based field emitters and the lowering of the effective electron affinity of GaN field emitters by using the piezoelectric effect in a thin, strained InGaN film grown on top of GaN field emitter pyramids.

# (1.7) Vacuum Microelectronics & Applications

The study of field emission has been ongoing for more than a century, but most of the work on field emitters since the late 1960s has involved efforts to miniaturize field emitters in order to lower their operating voltage. The use of microelectronic processing methods to fabricate devices that make use of vacuum as a transport "medium" has been termed vacuum microelectronics. The concept of vacuum microelectronics was first introduced by Ken Shoulders of the Stanford Research Institute in the late 1950's and first published in 1961.[66] In this seminal work, predictive of both vacuum microelectronic and computer based developments, Shoulders proposed many devices on vacuum microelectronics that are still being developed today such as vacuum microelectronic displays, vacuum microtriodes, and amplifiers. In fact, the basic building blocks of an entirely vacuum microelectronic computer, including memory, were discussed! Shoulders also foresaw many of the technological advances that would need to be made concerning vacuum encapsulation and component lifetime. Since Shoulders first introduced the concept, research has been on going and has accelerated since the mid-1980s. The improved fabrication of smaller and smaller microelectronic structures allows the production of very small extraction electrode-to-cathode spacing which allows even lower voltage operation of field emitters. The interested reader may turn to many fine reviews of vacuum microelectronics that have appeared in the literature.[2, 67-69]

Crucial to the development of vacuum microelectronics, a reliable source of electrons must be realized. Consequently, most vacuum microelectronics research has been aimed at producing microelectronic cold cathodes. Work on various types

of planar cold cathodes has been ongoing since the late 1960s with varying degrees of success. The best results for planar cold cathodes show current densities of 8000 A/cm<sup>2</sup>[16] and efficiencies of 1.5%[28] using cesium coatings. As stated earlier, most planar cold cathodes have required a cesium coating to achieve acceptable efficiencies and most researchers agree that cesium coatings are not acceptable for commercialization. The pioneer in the fabrication of vacuum microelectronic field emitter cathodes is Charles Spindt who was also at Stanford Research Institute in the 1960s (now SRI International). The most common structure for microelectronic field emission cathodes now carries his name.[70-72] The "Spindt cathode" is illustrated in Figure 1.1. In the Spindt structure, the extraction (or gate) electrode is separated from the substrates by a dielectric layer but is closely positioned around the field emission tips. The array of field emitters can be shaped to suit the design requirements and extremely dense arrays of field emitters can be produced using microelectronic fabrication. The close proximity of the extraction electrode to the emitter lowers the operating voltage necessary to produce a large electric field at the tip. Proper design of the structure ensures that

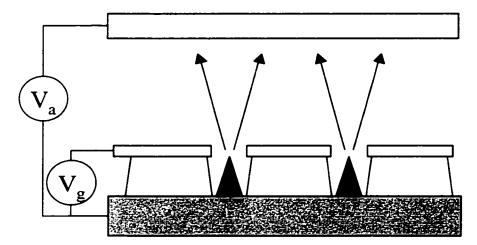


Figure 1.1. Cross-sectional schematic of Spindt-type field emitter array in a triode-like configuration. An extraction electrode (striped) surrounds the field emitter tips (black). The field created by the voltage applied to the extraction electrode,  $V_g$ , modulates the electron emission. If the anode voltage,  $V_a$ , is sufficiently larger than the extraction voltage, the electrons will be accelerated toward and collected by the anode.

the extraction electrode will intercept a negligible fraction of the emitted electrons. Once the electrons have passed the extraction electrode, they are attracted in the direction of the anode.

Cold cathodes find uses in a myriad of applications too numerous to cover completely here. Table 1.3 presents a list of some of the applications of vacuum microelectronic field emitters and cold cathodes. Some of these applications already make use of thermionic cathodes but could benefit from a cold cathode that provides higher current density, higher efficiency, or lower energy spread. Examples in this category are simple thermionic cathode replacement in devices such as CRT displays. Next, surface scientists have taken advantage of the properties of field emission to study the properties of surfaces and adsorbates. Of all the applications for field emitter arrays currently being investigated, two types of devices have generated the most research and show the most promise for taking advantage of the emission properties of field emitters. The first type is flat panel displays that can take advantage of low voltage and small size of field emitter arrays and the second are high power vacuum tubes that can take advantage of the high current density and direct modulation of the emission current. The basics of these two important devices will be briefly introduced in the following sections.

# Flat Panel Emissive Displays

Flat panel displays based on cold cathodes have been the most heavily targeted application of cold cathode research. The flat panel display market is currently dominated by active-matrix liquid-crystal displays (AMLCDs) that have the advantage of being a mature technology that can provide bright, full-color displays in a small package capable of reasonable operation times on battery power.[73] The basic weakness of the LCD is that it produces images by blocking and filtering a backlight and thus much of the energy used by the display is wasted. LCDs also suffer from slow refresh rate and restricted viewing angle although these deficiencies may be eliminated with advanced (but less mature and more

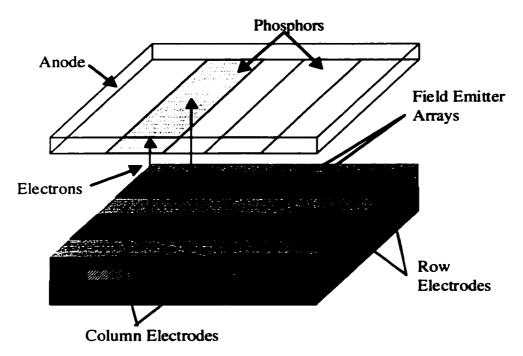


Figure 1.2. Schematic diagram of flat-panel display based on field emission arrays. The field emitters are connected to the column electrodes and the emission current is switched on and off by the row electrodes. In the simplest design, the anode-cathode separation is made small enough so that the electrons strike the phosphors above the array without the need for focusing electrodes.

expensive) LCD technologies. The cathode-ray tube (CRT), in which the light is produced by electrons striking a phosphor-coated screen, is an example of an emissive display. The CRT is considered the best quality display in terms of brightness, viewing angle, and refresh speed. Nevertheless, in order to scan the electron beam from a single thermionic cathode for the CRT, the design of CRTs requires them to have a depth comparable to the screen dimensions. A display combining the emissive properties of a CRT and the flat dimensions of an LCD would be an ideal technology for increasing the utility of consumer electronics. Flat-panel emissive displays based on cold cathodes are seen as a potential technology for realizing these applications.

The most commonly researched vacuum microelectronic display is the field emission display (FED). A simple schematic of an FED is shown in Figure 1.2. In an FED, each pixel of the display is supplied electrons from an array of field

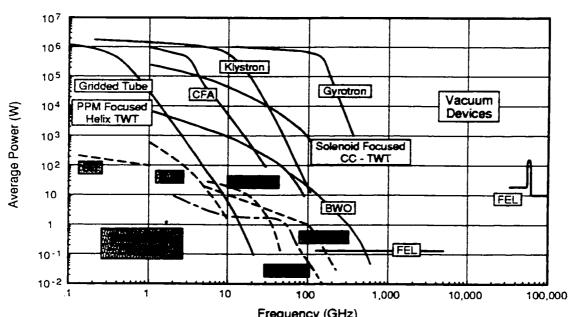
emitters. The array of pixels on the screen is directly in front of the arrays of field emitters, and thus, the voltage necessary to excite the phosphors governs the required thickness of the display, with higher voltage phosphors requiring larger front-to-back spacing. The main components of the display are the cold cathode, the anode screen, and the spacers that separate the anode from the cathode. The cold cathode is composed of the field emitter arrays and the gate electrodes which turn on and off the emission for the individual pixels. Initial work on FEDs was begun in the late 1980s by SRI International in the United States and by the Laboratoire d'Electronique, de Technologie et d'Instrumentation (LETI) in France.[74] Both groups produced prototype displays. Development has continued at companies such as Pixtech (France), Micron Display (U.S.), Candescent (U.S.), Samsung (South Korea), Daewoo (South Korea), and Futaba (Japan) and appears to be nearing commercialization. A related technology that has also received attention is field emitter-based lighting. Field emitter based lighting has the potential to produce highly efficient light sources if highly efficient phosphors are coupled with efficient field emitters.[75-79]

### **High-Power Vacuum Tube Amplifiers**

Solid state devices have yet to displace vacuum tube components for high power, high frequency sources.[80] Figure 1.3 shows a plot of the frequency-power ranges of various vacuum electronic and solid state devices take from Granatstein et al.[80] For applications requiring kilowatts or more or RF power, vacuum electronic devices are the only current option. Vacuum tube devices can operate at higher voltages and electron velocities than solid state devices. The higher voltage operation derives from the higher breakdown voltage of vacuum versus solid state device materials. Higher electron velocities in vacuum are a result of the reduced scattering of electrons in vacuum versus in solids. Cold cathodes have two main advantages over thermionic emitters for use in vacuum tube devices. The first is that cold cathodes can emit higher current density

electron beams. The higher current density increases the amount of power that can be generated in the tubes and relaxes the focusing requirements of the tubes.[80] The second advantage is the emission current from cold cathodes can be directly modulated. Because of the operating conditions of thermionic cathodes, placing a modulating grid near the hot filament involves difficult fabrication methods.[81] In conventional electron tubes, in order to modulate the emission current for electron beam devices using thermionic cathodes, long drift regions are necessary which adds weight and size to the tubes. Coupled with the their inherent higher efficiency, field emitter cathodes are a promising technology for use in high-power vacuum tubes, especial where portability (low weight, small size) and energy efficiency are required.

Compared to field emission flat panel displays, field emitter-based vacuum tubes have a much smaller market, and have generated fewer research programs and prototypes. In the U.S., the majority of research on field emitters for vacuum



Frequency (GHz)
Figure 1.3. Current state of technology for various vacuum and solid-state devices.
Reprinted with permission from Figure 3 of V.L. Granatstein, R.K. Parker, and C.M. Armstrong, *Proceedings of the IEEE*, vol. 87, no. 5, pp. 702-715, 1999.

tubes and designs of field emitter based tubes has been carried out by SRI International, Varian (now CPI), MIT/Lincoln Laboratory, MCNC, and the United States Naval Research Laboratory.[81, 82] Recently, demonstration of field emission cathode-based tubes has been made by researchers at NEC Corporation in Japan. Researchers there have reported miniaturized TWT results of 27.5 W at 10.5 GHz, 19.5-dB gain, and a bandwidth greater than 3 GHz using a lateral-resistor-stabilized Spindt-type field emitter array.[83] Another design by NEC, using vertical current limiters for high reliability from arc-related damage, resulted in a tube capable of 8 W output power, 22-dB gain at 11.5 GHz and stable operation for 5000 hours. These recent positive results may re-energize the efforts of the vacuum microelectronics community to develop high-power vacuum devices based on field emission cathodes.

Table 1.3. Some Applications of Cold Cathodes and Field Emitters.

Application	Description	Year of 1 <sup>st</sup> Prototype or Demonstration
Displays & Microscopes		
Cathode ray tube	Replace thermionic cathode with field emission cathode	1967[84]
Flat panel displays	Cold-cathode based flat panel	Alphanumeric: 1968[85] Monochrome & Color: 1988[74]
Field emission SEM & TEM	Field emitter cathode gives higher resolution at lower voltage than thermionic cathode	1968[86, 87]
Miniature electron beam column	For smaller SEMs using integrated miniature electron optics	1991[88]
Sensors & Gauges		
Pressure sensors	High sensitivity of field emission to changes in electric field; pressure changes anode-cathode spacing	1991[89, 90]
Accelerometer	Acceleration changes tunnel gap	1996[91]
Magnetic field	Magnetic field alters trajectory of field emitted electrons	1995[92]
UHV gauge	Relates field emission current changes to measure vacuum	1972[93]
Surface Science		
Field emission microscope	Projection of field electron emission on a phosphor screen reveals atomic structure of field emitter tip	1937[94]
Adsorbate & surface studies	Study the change in field emission currents and field emission microscope patterns caused by various adsorbates on field emitters	1951[95]
Electron holography	Coherent electron beam from single- atom field emitters	1987[96]
Vacuum Tube Devices		
Microelectronic triode	Based on field emitters	1986[97]
Conventional beam tube	Traveling-wave tube	1997[83]
Other		
Mass spectrometer ionizer	Vacuum microelectronic field emitter- based mass spectrometer used in the 1986 Vega spaceflight to analyze Halley's comet tail	1975[98] 1986[99]
Massively parallel electron beam lithography	Multiple electron sources speed e- beam lithography throughput	1987[100]
X-ray source	High current density electron beam for the production of flash x-rays	1961[101]

# (1.8) References

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# **Chapter Two**

# **Field Emission**

# "After considerable experimenting I have succeeded in finding a method of producing the rays by what appears to be a new form of cathode discharge, which manifests itself as a bright blue arc between two minute balls of platinum in a very high vacuum."—R.W. Wood, "A New Form of Cathode Discharge and the Production of X-Rays, Together with Some Notes on Diffraction," The Physical Review, vol. 10 (series I), pp. 1-10, i897.

# (2.1) History and Background

The emission of electrons from sharp points has been observed since 1744 when Johann Winkler observed electron emission from sharpened wires while teaching at a school in Leipzig.[1] The poor vacuum levels achievable then compared to present day preclude the conclusion that the observed emission was definitely field emission and Winkler did not use that term. The first work to experimentally describe field emission in detail was made by R.W. Wood in 1897.[2] Experimental work on field emission would increase of the next few decades with Julius Lillienfeld at the University of Leipzig, and Franz Rother publishing papers on the effect in the 1910s and 1920s. About 1920, Robert Millikan's group at the California Institute of Technology also began to look at the problem of electron emission in intense fields.[3-6] The commercial appeal of field emission-based cathodes can be attested to by the early research of Gossling at the General Electric Company in 1926.[7]

Walter Schottky's theory to explain field emission appeared in 1923.[8] Schottky attempted to explain field emission using a classical approach, hypothesizing that field emission was a result of the image force of electrons above a metal surface reducing the potential barrier to zero at some critical field. At low fields, the reduction of the thermionic work function with applied field had been experimentally confirmed, however, the field emission experiments of Gosling failed to confirm the Schottky theory for high fields. Gossling came to the general conclusion that application of the new quantum theory may be necessary to explain field emission. An important experimental discovery was made in 1929 by

Millikan and Lauritsen[9] where they showed empirically that the current-voltage characteristics followed a relationship given by  $I = A \exp(-B/F)$ , where A and B are constants and F is the field at the cathode surface.

The quantum mechanical theory of field emission was first published by R.H. Fowler and L. Nordheim in 1928 in which they made a clear application of Sommerfeld's electron theory of metals.[10] The key theoretical breakthrough was the realization that electrons did not have to possess enough energy to surmount the surface barrier, but, because the electron's wave function was spread out in space, there exists a finite probability that the electron can "tunnel" through the barrier and be emitted into vacuum. Fowler and Nordheim applied Fermi-Dirac statistics to determine the energy distribution of electrons striking the surface of a metal (the supply function) and then solved the Schrödinger equation to calculate the fraction of electrons that could tunnel through the surface barrier at a given energy (the transmission function). The emission current is calculated by taking the product of the supply function and transmission function and integrating over all energies. The result is an equation,  $I = AF^2 \exp(-B/F)$ , which differs in form from the Millikan and Lauritsen result only in the pre-exponential factor of  $F^2$ . This factor is difficult to observe experimentally. Nordheim improved the accuracy of the theory by incorporating Schottky's image lowering effect in a subsequent paper.[11]

Research on field emission and field emission cathodes continued at a rapid pace through the following decades. The most significant result of the 1930s was E. Müller's invention of the field emission microscope (FEM) in 1937[12] based on the work of Johnson and Shockley.[13] A schematic of the FEM appears in Figure 2.1. The FEM consists of a tungsten point cathode at the center of a glass bulb. The tungsten tip is mounted to a loop through which a current can be passed through, in order to heat and thereby clean the tip. The electrons pass through the vacuum and impinge on the anode, which is a phosphor screen on the glass vacuum envelope. The electrons striking the phosphor produce a magnified image of the

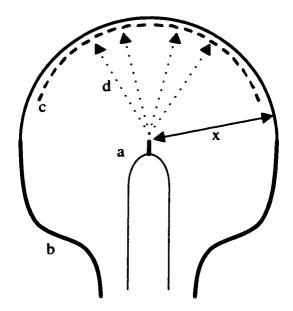


Figure 2.1. Schematic of field emission microscope. (a) tungsten loop with tungsten tip field emitter, (b) glass vacuum envelope, (c) phosphor screen, (d) electron trajectories from cathode to anode. The separation of the tip from the screen is x.

electron emission at the tungsten tip. The electron emission is dependent on the shape of the tip and the differing work functions of the various tungsten crystal planes. The ideal magnification of the FEM is x/r where x is the cathode-to-anode separation and r is the tip radius of the tungsten emitter. For a tip of 1000 Å and tube dimensions on the centimeter scale, magnifications in  $10^5$ - $10^6$  range are obtained.[14]

The first major effort to make use of field emitters as practical sources of electron beams was undertaken by W.P. Dyke and W.W. Dolan at Linfield College in Oregon. Dyke and Dolan concentrated on improving field emitter performance of tungsten field emitters, operating the emitters at temperatures and fields that gave stable emitter performance.[15] Their work on tungsten field emitters eventually lead to their use in such devices as flash x-ray tubes.[16]

The above discussion is but a brief introduction to the history and development of field emission theory and experimentation. The interested reader can obtain a fuller picture of the history of field emission research from the many fine review articles and manuscripts that have appeared on field emission and field emission microscopy over the past century.[1, 14, 15, 17-26].

The remainder of this chapter will be concerned with the development of the field emission equation for n-type GaN. The development will proceed from the treatment for metals and refinements will be made to account for the semiconductor nature of GaN. The theory of field emission from semiconductors was first undertaken by R. Stratton[27] in 1955 and later refined in 1962.[28] Stratton gives a detailed and rigorous derivation of the physics of emission from both the conduction and valence bands, but his resulting equations are complex. To be clear, the approach of the following sections will be to follow the development of the theory as given by Good and Müller[21] making the appropriate changes to account for an n-type, wide band gap semiconductor. The specification of wide band gap and n-type semiconductor suggests that field emission from the valence band, which is several eV below the conduction band, can be ignored relative to that from the conduction band. In addition, the consequences of surface states are not included in this derivation, and current research, although not complete, suggests that the surface state density of the nitride semiconductors is low. The fact that Schottky contacts on GaN appear to follow the Schottky-Mott model indicates that the surface state density is low enough to prevent surface Fermi level pinning.[29]

# (2.2) The Band Diagram

In order to calculate the field emission current from a metal or semiconductor, a model of the electron potential energy of the material is necessary. The model must include a description of the potential energy of an electron in the material and vacuum and at the surface. A schematic of a one-dimensional model of a metallic field emitter is given in Figure 2.2(a). For metals,

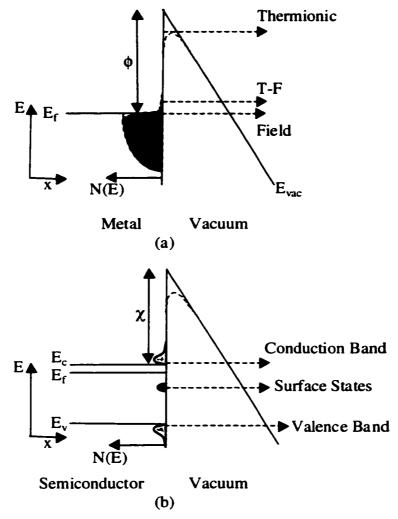


Figure 2.2. Band diagrams of (a) metallic field emitter and (b) n-type semiconductor field emitter. The vacuum level is shown with a field applied and the image lowering is shown by a dotted line near the apex of the barrier.

field emitted electrons originate from energy levels near the Fermi level of the metal. Field emission currents are generally calculated assuming a temperature of 0 K. As the temperature of a metal is increased, the Fermi-Dirac function will develop a finite slope about the Fermi level and electron states above the Fermi level will be filled. Electrons above the Fermi level have a thinner barrier to penetrate and thus under a moderate-to-high applied field and increased temperature, enhanced field emission will result which is termed thermionic-field (T-F) emission. Thermionic emission results under low field conditions when the metal has been heated to the point that tail of the Fermi-Dirac distribution reaches energies above the maximum of the surface barrier. A similar band diagram for a semiconductor is shown in Figure 2.2(b). In a semiconductor, the situation is complicated by the fact that emission is possible from both the valence and the conduction bands. In addition, semiconductors may have surface states that effect the band diagram at the surface and electrons may tunnel from surface states that trap electrons.

To calculate the field emission from a material, two functions must be derived. The first function, the supply function,  $N(E_x)$ , specifies the number of electrons per second per unit area traveling in the x-direction with momentum in the range of  $dp_x$  where  $E_x$  is x-part of the electron energy. The second function, the transmission function,  $T(E_x)$ , gives the probability that an electron of energy  $E_x$  is able to penetrate the surface barrier. The current density is found by multiplying these functions and integrating over all possible energies. First, we will calculate the supply function.

# (2.3) The Supply Function

The supply function is calculated by combining the free-electron gas model of a solid with Fermi-Dirac statistics, the so-called Sommerfeld model. Descriptions of this model can be found in any text on solid state physics.[30, 31]

The number of electron states in a volume, V, with momenta in the range  $dp_x dp_y$   $dp_z$  is given by

$$dn = \frac{2V}{h^3} \frac{dp_x dp_y dp_z}{1 + \exp(\varepsilon - \mu/k_b T)}$$
(2.1)

where  $\varepsilon$  is the total electron energy,  $\mu$  is the electrochemical potential,  $k_b$  is Boltzmann's constant, h is Planck's constant, and T is the temperature. Next, the number of electrons moving toward the surface (in the x-direction) per second per unit area with momentum within  $dp_x$  is found by multiplying the number per unit volume in the momentum range  $dp_x dp_y dp_z$  (given in equation (2.1)) by the velocity in the x-direction ( $v_x = p_x/m_\varepsilon$ ) and integrating over all  $p_y$  and  $p_z$ . This gives

$$N(p_x)dp_x = \int_{p_y = -\infty}^{+\infty} \int_{p_z = -\infty}^{+\infty} \frac{2}{h^3} \frac{p_x}{m_e} \frac{dp_x dp_y dp_z}{1 + \exp\left(\frac{\varepsilon - \mu}{k_b T}\right)}$$
(2.2)

where  $m_e$  is the effective mass of electrons in the conduction band. In this work, the effective mass is assumed isotropic and all bands will be assumed to follow the parabolic approximation. The energy in the x-direction can be calculated by

$$E_{x} = \varepsilon - \frac{p_{y}^{2} + p_{z}^{2}}{2m_{e}}$$

$$E_{x} = \frac{p_{x}^{2}}{2m_{e}} + E_{c}$$

$$(2.3)$$

where  $E_c$  is the conduction band minimum energy. Substituting this and  $p_x dp_x = m_e dE_x$  (derived from the second of equations (2.3)) into equation (2.2) gives

$$N(E_{x})dE_{x} = \frac{2}{h^{3}}dE_{x} \int_{-\infty}^{+\infty} \frac{dp_{y}dp_{z}}{1 + \exp\left(\frac{E_{x} - \mu + \frac{p_{y}^{2} + p_{z}^{2}}{2m_{e}}}{k_{b}T}\right)}$$
(2.4)

The above equation can be integrated by transforming to polar coordinates and yields the final supply function

$$N(E_x)dE_x = \frac{4\pi m_e k_b T}{h^3} \ln \left(1 + \exp\left(-\frac{E_x - \mu}{k_b T}\right)\right) dE_x$$
 (2.5)

which gives the number of electrons with energy  $E_x$  impinging on a unit surface per second. This expression differs from Good and Müller's only by our use of the conduction-band effective electron mass instead of the free electron mass.

# (2.4) The Transmission Function

The transmission function is a measure of the probability that an electron of energy  $E_x$  can penetrate the surface barrier. The transmission function can be calculated exactly by solving the one-dimensional, time-independent Schrödinger equation in the direction of the barrier

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left[ E_x - V(x) \right] \psi = 0$$

where  $\psi$  is the one-electron wave function, V(x) describes the potential variation in the barrier region and  $\hbar$  is the modified Planck's constant. For a triangular barrier, the potential is given by

$$V(x) = \begin{cases} E_c & \text{where } x < 0 \\ \chi - qFx & \text{where } x > 0 \end{cases}$$

where q is the electron charge and F is the applied electric field and the barrier is shown schematically in Figure 2.3. For the given triangular barrier, the transmission probability is given by  $T = k(b)|\psi(b)|^2/k(0)|\psi(0)|^2$  which is

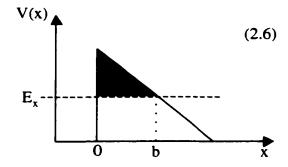


Figure 2.3. Schematic of a triangular barrier for calculation of transmission probability.

ratio of the amplitude of the wave function times the wave vector at right side of the barrier to the left side. This can be evaluated by solving the Schrödinger equation exactly if the potential is simple, using the scattering matrix approach for a numerical solution, or by making use of the Wentzel, Kramers, and Brillouin (WKB) approximation for calculating tunneling probabilities. Here, we will make use of the WKB approach because it allows us to preserve the physical significance of the parameters in the final field emission equation and gives results that agree reasonably with more rigorous calculations and experimental results. The WKB approximation fails when the change in potential, over one electron wavelength, due to slope or curvature of the potential, is too large.\* Thus, in the case shown in Figure 2.3, the WKB approximation fails near the top of the triangle and at the left side of the barrier. For energies of interest,  $E_x$  is generally a few eV below the top of the barrier and the WKB approximation gives close-to-exact results. In spite of these difficulties, for the case of a triangular barrier, the WKB approximation is remarkably successful (for a comparison of the exact solution and WKB approximation for a triangular barrier, please see Appendix A). For cases where this is not true, application of another WKB-like approximation may be used to obtain improved results.[33] In the WKB approximation the transmission coefficient is given by

$$T(E_x) = \exp\left(-\int_a^b \sqrt{\frac{8m}{\hbar^2} [V(x) - E_x]} dx\right)$$
 (2.7)

where, here, m is the free electron mass because the barrier is outside the material, and a and b are the classical turning points of the potential. For the triangular barrier, the left turning point is taken as the reference and the right turning point is given by  $b = (\chi - E_x)/qF$ . In Figure 2.3, the shaded area shows the energy range being integrated over at a given  $E_x$ . The result of carrying out this integration is

<sup>\*</sup>The interested reader is encouraged to consult Chapter 6 of H. Kroemer's quantum mechanics text.[32]

$$T(E_x) = \exp\left(-\frac{4\sqrt{2m}}{3\hbar qF}(\chi - E_x)^{3/2}\right).$$
 (2.8)

### (2.5) Image Force Correction to the Transmission Function

The transmission function calculated above ignored the image force that acts on electrons as they exit the surface of the emitter. The image force is created by the positive charge that is drawn to the surface of the material by the electron. This effect on field emission characteristics was first studied by Nordheim.[11] The effect on the potential for a metal is given by a term  $-q^2/(16\pi\epsilon_o x)$ , which would be added to the second of equations (2.6), where  $\epsilon_o$  is the permittivity of free space. For a semiconductor, this factor must be multiplied by  $v = (\epsilon_r - 1)/(\epsilon_r + 1)$ , where  $\epsilon_r$  is the low frequency dielectric constant of the semiconductor. The solution to this more realistic and complicated potential is exactly solvable (still within the WKB approximation) and involves the use of elliptic integrals and was given by Good and Müller.[21] The end result is

$$T(E_x) = \exp\left(-\frac{4\sqrt{2m}}{3\hbar qF} (\chi - E_x)^{3/2} v(y)\right)$$
 (2.9)

where  $y = \sqrt{\upsilon} \sqrt{q^3 F} / (2\sqrt{\pi \varepsilon_o} (\chi - E_x))$  and v(y) is a tabulated function. [34]

# (2.6) A Fowler-Nordheim Equation for n-type Wide Band Gap Semiconductors

The final step to deriving the Fowler-Nordheim equation is to multiply the supply function (equation (2.5)) by the transmission function (equation (2.9)) and integrate over all the energies of the electrons. The integrand,  $P(E_x)$  is given by

$$P(E_{x})dE_{x} = \frac{4\pi m_{e}k_{b}T}{h^{3}} \exp\left(-\frac{4\sqrt{2m}}{3\hbar qF}(\chi - E_{x})^{3/2}v(y)\right) \ln\left(1 + \exp\left(-\frac{E_{x} - \mu}{k_{b}T}\right)\right) dE_{x}$$
(2.10)

which cannot be integrated analytically. For a metal, the usual practice is to expand the transmission function as the first two terms of a Taylor expansion about  $E_x=\mu$  because most of the emitted electrons originate from around the Fermi level. For the conduction band of a semiconductor, Stratton has shown that the expansion should be taken about either the Fermi level for a degenerate semiconductor or the conduction band minimum for a non-degenerate semiconductor. Stratton shows that both of these expansions are equivalent if the Fermi level is close to the conduction band as one would expect and it will be assumed that the Fermi level is near the conduction band (i.e. a non-degenerate, n-type semiconductor). The expansion will be taken about  $E_x=\mu$  (the Fermi level) in order to simplify the evaluation of the integral.

Taking the expansion of the exponent of the transmission function results in an exponent given by

$$-\frac{4\sqrt{2m\chi^3}}{3\hbar qF}v(y') + (E_x - \mu)\frac{2\sqrt{2m\chi}}{\hbar qF}t(y')$$
 (2.11)

where

$$t(y) = v(y) - \frac{2}{3}y \frac{dv(y)}{dy}$$
 (2.12)

and

$$y' = \sqrt{\upsilon} \sqrt{q^3 F} / (2\sqrt{\pi \varepsilon_o} \chi). \tag{2.13}$$

From Good and Müller (equation (5.16) in [21]) the supply function at low temperature can be approximated by

$$k_b T \ln \left( 1 + \exp \left( -\frac{E_x - \mu}{k_b T} \right) \right) = 0 \qquad \text{when } E_x > \mu$$

$$= (\mu - E_x) \text{ when } E_x < \mu$$
(2.14)

Substituting equations (2.11) and (2.14) gives

$$P(E_x) = 0 \qquad \text{when } E_x > \mu$$

$$= \frac{4\pi m_e}{h^3} \exp\left(-\frac{4\sqrt{2m\chi^3}}{3\hbar qF}v(y') + (E_x - \mu)\frac{2\sqrt{2m\chi}}{\hbar qF}t(y')\right)(\mu - E_x)$$
when  $E_x < \mu$  (2.15)

Equation (2.15) is valid for a semiconductor where the Fermi level is near the conduction band edge, i.e.  $\mu \approx E_c$ . The integration of the resulting equation is relatively straightforward and results in an equation displaying the essential features of the Fowler-Nordheim equation.

The field emitted current density, j, is found by multiplying  $P(E_x)$  by the electron charge and integrating over all electron energies

$$j = \int_{-\infty}^{+\infty} qP(E_x)dE_x \tag{2.16}$$

Substituting the exponent of the transmission function given in equation (2.11) and integrating

$$j = \int_{0}^{+\infty} \frac{4\pi m_{e}}{h^{3}} \exp\left(-\frac{4\sqrt{2m\chi^{3}}}{3\hbar qF}v(y') + (E_{x} - \chi)\frac{2\sqrt{2m\chi}}{hqF}t(y')\right)(\mu - E_{x})dE_{x}$$
 (2.17)

results in

$$j = \frac{q^3 F^2}{8\pi h \chi t^2(y')} \frac{m_e}{m} \exp\left(-\frac{4\sqrt{2m} \chi^{3/2}}{3\hbar q F} v(y')\right)$$
(2.18)

Equation (2.18) gives the current density field emitted from a planar surface at a given field, F, for an n-type, degenerate, wide band gap semiconductor. The equation is analogous to Good and Müller's equation for a metal with the metal's work function replaced by the semiconductor's electron affinity and the electron mass no longer cancels in the pre-exponential factor.

Stratton's derivation of the field emission current from the conduction band of a semiconductor uses the same approximation for the transmission function, but Stratton retains the full supply function and integrates the resulting expression. The

interested reader may consult the references for the mathematical details.[27, 28] The result of Stratton's calculation for the field emission from an *n*-type semiconductor is

$$j = \frac{q^{3}F^{2}}{8\pi\hbar\chi t^{2}(y')} \exp\left(-\frac{4\sqrt{2m}\chi^{3/2}}{3\hbar qF}v(y')\right) \times C(F,\chi)$$
 (2.19)

where  $C(F,\chi)$  is a correction function which is weakly dependent on F and  $\chi$  and therefore will be ignored here. This equation is essentially the same as equation (2.18). Stratton's equations do not include the factor (m / m), as he takes the effective mass to be one.

Further simplification of the Fowler-Nordheim equation can be obtained by approximating the tabulated functions, v(y) and t(y). Brodie and Spindt give approximate expressions for these functions as [35]

$$v(y) \approx 0.95 - y^2$$
 and  $t^2(y) \approx 1.1$  (2.20)

and inserting these factors into equation (2.18) and evaluating the constants numerically gives

$$j = \frac{2.8 \times 10^{-7} F^2}{\chi} \exp\left(\frac{7.97}{\sqrt{\chi}}\right) \exp\left(-\frac{6.49 \times 10^7 \chi^{3/2}}{F}\right) [A/cm^2] \quad (2.21)$$

where j is in A·cm<sup>-2</sup>, F is expressed in V/cm,  $\chi$  is expressed in eV, and the numerical value of the constants and material parameters are

$$\varepsilon_r = 9.5$$
 for GaN  
 $m_e = 0.2m$  for GaN  
 $q = 1.602 \times 10^{-19}$  C  
 $m = 0.91095 \times 10^{-30}$  kg  
 $\varepsilon_o = 8.85418 \times 10^{-12}$  F/m  
 $h = 6.62617 \times 10^{-34}$  J·s

# (2.7) Field Enhancement

The above derivation assumes that the surface of the sample is a planar surface. A simple method to determine the order of magnitude of electric field necessary for field emission makes use of Heisenberg's uncertainty principle.[14] The uncertainty principle states that there is a fundamental inequality relating the uncertainty of momentum and position of a particle. Stated mathematically, the uncertainty principle is  $\Delta x \Delta p \ge \hbar/2$ . For electrons tunneling from the Fermi level of a metal, the relevant uncertainty in momentum is related to the energy barrier (the work function), or  $\Delta p = \sqrt{2m\phi}$ . Thus, the uncertainty in position is  $\Delta x = \hbar/2\sqrt{2m\phi}$ . When the uncertainty in position of the electron is of the order of the barrier width, there will be a reasonable tunneling probability. Recall that, for the triangular barrier, the barrier width at the Fermi level is  $\phi/Fq$ . Setting the barrier width equal to the uncertainty in position, and solving for the required field gives  $F = (\sqrt{2m}\phi^{3/2})/q\hbar$ . For a work function of 3.5 eV, this gives an electric field of about 10<sup>10</sup> V/m. Fields of this size far exceed the breakdown potential of standoff dielectrics which must be present to separate the field emitter from the anode and require an extremely good vacuum to avoid vacuum arcing which would destroy the emitter. The above discussion was for a triangular barrier, which ignored the image effect, and thus predicts too large of an electric field by about an order of magnitude.

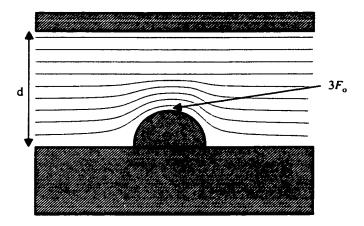


Figure 2.4. Illustration of field enhancement for hemisphere on plane. The dotted lines indicate the equipotentials and the compression of the near the sphere represents the field enhancement ( $F = -\nabla \Phi$ , where  $\Phi$  is the potential).

Large fields such as discussed above can be produced by the intensification of electric field that occurs at sharp projections. One example of field enhancement that is exactly solvable is the problem of a hemisphere on an infinite half plane separated by a large distance  $(d \gg r)$ , where r is the radius of the hemisphere) from an anode in a plane-parallel geometry as illustrated in Figure 2.4.[36] The field at the top of the hemisphere is three times the field that would exist at that point without the presence of the hemisphere. For actual field emitter geometries, analytical solution may be intractable or impossible to obtain. Numerical calculations of the solution of Laplace's equation  $(\nabla^2 \Phi = 0)$  for boundary conditions determined by the cathode geometry are often used to calculate the field enhancement.[37-45]

For a point electron source, one simple model of the electric field around a field emitter is the concentric sphere model. [46] The field emitter is modeled as sphere of radius, r, and the anode is modeled as a sphere of radius, R, concentric with the field emitter sphere. This model is accurate for a field emitter if the field lines about the point are radial and this condition is fulfilled if r << R. It is a simple

electrostatic problem to calculate the field at the surface of the inner sphere and the resulting field enhancement factor,  $\beta$ , is given by

$$\beta = \frac{R}{r(R-r)} \ . \tag{2.23}$$

The field enhancement factor relates the field at the emitter to the potential applied between the anode and the cathode (i.e.  $F = \beta V$ ) and thus the field enhancement factor has units of [length<sup>-1</sup>]. In reality the field at the point of the tip will be reduced from the free-sphere case given above because of the influence of the conical shank portion of the field emitter.[14] Based on the work of Gomer, Brodie has multiplied the field enhancement factor given for the spherical case by a correction factor (1/k) where 1 < k < 5. Thus, the field enhancement factor for a point source field emitter modeled as a truncated cone with a hemispherical top can be given by

$$\beta = \frac{R}{kr(R-r)}. (2.24)$$

With the anode-cathode separation in the range of 1  $\mu$ m and the radius of curvature of the field emitter point in the range of 10 nm gives a field enhancement factor in the range of  $(1/k)\times10^8$  m<sup>-1</sup>. Above we calculated that the electric field necessary for field emission is in the range of  $10^{10}$  V/m, and with the field enhancement in the range of  $10^8$  m<sup>-1</sup>, the required voltage to produce these fields is in the range of  $10^0$  V. For micron-sized spacing, turn-on voltages of field emitters are typically of that order of magnitude.[47]

### (2.8) Current-Voltage Characteristic & the Fowler-Nordheim Plot

The Fowler-Nordheim equation given above (equation (2.21)) relates the current density to the field at the surface of the emitter. The current density and field are not generally available to the experimentalist. The current density and field enhancement can be related to the experimentally observable current and voltage by the following equations

$$F = \beta \cdot V$$

$$I = A \cdot j$$
(2.25)

where A is the emission area and  $\beta$  is the aforementioned field enhancement factor. There is a serious assumption made in applying equations (2.25) to the Fowler-Nordheim equation. Use of a constant field enhancement factor implies that the electric field is constant over the emission area, which is generally not true. A rigorous procedure for obtaining the current-voltage characteristic would be to integrate the current density over the emission area with the field as a position-dependent quantity. Experimentally, it is seen that this procedure is not necessary and the approximation made in using equations (2.25) is valid, but with  $\beta$  representing a weighted average of the field enhancement factor over the emission area. For microelectronic field emitters, the emission area per tip is generally so small that the field enhancement can be taken as constant. The resulting field emission current-voltage characteristic is given by

$$I = \frac{2.8 \times 10^{-7} A \beta^2 V^2}{\chi} \exp\left(\frac{7.97}{\sqrt{\chi}}\right) \exp\left(-\frac{6.49 \times 10^7 \chi^{3/2}}{\beta V}\right)$$
(2.26)

where I is in amperes, A is in cm<sup>2</sup>, and V is in volts. The current voltage characteristic is dominated by the last exponential term, which depends on the electron affinity and field enhancement factor. One of the desires of microelectronic field emission researchers is to reduce the turn-on voltage of field emitter cathodes. [48] From the above equation, it can be seen that lowering of the turn-on voltage of the emitter requires either that the electron affinity be reduced or the field enhancement be increased. The total current can be increased by increasing the area of emission, which is the prime reason for using arrays of field emitters together.

Manipulation of equation (2.26) by dividing both sides by  $V^2$  and taking the logarithm of both sides results in

$$\ln(I/V^2) = \ln a - b(1/V) \tag{2.27}$$

where

$$\ln a = \ln \left( \frac{2.8 \times 10^{-7} A \beta^2}{\chi} \exp \left( \frac{7.97}{\sqrt{\chi}} \right) \right)$$
 (2.28)

and

$$b = \frac{6.49 \times 10^7 \, \chi^{3/2}}{\beta} \,. \tag{2.29}$$

Equation (2.27) is simply the equation of a line with (1/V) as the ordinate,  $\ln(I/V^2)$  as the abscissa,  $\ln a$  as the y-intercept, and -b as the slope. A plot of experimental current-voltage data with (1/V) for the x-axis and  $\ln(I/V^2)$  for the y-axis is called a Fowler-Nordheim plot. The slope and intercept of a linear, least-squares fit of the Fowler-Nordheim plot gives equations that allow the extraction of any two of the field enhancement factor, emission area, or electron affinity when the third is known. For example, in most field emission experiments, the work function of a metal is approximately known from other experiments, and the field enhancement and emission area can be calculated using the known work function.

# (2.9) Engineering Considerations and Refinements to Field Emission Theory

Brodie and Schwoebel, in their review of vacuum microelectronics, list a number of considerations important to field emission devices in addition to considerations that arise from the current-voltage characteristic worked out above. These additional considerations include fundamental properties of field emitters such as emission noise, and space-charge effects[49], and engineering concerns such as lifetime problems, current limiting resistors, leakage currents, electron trajectories, device capacitance, and packaging.[50] A discussion of all of these factors is outside the scope of this dissertation but a brief discussion of two of these considerations will be given. Emission fluctuation and emitter lifetime will be discussed because the use of nitride semiconductor-based field emitters may have

an impact in these areas. In addition this section will conclude with a brief list of refinements to field emission theory that have been studied by other researchers but not included in this dissertation.

### **Emission Fluctuation**

Emission noise from field emitters has a complicated structure and much about the sources of noise in field emission remains unknown. Probably the most important source of noise in field emitters comes from modulation of the work function or electron affinity.[51-54] The surface barrier can be modified by the adsorption, desorption, and diffusion of foreign atoms and molecules on the surface of the emitter. Adsorbates interacting with the surface can produce a dipole that may increase or decrease the effective work function at the surface,  $\phi_{eff} = \phi \pm \Delta \phi$ . The fluctuations in the barrier height will produce fluctuations in the emission current. Taking the derivative of the current-voltage characteristic (and ignoring the pre-exponential factor) with respect to electron affinity gives

$$\frac{1}{I}\frac{dI}{d\chi} = \frac{-6.4 \times 10^7}{\beta V} \sqrt{\chi} \ . \tag{2.30}$$

The above equation shows that as the electron affinity decreases, the contribution of small changes of the electron affinity to the noise decreases as well. This leads to the conclusion that materials with smaller electron affinity are desirable for field emitters from a low current-fluctuation perspective. The above equation ignores the influence of the pre-exponential factor. This approximation breaks down at small electron affinity. Taking the derivative of the full equation (2.26) and substituting typical values of field enhancement (64,000 cm<sup>-1</sup>) and voltage (100 V) gives

$$\left|\frac{\Delta I}{I}\right| = \left(\frac{4.0 + \sqrt{\chi} + 15.2 \chi^2}{\chi^{3/2}}\right) \Delta \chi \tag{2.31}$$

The last term in the parentheses is the approximation given in equation (2.30) and when this term dominates, we can use that approximation. A plot of equation (2.31) and the approximation given in equation (2.30) over the electron affinity range of 0 to 4.5 eV, and using a  $\Delta\chi$  of 0.01 eV is shown in Figure 2.5. The plot indicates that decreasing the electron affinity from 4.5 eV to about 1 eV will decrease the relative current fluctuations caused by adsorbates. Below about 1 eV, however, the plot shows that the current fluctuations will rapidly increase with decreasing electron affinity, and the approximation given in equation (2.30) no longer agrees with the full expression (equation (2.31)). One should take caution when applying this interpretation to low electron affinity emitters because the Fowler-Nordheim equation breaks down at low barrier heights because of the limitations of the WKB approximation. At very low electron affinity, a more rigorous derivation of the current-voltage characteristic would be necessary. With this caution in mind, the above analysis suggests that lowering the electron affinity, in the range most commonly available for field emitters, 1-5 eV, will reduce the

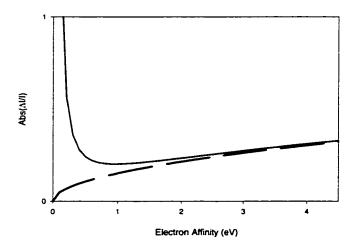


Figure 2.5. Relative current fluctuation versus the electron affinity of a field emitter. The full dependence (equation 2.31) is given by the solid line and an approximation (equation 2.30) is given by the dashed line. The approximation fails below about 2 eV.

amount of adsorption-based emission fluctuation. In reality the situation is further complicated by the fact that adsorbates effect the emission not only through modulation of the surface barrier, but also by modifying the field enhancement and the emission area.[50]

### Lifetime Issues

The lifetime of a field emitter is limited by two main factors: destruction by a vacuum arc or excessive currents, and an overall change in current-voltage characteristic caused by 1) contamination of the emitter surface by the residual gases in the vacuum, or 2) ion bombardment of the emitter. Destruction of emitters or emitter arrays by vacuum arc represents a catastrophic failure mode, and is generally related to the quality of vacuum in the field emission device. Poor vacuum can lead to vacuum arc and the resulting high currents can destroy the emission tips or extraction and anode electrodes. Operation of the cathodes at excessive currents can lead to cathode destruction by either melting or fracturing of the emitter tip. Contamination of the emitters is also dependent on the quality of the vacuum, but also depends on the reactivity of the emitter material. A highly reactive surface is more likely to be contaminated by the residual gases in the vacuum than a stable surface. As we have seen from the last section, adsorbed gases can change the surface barrier height, field emission factor, and emission area of an emitter.

Vacuum arc results when a high current flows from anode to cathode and, at the same time, the voltage between the anode and cathode is greatly reduced. Arcing in a gas environment may be initiated by the ionization of the gas atoms, but at high vacuum, there are not enough residual gas molecules in the vacuum to initiate an arc. Many theories for the initiation of vacuum arcs exist.[55] In fact, one theory of vacuum breakdown suggests that field emitted electrons cause intense heating of the anode material and the evaporating anode material helps supply the

conditions for an arc.[56-61] Still another theory proposes that vacuum arc is initiated at non-metallic particles or surface oxides.[62] Regardless of the initiation mechanism, the large currents in vacuum arcs lead to melting of electrodes and emitters and can lead to the destruction of the field emission cathode. Arrays of cathodes are somewhat safer than single emitters are because the failure of one or a few of the tips may not cause the destruction of the entire array. In general, it is seen that arcing between the gate and emitter tip of an array of electrodes leads to localized failure and destruction of the tip while arcing between the gate and anode electrodes leads to destruction of larger areas of the gate.[35]

Field emitters can also fail from excessive currents. The field emitter heats up by a combination of Joule heating and the Nottingham effect. The Nottingham effect is the result of the difference of the average energy of emitted electrons and the average energy of replacement electrons (i.e. electrons supplied by the circuit to replace the emitted electrons). The average energy of the replacement electrons was assumed by Nottingham to be the Fermi level[63] and the work of Charbonnier et al. supports that contention. [64] This assumption has created some controversy, however, and a rival hypothesis that the replacement electrons come from states below the Fermi level has been proposed by Fleming and Henderson[65] and improved upon recently.[66] Regardless of the correct theory, electrons that are emitted from energy levels above the average energy of replacement electrons serve to cool the material. Conversely, electrons emitted from levels below the average energy of the replacement electrons heat the material. For a metal, all emission at low temperatures is assumed to come from below the Fermi level so the Nottingham effect should serve to heat the electrons. As the material is heated, either by an outside source or by the emission itself, more electrons will be emitted from above the Fermi level and eventually a critical temperature will be reached where the Nottingham effect will cool the emitter. To avoid damage, field emitters must be able to transfer heat from the emission area to the substrate, but sharp

emitter tips lead to small tip base area and increased thermal resistance. The temperature rise in the tips can be reduced without the penalty of decreasing the field enhancement by using cathode materials that have high thermal conductivity. The higher the thermal conductivity is, the higher the emission currents than can be supported.[67-69] The nitride semiconductors excel in this material property. The thermal conductivity of GaN is 1.3 W/cm K[70] and is in the same range as the commonly used metals (Mo and W), and is higher than other semiconductors studied for field emitter applications, such as Si and GaAs. Diamond, which is a much-studied material for field emission, has the highest thermal conductivity at 20 W/cm K.[71] In addition to thermal effects causing failure of cathodes, some researchers have investigated the effects of both thermal and electrical stresses on field emitters as a cause of failure in some field emission cathodes.[72]

Other than cathode destruction, the lifetime of field emission cathodes can be cut short by contamination of the tip or the eroding of the tip by ion bombardment, both of which change the current-voltage characteristic of the field emitter over time. For field emitters operated at room temperature, contamination comes from the vacuum environment. "Poisoning" of the emitter surface happens when residual gases react with the surface and change the surface work function, usually increasing the barrier.[73-76] The nature of the contamination depends on both the emitter material and the residual gas content. Thus in terms of stability, a chemically inert surface is desirable for field emitters. Materials such as diamond and carbon have low reactivity and thus are good choices.[77]

Ion bombardment of the emitter tip is a second important effect that limits the lifetime of field emitters. Positive ions are created in the vacuum space between the anode and cathode by the collision of the emitted electrons with the residual gas atoms.[78-81] Smith has shown that positive ions created in the vacuum gap carry an average energy of  $V_{ac}/10$  to the surface of the cathode where  $V_{ac}$  is the applied anode-to-cathode voltage. Operation voltages of field emitters

are such that the average energy of the positive ions is near or above the physical sputtering threshold of cathode materials.[82] The surface morphology changes that can result from the ion sputtering include sharpening of the emitter tip[78, 83] or the creation of nanometer-sized protrusions that increase the local field enhancement that can increase current to the point that the emitter tip can be destroyed. Emitter materials that are resistant to sputtering can thus be operated at higher voltages than materials with a lower threshold for sputtering.

It is anticipated that the nitride semiconductors are good candidates for field emitters based on the criteria of high chemical inertness and high resistance to sputtering discussed above. The low reactivity and high sputtering energies of the nitride semiconductors are a result of the strong bonds between the atoms in the nitride crystals. The difficulty of wet chemically etching the nitride semiconductors indicates the low reactivity of the nitride semiconductors. Currently no practical chemical etches are known for the nitride semiconductors. Dry etching, such as reactive ion etching (RIE) of nitride semiconductors generally requires a high plasma voltage which indicates a physical etch, dependent on the sputtering of atoms. While resistance to reactions is beneficial for all field emitters, resistance to sputtering only effects field emitters operated at high voltage. Thus for vacuum microelectronic field emitters operated at low voltage, the resistance to sputtering of the nitrides will not be so important as their chemical inertness.

# Refinements to Field Emission Theory

The above treatment of field emission theory made use of several simplifying assumptions: low temperature (in fact, 0 K), parabolic bands, emission from only the conduction band, ignoring of surface states, a planar surface, simple image theory, no account of space charge effects, and an implicit assumption that, in an array, all tips have the same parameters. Removing each of these assumptions complicates the theory but also elucidates interesting physics. The

effect of finite temperature has been treated by a number of authors.[21, 84-86] Band structure and surface state effects have also been actively studied, largely because of the information about the surface band structure that may be obtained from field emission measurements.[87-97] Several researchers have attempted to calculated more accurate theories of field emission using more realistic models for the surface barrier.[98-106] Electron space charge in the volume surrounding a field emission tip will tend to lower the field at the tip and thus will cause the amount of field emission current to saturate.[39, 49, 107-112] Jensen et al. have studied the effects of the statistical distribution of field emitter parameters, such as the field enhancement and work function,[113] and the effect of neighboring tips in an array has also been studied.[114]

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# **Chapter Three**

# **GaN Field Emitter Development**

# (3.1) Introduction

Development of vacuum microelectronic GaN field emitter arrays (FEAs) involves the production of the field emission tips, microelectronic fabrication of the field emitter device, and testing of the emission characteristics of the field emitter. GaN, as a material for field emission tips, possesses several properties that make it attractive: n-type doping to increase electron concentration in the conduction band, a hard and non-reactive surface which may potentially benefit the stability and lifetime of GaN-based field emitters, and a method by which uniform arrays of field emitters can be formed. The technology by which GaN field emitters are produced is selective area, metalorganic chemical vapor deposition (MOCVD) which will be the concern of section (3.2). Then the fabrication and testing of the first GaN field emitter arrays, making use of an external anode, will be presented in section (3.3). Finally, in section (3.4) we will detail the fabrication and testing of GaN field emitter arrays with an integrated anode which allows more reproducible results at lower voltages than the arrays with external anodes.

#### (3.2) GaN Field Emitter Growth

There are several options for producing the sharp, tip-like features necessary for field emitter arrays (FEAs). The first reproducible field emitters were made by electrolytically etching the ends of tungsten wires.[1] The first microscopic field emitter arrays were fabricated by Spindt in 1968.[2] Spindt used angled electron beam evaporation of molybdenum through lithographically

produced holes in a silicon dioxide layer to form metallic cones.[3] The first microelectronic semiconductor field emitters were produced from silicon by Thomas and Nathanson in 1972 by employing wet chemical etching.[4] Isotropic and orientation-dependent etching, and plasma etching have also been used to produce Si field emitter arrays.[5-7] Another method for production of field emitters is the directionally solidified eutectic technique, which has also been termed the vapor-liquid-solid technique.[8, 9] In this technique, a eutectic of two compounds is used to grow a needle of one of the constituents. Field emitter arrays can also be produced by the use of the transfer mold technique.[10] The transfer mold technique uses a substrate with etched pits (the mold). The pits are filled by evaporation or deposition, and the mold is removed to produce a freestanding FEA. The transfer mold technique is versatile, in that, almost any material can be evaporated into the mold to produce an FEA. A final technique for producing FEAs is the selective area metalorganic chemical vapor deposition (MOCVD) epitaxial growth of field emitter arrays. This technique has been used for the production of GaAs FEAs[11] and was the method used in this work to form GaN field emitter arrays.

Selective-area epitaxial growth is the growth of epitaxial layers of semiconductors in the unmasked regions of a patterned template. The template can be a substrate or a previously grown planar epitaxial film. The mask is a thin layer of a different material deposited on the substrate. Selective growth occurs when the masked template is placed back into the growth system and additional growth is accomplished. MOCVD growth involves the use of metalorganic gases to deliver the semiconductor species to the substrate. GaN MOCVD uses trimethylgallium to provide the Ga and ammonia (NH<sub>3</sub>) to provide the N, and these precursors are carried to the reactor by a hydrogen carrier gas. In the reactor, the precursors decompose at the heated surface of the substrate, leaving the desired element on the surface. The growth is selective if the new material does not deposit on the mask

and growth occurs only in the unmasked regions. Depending on the growth conditions, the selective growth may rise vertically up from the unmasked regions or it may begin to grow laterally over the masked regions. The later condition is termed lateral epitaxial overgrowth (LEO) and has been used to reduce the defect density in films of nitride semiconductors.[12, 13] LEO has the potential of providing a better substrate than sapphire or SiC for nitride-based electronic and optoelectronic devices.

Kitamura et al. were the first to grow arrays of GaN pyramids using selective area epitaxial growth in 1995.[14] The template they used was a 2  $\mu$ m thick layer of GaN grown on a sapphire substrate with an AlN buffer layer. They used a thin silicon dioxide layer patterned with an array of 5  $\mu$ m hexagonal openings as the mask. In addition, in 1995, selective growth studies of GaN were beginning at the University of California, Santa Barbara (UCSB). In the first UCSB experiment, the silicon dioxide mask was patterned into intersecting, perpendicular openings exposing the underlying GaN that was grown on a c-plane

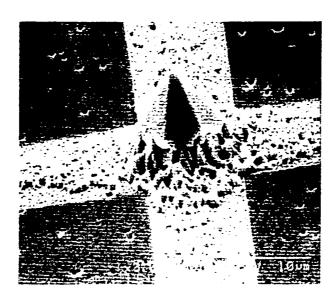


Figure 3.1. SEM picture of the first UCSB MOCVD GaN pyramids grown by selective area epitaxial regrowth. The dark gray regions are the SiO<sub>2</sub> mask and the light gray is the GaN.

sapphire substrate. The growth conditions for the planar GaN films are given elsewhere. [15] Selective growth was performed on the samples and GaN growth in the lines was observed. At the intersections of the lines, GaN pyramids grew as shown in Figure 3.1. The pyramids showed poor morphology and little uniformity in the early growths. The six sides of the hexagonal pyramid are the  $\{1\overline{1}01\}$  planes of the hexagonal crystal lattice.

Next, research was begun into characterizing and optimizing the growth of the pyramids in regular arrays using a dot-patterned mask of SiO<sub>2</sub> on a layer of MOCVD-grown GaN. The shape of the openings was circular and not hexagonal The resulting GaN pyramids grow oriented to the as in Kitamura's work. underlying GaN and it is not necessary to try to align the mask with the GaN layer. The mask pattern variations that were studied involved varying the size of the pyramid base and the density of openings in the mask. The height of the pyramids is fixed by the geometry of the GaN crystal and is given by  $h = rc/a\cos 30^\circ$ , where c and a are the lattice constants of the crystal (see Appendix B for a table of physical constants of GaN) and r is the radius of the inscribed circle at the base of the pyramid. When the numerical values are plugged into the equation for the height, the result is h = 1.8r, or the height is 0.9 times the separation of opposite sides of the pyramid at the base (hereafter noted as the base width). To put it a different way, the pyramids are about as tall as they are wide. The angle of the sides of the pyramid to the substrate is 61.96°. The MOCVD parameters that can be varied to affect the selective growth are the pressure, temperature, flow rates of the precursors, and the III/V ratio of the precursors.

The characterization and optimization of the GaN selective area growth was the doctoral dissertation research of David Kapolnek in the Materials Department at UCSB.[16] Dr. Kapolnek and UCSB graduate students Peter Kozodoy and Huili Xing performed all of the selective area MOCVD growth for the samples described herein. In addition, the MOCVD template layers were grown by Dr. Kapolnek,

Dr. James Ibbetson, Paul Fini, and Peter Kozodoy, all of UCSB. In addition to the original work of Kitamura et al., [14, 17] other selective growth studies of GaN and its alloys have been reported. Akasaka et al. have produced selectively grown GaN hexagonal prisms with facets perpendicular to the growth plane, [18] and selective overgrowth with rectangular cross-sections have been produced for LEO.[19] Bidnyk et al. have produced and are studying GaN pyramids for use as the cavity of a semiconductor laser. [20] GaN pyramids for field emission are also being studied by Nam et al. at North Carolina State University, [21], Kozawa et al. at Toyota Central R&D Labs and Kyoto University[22], and their results will be compared to our work below. Recently, Kawaguchi et al. have presented growth of GaN pyramids on a Si substrate for use in FEAs but they have not presented any emission current results to-date. [23]

An important result of Dr. Kapolnek's dissertation work was the determination of growth conditions at which GaN regrowth is not only selective-area, but also *self-limiting*. The self-limitation of the pyramid growth has important implications for the use of GaN pyramids in FEAs. The self-limited growth of the pyramids results when the growth of the  $\{1\overline{1}01\}$  planes (the pyramid sides) is much slower than the growth of the (0001) plane (the basal plane). Thus when the

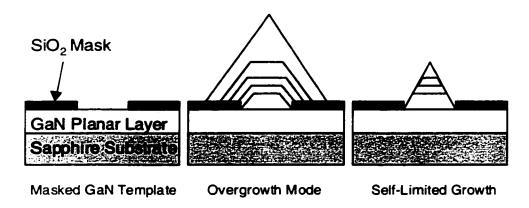


Figure 3.2. Comparison of the overgrowth mode and self-limited growth mode of GaN FEA pyramids.

pyramid formation is complete, the growth of the pyramid slows or stops altogether. This process is illustrated in Figure 3.2. The figure also depicts the overgrowth mode, in which the GaN continues to grow laterally over the masked regions after it has grown above the mask surface. In the overgrowth mode, inhomogeneities in the MOCVD reactor can lead to large differences in the size and shape of the pyramids over the array. The self-limited mode helps to mitigate the effects of the inhomogeneities. Transmission electron microscopy and double crystal x-ray diffraction experiments conducted by Dr. Kapolnek indicated that the structural quality of the GaN pyramids was similar to the underlying GaN layer.[24] The optimal conditions for selective area, self-limited growth of GaN pyramids are given in Table 3.1.[25]

Table 3.1. Selective Area, Self-limited GaN Growth Parameters.

Growth Parameter	Value	
Temperature	980°C	
Pressure	76 Torr	
Trimethylgallium flow	18.4 μmol/min	
Ammonia flow	0.22 mol/min	
Disilane flow	0.9 nmol/min	

#### (3.3) GaN FEAs with an External Anode

Field emission experiments using the GaN pyramids grown as described above will be the subject of this section. Although Kitamura et al. were the first to report the growth of GaN pyramids, they apparently did not try to use them as field emitter arrays. The first UCSB-grown GaN FEA samples were composed of arrays of GaN pyramids of differing size and density. The pyramid sizes varied from 2-12 µm base width and tip-to-tip spacing varied from 3-13 µm. The samples were characterized by viewing with scanning electron microscopes, processed to include an ohmic contact, and finally, field emission measurements were taken.

Fabrication of the GaN FEAs began with a template. As noted above, the template consists of a clean, planar GaN film, 2 µm thick, grown on a c-plane oriented sapphire substrate. Then, a layer of SiO<sub>2</sub> is deposited by either electronbeam evaporation or plasma-enhanced chemical vapor deposition (PECVD) to a thickness of 200-400 nm. The SiO<sub>2</sub>-mask layer was patterned by contact lithography and buffered HF etching to expose circular regions of GaN for selective area MOCVD. Dry etching of the oxide was also tried by reactive ion etching (RIE) but produced poor regrowth results, presumably because of damage caused by the RIE. The photoresist used to pattern the mask was removed by solvent cleaning and photoresist stripper. The cleanliness of the exposed GaN is crucial to the success of the selective growth. To secure this end, the sample was treated by five minutes of ultraviolet light and ozone to clean hydrocarbon contaminants from the surface. Immediately before being placed into the MOCVD reactor for the selective area growth, the sample was dipped into a dilute buffered HF solution to remove any surface oxide. After the selective MOCVD growth, the SiO<sub>2</sub> mask was removed by an HF etch. Because of the high temperature of the growth process, the mask was difficult to remove after growth, and long etch times in concentrated HF solutions (1:1 HF:H<sub>2</sub>O) were necessary to completely remove the mask. The

difficulty could have resulted from both the densification of the  $SiO_2$  mask material or the nitridization of the mask while in the MOCVD reactor. Changes in the mask thickness and index of refraction were observed using ellipsometry. Contact to the GaN template layer was made by thermal evaporation of Al and e-beam evaporation of Ti/Au metals. Al is used because it forms a non-alloyed ohmic contact to n-type GaN and the Ti/Au metalization provides a surface for Au-wire bonding.

SEM characterization was the primary method used to characterize the growth and morphology of the GaN pyramids. Depending on the growth conditions and the time of growth, various states of completion of the pyramids could be observed. Figure 3.3 shows two SEM micrographs of different arrays on a single sample. The less dense array completes in a shorter time than the denser array. For FEAs, the sharpness of the tips is the most important physical feature of

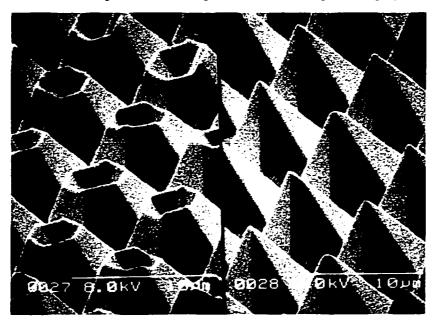


Figure 3.3. SEM micrograph of two GaN pyramid arrays on the same sample with different levels of completion. The array on the left side is 7.5  $\mu$ m base width pyramids on 8.5  $\mu$ m centers and the array on the right side is 5  $\mu$ m base width pyramids on 8.5  $\mu$ m centers.

the array. The sharpness of the tips is difficult to measure with a conventional SEM because the dimensions of the tips are below the typical resolution. Higher resolution can be achieved by using a low-voltage field emission-based SEM (FE-SEM). An example of an image of the top of a pyramid is shown in the inset of Figure 3.4 in which the sample was tilted by nearly 90°. The magnified tip has a radius of curvature of about 70 nm. Over a typical array, a range of tip radii between 70 and 100 nm was observed. As compared to Si field emitter tips that can have radii of less than 1 nm,[26] these radii are quite large. It appears from the micrograph that the pyramids are not terminating at a single atom. No attempt was made to optimize the growth of the GaN pyramids with respect to tip sharpness, but this would be an important direction for future growth study of GaN pyramids. Using the field enhancement equation given in Chapter 2, the field enhancement for

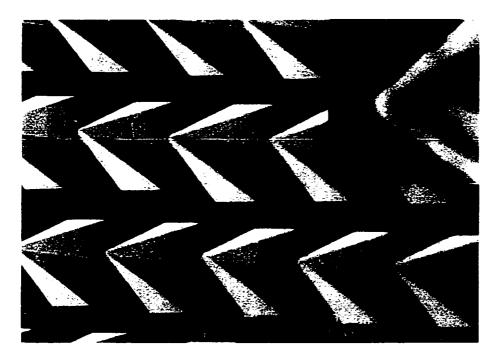


Figure 3.4. SEM micrograph of an array of completed, self-limited GaN pyramids. The inset shows a close-up image of a pyramid top with a radius of about 70 nm.

a tip of 70-nm radius (for a 1-mm anode-cathode separation) is between  $3 \times 10^6$  and  $1.4 \times 10^7$  m<sup>-1</sup>.

Electrical tests were made in ultra-high vacuum (UHV) using a custommade stainless steel electrical test chamber. The vacuum system is oil-free and can maintain base pressures below 10<sup>-9</sup> Torr. Rough pumping is accomplished first by a Venturi pump and then by liquid-nitrogen-cooled sorption pumps. Two sorption pumps are used in succession to bring the pressure to the  $1\times10^{-4}$  Torr range. Then final pumping to UHV is accomplished using a CTI Cryogenics 8F on-board cyropump and a Varian Model 921-0066 VacIon® ion pump. Intermittent use of a Varian Ti-sublimation pump was made to lower the pressure even further. Pressure measurements of the measurement chamber were made by a Granville-Phillips nude ion gauge placed near the sample holder. The system in composed of two chambers. The lower chamber is separated from the measurement chamber by a gate valve and is maintained at UHV to speed the pump down time from roughing to UHV. The total volume of the system is about 70 L. Twelve pin-type electrical feedthroughs are available for device measurements as well as are three MHV coaxial feedthroughs. Another port contains two thermocouple feedthroughs and three more pin feedthroughs, which are used to supply current for the sample heater for sample degassing. The system also contains a Cs dispenser and shutter for Cs coating of surfaces, although Cs was not used in this study. The entire system is bake-able to 200°C to increase the rate of removal of water vapor from the system.

The samples are placed into the vacuum system mounted to a custom-built sample holder (see Figure 3.5). The sample holder is made of machinable ceramic and has an integrated resistive sample heater and thermocouple for degassing of the sample. Twelve Cu pins are available for wire bonds from the sample. The pins can be connected by wires to the electrical pin feedthroughs of the system. The sample is bonded using indium to a silicon spacer that is clipped to the sample holder. A ceramic spacer is placed between the sample holder and the anode to

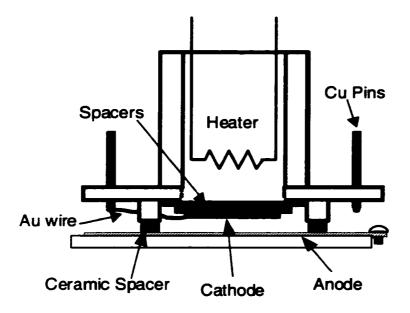


Figure 3.5. Schematic of UHV sample holder. The spacers are used to vary the anode-cathode separation. Au wire bonds connect the sample contacts to the Cu pins on the holder, which are attached by wires to the system feedthroughs.

control the anode-to-cathode distance. The anode is a flat, rigid foil of tantalum. Tests of leakage currents using planar GaN samples in the sample holder were performed and showed no measurable currents up to the 3000 V maximum voltage available.

Electrical measurements of the field emitters were made with several instruments. After pump-down, a low-voltage measurement, from 0 to 100 V, was made using a Hewlett-Packard 4145B semiconductor parameter analyzer. This measurement was useful for detecting shorts and for measurement of field emission at voltages below 100 V. Most of the field emission measurements were made using a computer-controlled picoammeter and high voltage power supply. A Bertan Series 225 high voltage power supply (DC) and Keithley 486 picoammeter were connected by a general purpose instrumentation bus (GPIB; IEEE-488) to a computer running National Instruments Labview<sup>TM</sup> instrumentation control

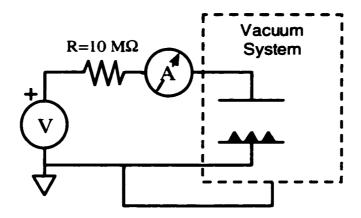


Figure 3.6. Schematic of electrical circuit used to measure the field emission from GaN FEAs. The resistor is used to protect the picoammeter and the arrays from vacuum arcs.

software. A custom Labview program was written to take the current and voltage measurements. In addition to selecting the voltage range and step-size, the program allowed control of the number of current readings to average at each voltage point and the standard deviation and standard error of the emission current were calculated. Several seconds were allowed between changing the voltage and measuring the current in order to allow time for the transient RC charging currents of the cables to decay. The last of the instruments used to take field emission measurements was a Tektronix 371a high power curve tracer. This instrument allowed measurements at higher voltage than the HP 4145B and faster sweeps than could be achieved with the picoammeter setup. The Tektronix curve tracer has a lower current resolution ( $\mu$ A) compared to the HP 4145B and picoammeter, so that only FEAs that could support relatively large currents could be measured this way.

The electrical measurements of the emission current by the picoammeter system were made using the circuit shown in Figure 3.6. The voltage supply was connected by MHV coaxial cable to a current-limiting resistor. Current-limiting resistors of 99 k $\Omega$ , 1 M $\Omega$ , and 10 M $\Omega$  were used. The lower the current-limiting resistor, the more susceptible the arrays were to failure by destructive current

surges. The current-limiting resistor was connected to the picoammeter, which was connected to the anode of the field emitter through the electrical feedthroughs. The field emitters were connected to the ground of the high-voltage power supply.

The first emission measurements of GaN field emitters took place in September of 1995. Two large area Al/Ti/Au contacts were deposited on a planar region of a growth sample that had several arrays with different sized tips and varying levels of tip completion. The separate contacts allowed the conductivity of the unintentionally doped *n*-type GaN and the nature of the contacts to be assessed. The contacts appeared ohmic and the GaN was conductive. The conductivity of the tips appears to be similar to the planar GaN layers as tested by probing the pyramids with a tungsten probe and observing the current-voltage characteristic between the probe at the pyramid and an ohmic contact on the planar region. The point contact between the tungsten probe and the pyramid showed a characteristic similar to a point contact between the probe and planar region of GaN. Thus, we can be reasonably certain the GaN pyramids have conductivity similar to the planar GaN. The first current-voltage characteristics of GaN field emission is shown in Figure 3.7 along with the Fowler-Nordheim (F-N) plot of the data. The emission

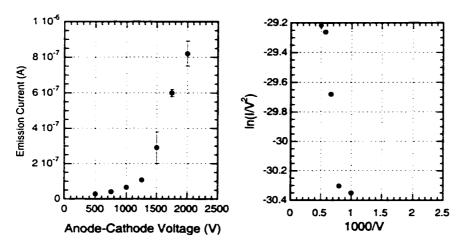


Figure 3.7. First GaN field emission measurements (left) and Fowler-Nordheim plot (right).

was quite low  $(0.8 \,\mu\text{A}$  at 2000 V) and the F-N plot was linear over a quite narrow region. The anode-cathode separation in this case was approximately 0.5 mm and the turn-on voltage was about 1200 V (found by extrapolating the linear high-current region to the voltage axis). As stated above, this sample had many different sized pyramids with varying morphology and, therefore, the field emission parameters were not calculated because they are essentially meaningless in this case.

Improved field emission results were obtained from FEAs grown specifically for field emission measurements (as opposed to the growth study samples). The arrays had a single tip size and density, and the pyramids were grown to completion. The array consisted of approximately 245,000 pyramids in a close-packed array. The pyramids had 5  $\mu$ m base width and were separated by 11  $\mu$ m tip-to-tip. The total array area was approximately 0.26 cm<sup>2</sup> giving a final tip density of  $9.4 \times 10^5$  cm<sup>-2</sup>. The anode-cathode separation was set to 0.25 mm using a

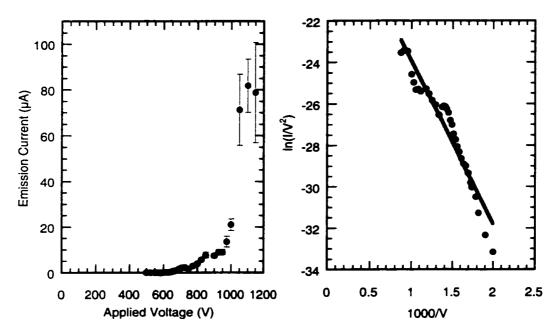


Figure 3.8. Field emission I-V (left) and F-N plot (right) for an array of 5  $\mu$ m pyramids on 11  $\mu$ m centers. The F-N plot is shown with a linear fit over several orders of magnitude indicating field emission.

ceramic spacer. The emission results of this array were much better than the previous one, giving 81.7  $\mu$ A at only 1100 V as shown in Figure 3.8. The turn-on voltage, which is defined for the remainder of this dissertation as the voltage at which the total array current was 10 nA, was about 560 V. These voltages were about half of what was obtained from the first array, as one would expect because the anode-cathode separation was halved in this experiment compared to the previous. The field enhancement factor and emission area could be extracted from this data, assuming that the electron affinity of GaN is 3.5 eV. The field enhancement factor extracted was about 54,000 cm<sup>-1</sup> and the emission area was  $6.1 \times 10^{-12}$  cm<sup>2</sup>. If we model the emission area as a hemisphere with a radius of 90 nm, the emission area for a single tip is about  $1 \times 10^{-9}$  cm<sup>2</sup>. Thus, the emission area extracted for the whole array is smaller than the area of the tip of a single pyramid. This suggests that the emission is coming from relatively few pyramids, and the emission is most likely being emitted from nanometer-sized features on the pyramids.

The above results bear remarkable agreement with other researchers' results on GaN FEAs. Comparison of field emission measurements is often difficult because of different emitter and anode geometries. One measurement commonly used to compare field emission data between different measurements is the macroscopic or plane-parallel electric field at turn-on. This is calculated by taking the turn-on voltage and dividing by the anode-cathode separation. The data given above give the plane-parallel turn-on fields of 2.4 V/µm and 2.2 V/µm. Nam et al., at North Carolina State University (NCSU), reported a turn-on field of 25 V/µm using a moveable Mo anode (5 mm diameter).[27] Later measurements from NCSU have reported a turn-on field of 7 V/µm (using a 3 mm diameter Mo anode).[28, 29] Calculation of the turn-on field from the data given by Kozawa et al. indicate at turn-on field of 133 V/µm, using a gold ball anode of 1 mm diameter, 1.5 µm above the sample.[30] Comparison of our data and NCSU's data versus

Kozawa's is aggravated by the differences in measurement geometry. Whereas NCSU's and our experiments used an anode geometry that applied the field over a large portion of the arrays, the experiment of Kozawa et al. used a geometry in which only a few pyramids likely contributed to the emission current. published SEM micrographs of the emitter arrays and the top of the pyramids of Kozawa et al. and Nam et al. are virtually indistinguishable from our micrographs, indicating the reproducibility of the pyramid growth. Ward et al. [28] and Nemanich et al.[29] have also been able to image the emission of GaN field emitter arrays on phosphor screens using field emission electron microscopy (FEEM) and photoemission electron microscopy (PEEM). The images of the electron emission show relatively uniform emission over the arrays. In addition, experimental analysis of the electron energy distribution by Ward et al. of the field emitted electrons showed no voltage-dependent energy shift of the distribution, which indicated that no significant potential drop is occurring in the GaN sample from the contacts to the pyramids. This suggests a high conductivity in the GaN planar films and pyramids.[28] In addition to the above mentioned studies of GaN FEAs, studies on the field emission from planar GaN films on Si(111) substrates have be reported,[31] and the negative electron affinity of AlN and AlGaN alloys has sparked interest in those materials for field emission.[32]

Table 3.2. Comparison of Plane-Parallel Turn-on Fields of GaN FEAs.

Research Group	Plane-Parallel Turn-On Field (V/µm)		
Kozawa et al., Toyota Central R&D	133		
Ward et al., NCSU	7		
	25		
UCSB	2.2		
	2.4		

Our experiments involving the external anode had several difficulties. First, the minimum separation available was limited to the minimum thickness that

machinable ceramic spacers could be fabricated. This limit was about 0.1 mm for the physics machine shop at UCSB. The rather large separation dictated that large voltages would be necessary for field emission. The large voltages necessary increased the likelihood that the arrays would be damaged in the case of a vacuum arc. The damage from an arc is related to the energy stored in the circuit. In this case, the field emitter-anode combination formed a capacitor so the stored energy is proportional to the capacitance times the square of the voltage so high voltages can lead to very destructive arcs. The second difficulty was the poor accuracy in determining the anode-cathode separation and maintaining parallelism between the anode and the sample. As discussed in Chapter 2, the field-emitted current is extremely sensitive to the value of the field at the emitter tip, and small changes in the anode-cathode separation could lead to large changes in emitted current. The final disadvantage of the external anode structure, was the fact that only one array could be placed into the vacuum system at a time. Pump-down typically lasted from half a day for a clean system, to several days when the system required a bake. This presented a severe bottleneck for performing the measurements. A solution to this difficulty was to integrate the anode onto the wafer with the FEAs, and this will be the subject of the next section.

#### (3.4) GaN Field Emitter Arrays with Integrated Anode

To decrease and provide better control of the anode-cathode separation, a design integrating the anode on wafer with the FEA was proposed. The anode was fabricated as an air-bridge over the field emission array. The integrated anode design in this work is similar to the integrated anode developed by Yoon *et al.* for planar cold cathodes.[33] Thus, the anode can be controllably placed on the order of microns away from the pyramid tops. First, the fabrication of the field emitter arrays and integrated anode are detailed. Next, experimental measurements of the physical and electrical characteristics of the FEAs are presented and the results discussed.

Fabrication of the GaN FEAs involved the following steps in a five mask process: patterning of the growth mask to define the arrays, selective epitaxy of the hexagonal GaN pyramids, and definition of the cathode mesa, contacts, and anode air-bridge. A schematic process flow is illustrated in Figure 3.9(a)-(h) and an example process sheet is given in Appendix C. To begin, planar GaN films of nominally 2 µm thickness were grown by atmospheric pressure MOCVD. Unlike the arrays describe above which were unintentionally n-type, the conductivity of these layers was controlled by doping and the films and pyramids were doped with Si for a carrier concentration of about  $3\times10^{18}$  cm<sup>-3</sup>. On the planar GaN layer, a mask film of 2000 Å of SiO<sub>2</sub> was deposited by PECVD. The SiO<sub>2</sub> was patterned with arrays of 2 µm diameter holes on 12 µm centers by contact lithography and buffered HF etching (Figure 3.9(a)-(b)). Devices were arranged in suites with four devices per suite. Each suite had a single-tip emitter, 5-tip array, 10-tip array, and a 40-tip array. Then, the sample was cleaned using resist stripper, solvents, and ultraviolet-light-activated ozone to ensure a low level of contamination. Finally, immediately prior to introduction into the regrowth reactor, the sample was given a brief dip in dilute buffered HF to ensure an oxide-free GaN surface.

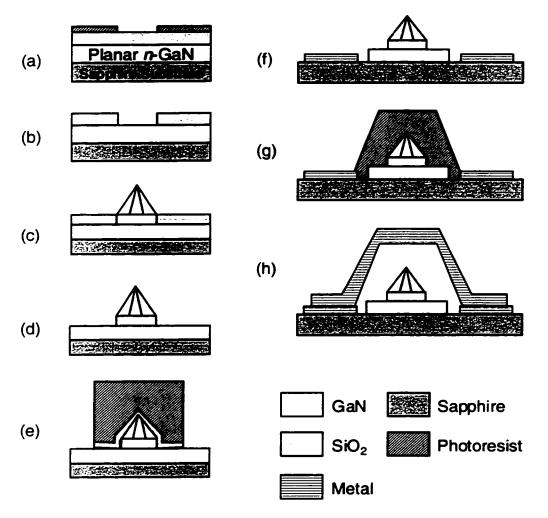


Figure 3.9.(a)-(i) Process flow of integrated anode field emission array.

After growth of the GaN pyramids (Figure 3.9(c)), fabrication proceeded with the definition of the cathode mesa. First, the selective-area growth mask was removed in an HF etch (Figure 3.9(d)). Then, the FEA mesa was defined by Cl<sub>2</sub>-based reactive-ion etching (RIE) using photoresist (3 μm) and SiO<sub>2</sub> as an etch mask (Figure 3.9(e)). The etch parameters were 5 mTorr chamber pressure, 10 sccm of Cl<sub>2</sub> flow and, 200 W of plasma power giving an etch rate of about 1250 Å/minute. The protection of the pyramid tops by the SiO<sub>2</sub> layer was crucial

to the survival of the emitters during the RIE etch. Thick resists (>6  $\mu$ m) were tried but they tended to deform during the etching. The SiO<sub>2</sub> and photoresist combination proved to be acceptable and only slightly increased the complexity of the process. The GaN was etched down to the sapphire to isolate the cathodes and provide an insulating substrate for the anode.

The cathode contact pads and the anode supports were patterned next (Figure 3.9(f)). Contact lithography and image reversal resist was used in a lift-off process to define the contact pads and anode air-bridge supports. The contact metalisation layers were 100 Å of Ti and 5000 Å of Au. The excess metal was lifted off in acetone with brief ultrasonic agitation. The cathode contacts were completed by an alloying step in a rapid thermal annealer at 700°C for 15 seconds. The next mask step consists of opening the air-bridge supports and anode contact pads. Two layers of Nano<sup>TM</sup> PMGI SF15 positive photoresist were spun on the sample. The thickness of the PMGI is controlled by selecting the spin speed and the thickness of the PMGI defines the anode-cathode separation. On top of the PMGI, a positive resist was spun and patterned to expose the PMGI where the airbridge supports were to be located. This positive resist served as the exposure mask for the deep ultraviolet exposure ( $\lambda$ =240 nm) of the PMGI. The PMGI was then developed in Microposit® SAL®-101 Developer. Figure 3.9(g) shows the pyramids and mesa coated by the PMGI resist that will form the sacrificial layer under the anode.

Finally, the air-bridge was patterned, the bridge metal evaporated, and the PMGI was laterally etched from under the bridge to form the vacuum cavity (Figure 3.9(h)). A tri-layer photoresist system was used to provide a thick lift-off profile for the thick air-bridge metalisation. The bridge metal was 200 Å of Ni and 1  $\mu$ m of Au. The excess metal was lifted-off in acetone with exposure to brief ultrasonic agitation. The final step in the process was the lateral etching of the

PMGI sacrificial layer to undercut the bridge and open the vacuum cavity. The cavity was not sealed by this fabrication but the structures can easily be modified to accomplish integral cavity sealing.[34, 35] The sample was then cleaned and given a brief HF dip to remove any residual oxide from the surface before being transferred to the UHV electrical testing system.

SEM and optical microscope observation served as the best means to characterize and monitor the processing results. Figure 3.10 shows an optical microscope image of a top view of a suite of GaN FEAs. A suite takes up a die area of  $2.2 \times 10^{-2}$  cm<sup>2</sup>. The cathode mesas are positioned around a centrally located Schottky bond pad. The Schottky bond pad is connected to Schottky contacts on each of the cathode mesas. The Schottky contacts were to be used to measure the temperature change of the emitter arrays during emission but this experiment was not carried out. Each FEA had its own cathode contact and anode contact so that damage would be limited to a single device in case of a vacuum arc. The bond pads were 250  $\mu$ m  $\times$  500  $\mu$ m. Figure 3.11 presents an SEM image of an array tilted

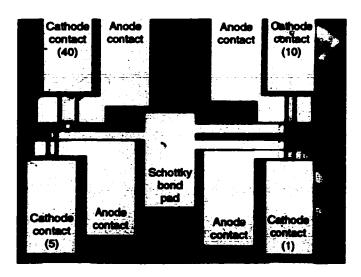


Figure 3.10. Optical microscope top-view of suite of GaN FEAs. The number of tips in the device array is indicated in parantheses. Each array has its own cathode and anode contact pads. The airbridges are connected to the anode contact pads and span the GaN FEAs.



Figure 3.11. SEM micrograph of completed air bridge anode.

at an angle so that the air-bridge is clearly shown. The air bridges over the narrow arrays (1, 5, and 10 tips) spanned a gap of about 50  $\mu$ m and the those for the 40-tip arrays spanned about 90  $\mu$ m and tall bridges sometimes showed a slight sag (<1  $\mu$ m) in the middle.

Lowering of the operating voltage of GaN FEAs with an integrated anode was observed by fabricating three samples, each with different anode-cathode spacing. The anode-cathode separation, defined as the distance between the anode and the top of the GaN pyramid, was measured by observation in an SEM. The separations, measured turn-on voltage, field enhancement, and emission area of each of the samples are listed in Table 3.3 and the *I-V* characteristics and F-N plots are given in Figure 3.12. The field enhancement and emission area was calculated from the F-N plots of the *I-V* data assuming that the electron affinity of GaN is 3.5 eV. The turn-on voltage decreased as the anode-cathode separation decreased, as would be expected. The field enhancement data in Table 3.3 was fit to the concentric sphere model given in equation (2.24) of Chapter 2. The fit and experimental points are shown in Figure 3.13. The fit appears reasonable in the

Table 3.3. Measured Parameters of GaN FEAs with Integrated Anode.

Sample Number	Anode- cathode separation (µm)	Turn-on voltage (V)	Field Enhancement (cm <sup>-1</sup> )	Emission Area (cm²)	Number of tips in array
1	2.35	435	60,000	4.1×10 <sup>-11</sup>	10
2	1.4	290	67,000	2.6×10 <sup>-8</sup>	40
3	0.4	176	125,000	1.1×10 <sup>-9</sup>	5

figure, but the k parameter from equation (2.24) extracted from the fit is 0.81, which is not in the range acceptable for the concentric sphere model (1<k<5). In addition, the extracted tip radius is 220 nm, which is over three times that measured by the SEM. The probable reason for the disparity of the fit with the data is that the concentric sphere model is most likely not a good model for sample #3, in which the anode-cathode spacing was only 0.4  $\mu$ m. Another difficulty in analyzing this data is that the tops of the tips of sample #1 were known to be etched during the mesa RIE, and this would decrease the field enhancement factor compared to the other samples, which had sharp tops.

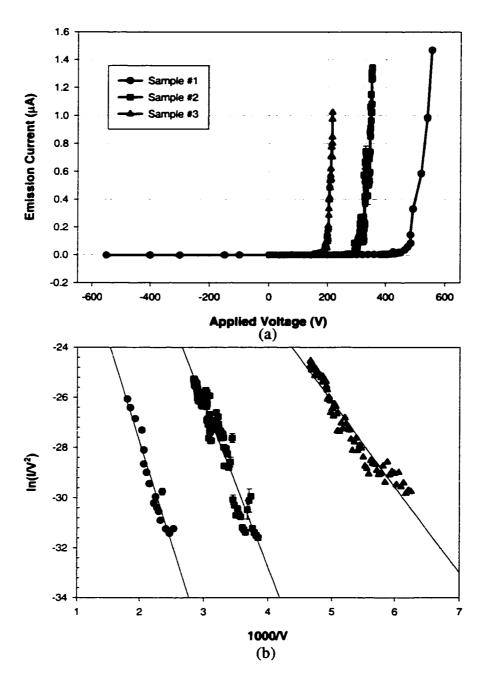


Figure 3.12. (a) *I-V* characteristic of the GaN FEAs listed in Table 3.3. (b) F-N plots for data given in (a) with weighted least squares fits.

Finally, it can also be seen in Table 3.3 that the emission area does not scale with the number of tips in the arrays. This suggests that the emission was likely

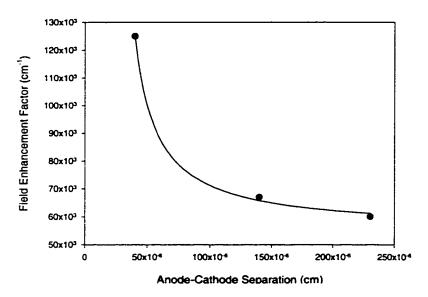


Figure 3.13. Field enhancement as a function of anodecathode separation and fit.

coming from one tip or a few of the tips in the arrays. Jenkins has also shown that the Fowler-Nordheim formalism tends to underestimate the emission area and overestimate the field enhancement factor.[36] The erroneous estimation of the Fowler-Nordheim formalism is a result of the assumption of a constant field enhancement factor over the tip surface and Jenkins has used a numerical approach to calculate the emission areas and field enhancements of vacuum microelectronic FEAs. The upshot is that in order to adequately compare field emission results from FEAs of significantly different geometry, one must have an accurate knowledge of the detailed geometry of the structures and numerical calculations must be used.

Various kinds of damage resulted from the arcing of the devices. The most common failure mode was melting and destruction of the anode. If the current was limited with a large resistor, damage was limited to the anode. An SEM image of a damaged anode is shown in Figure 3.14. As can be seen, the anode appears to have begun to melt and deform. A GaN tip can be observed in the area where the anode

deformed to expose the underlying structure. In all of the devices examined where the limited anode damage had occurred, none of the GaN pyramids showed any damage. If a smaller resistor was used to limit the current, damage was seen in the underlying GaN and more extensive anode damage extending out to the contact pad was observed. The conclusion that can be drawn from these observations is that the anode is the initiating component to the vacuum arc for these integrated anode structures. Lower voltage operation reduced the heating of the anode and increased the reliability of the emitters.

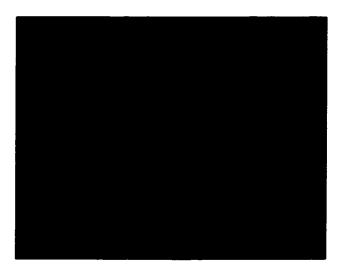


Figure 3.14. SEM image of anode damage caused by a vacuum arc. The field emitter tip shown on the mesa finger appears undamaged.

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# **Chapter Four**

# Piezoelectric Surface Barrier Lowering in InGaN/GaN Field Emitter Arrays

#### (4.1) Introduction

Paths to lowering the operating the voltage of field emitters include increasing the field enhancement, lowering the surface energy barrier height, and increasing the emission area. The two most important parameters are the surface barrier and the field enhancement factor because the emission current is exponentially related to both. The field enhancement factor can be increased by sharpening the emitters or making the device dimensions smaller as we showed with the integrated anode FEAs in Chapter 3. The fact that the GaN field emitters grow constrained by the crystal geometry gives the benefit of uniformity but with the disadvantage that the pyramids have a large tip angle (~60°) and thus a relatively low field enhancement factor. Methods have been demonstrated in other material systems to sharpen the emitters, either by the effects of oxidation[1-3] or by ion-beam milling[4-6], but no such method has been demonstrated for the nitrides, and it is also not clear if the methods would produce arrays of sufficient uniformity for practical FEA devices.

Lowering the effective surface barrier of the emitters is another method to increase the current at a given voltage for field emitters. The most common method to lower the work function or electron affinity of materials is the application of an electropositive adsorbate to the surface of the material. The most common adsorbate for reducing the surface barrier is cesium, and the mechanism of the cesium work function lowering and an estimate of the magnitude of the effect are given briefly in section (4.2). In Chapter 1, we discussed the fact that the use

of cesium has several drawbacks such as the requirement of UHV, migration of the cesium on the device, and possible compromising of the insulating components of the device. Section (4.3) presents an overview of the piezoelectric effect in III-V nitride semiconductors, which will form the basis of a new method to produce a large dipole at the surface of a field emitter. The effect of this dipole in lowering the electron affinity of InGaN/GaN FEAs is the subject of section (4.4). Using a strained layer of InGaN on the GaN pyramids, a large dipole can be grown into the crystal structure that lowers the effective electron affinity. Because the dipole is built into the crystal structure of the emitter, it will not suffer from the stability problems that mobile adsorbates, such as Cs, suffer. Finally, experimental measurements of the current-voltage characteristics of InGaN/GaN field emitters that show strong support for the model are presented in section (4.5).

#### (4.2) Surface Barrier Lowering Using Cesium

The use of electropositive adsorbates to lower the work function or electron affinity of materials has been investigated for cathode and photocathode applications.[7] The most technologically important electropositive adsorbates are the alkali metals which are known to have low ionization potentials, and the most important of the alkali metals for surface barrier modification has been cesium. Cesium has the lowest ionization potential of any element. The physics behind the surface barrier lowering of cesium adsorbates is still not completely understood for all material systems. The simplest model treats the cesium atom-surface interaction by way of a charge transfer from the cesium to the substrate. This is schematically represented, using a tight-binding approach, in Figure 4.1(taken after Fig. 4.1 in [7]). When the Cs atom adsorbs on the substrate, the highest energy electron in the Cs atom can transfer to the substrate, leaving the Cs ionized. A dipole is formed at the surface and this dipole counteracts the work function barrier of the substrate. In fact, each Cs atom does not transfer a full electron to the substrate, but rather, the

ionicity of the bond gives the fraction of the electronic charge transferred. The ionicity of the bond can be calculated from Pauling's electronegativity values for the elements. To calculate the order of magnitude of the charges involved in cesium-induced work function lowering, the case of GaAs will be considered because it is a well-studied system. For Cs on Ga or Cs on As, the ionicity of the bonds is about 0.19 and 0.35 respectively. For Cs on a GaAs surface, the effective work function is 1.4 eV, which is about 2.6 eV less than a clean GaAs surface

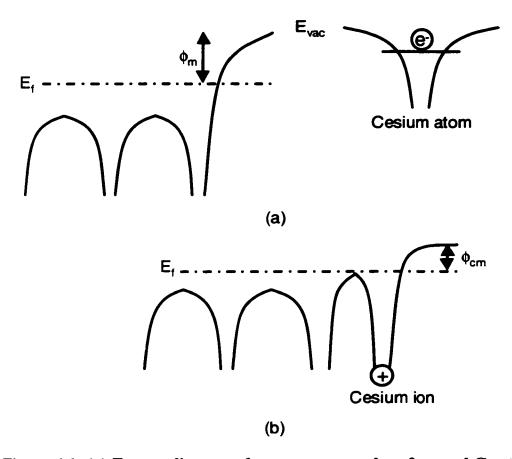


Figure 4.1. (a) Energy diagram of a separate metal surface and Cs atom with common vacuum level. The line on the Cs atom indicates the top-filled electron level. (b) As the Cs atom adsorbs on the metal surface, the Cs atom ionizes and the electron is transferred to the conduction band of the metal. The result is a surface dipole that counteracts the metal work function.

(4.0 eV).[8] The potential drop caused by a dipole is given by  $\Phi_d = \rho_s l/\varepsilon_o$  where  $\rho_s$  is the sheet charge of the dipole, and l is the length of the dipole. As an approximation, the dipole length is taken to be the length of Cs-Cs bond, about 4 Å. The dipole charge necessary to produce this change in potential is about  $3.6 \times 10^{13} q$  C/cm<sup>2</sup>. Given that each Cs contributes only a fraction of a charge to the dipole, the density of Cs atoms necessary to produce this charge density is in the range of  $1 \times 10^{14}$  atoms/cm<sup>2</sup>. This density is of the same order of the surface density of atoms of GaAs  $(4 \times 10^{14} \text{ atoms/cm}^2)$ . Thus, we see that in order to produce a large change in the surface energy barrier, a charge density of the order of  $10^{14}$  cm<sup>-2</sup> is necessary. Although, the use of cesium is a good method to achieve such large work function reduction, the instability of Cs in the vacuum environment, as discussed in Chapter 1, makes it an unsuitable technology for practical devices. A novel method to achieve dipoles of these magnitudes using the piezoelectric effect in the III-V nitrides will be the subject of the next two sections.

## (4.3) Piezoelectric Effect in Nitride Semiconductors

The piezoelectric effect was precisely defined by W.G. Cady as "electric polarization produced by mechanical strain in crystals belonging to certain crystal classes, the polarization being proportional to the strain and changing sign with it." [9] Stated mathematically, the relation between the electric polarization and the strain in the crystal (assuming no applied electric fields) is given by

$$P_i = e_{ij} S_j \tag{4.1}$$

where  $P_i$  is the polarization in the *i*-direction (in units of C/m<sup>2</sup>),  $e_{ij}$  are the piezoelectric stress constants (C/m<sup>2</sup>),  $S_j$  are the strain tensor components (m/m), i=1,2,3 represents the three Cartesian directions, j ranges from 1 to 6, and the Einstein summation convention has been employed. The above equation can be identified as a tensor equation where the strain tensor is a 6-component tensor and the stress constants form a  $3\times6$  tensor. The piezoelectric stress constant  $e_{ij}$  gives

the polarization in the *i*-direction caused by a *j*-stress. For j=1,2,3 the stress is a simple compressive or extensive stress component corresponding to the same *i*-directions, but for j=4,5,6 the stress components are shearing stresses. The piezoelectric polarization can also be given in terms of the stress tensor, **T**, and the piezoelectric strain constants,  $d_{ij}$  as

$$P_i = d_{ii}T_i \tag{4.2}$$

where stress has units of N/m<sup>2</sup>, and the units of the piezoelectric strain constants are given in C/N (or equivalently, m/V). Knowing that the strain and stress in a crystal are related through the elastic constants,  $c_{ij}$ , a relation between the piezoelectric strain and stress constants can be derived to yield

$$e_{mh} = \sum_{i=1}^{6} c_{ih} d_{mi} \tag{4.3}$$

where the elastic constants carry the units of N/m<sup>2</sup>. The above equations are the basic equations of piezoelectricity and the derivations are available in Cady's work cited above and other texts on piezoelectricity.[10, 11]

The piezoelectric polarization physically derives from the separation of

$$\mathbf{c} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix}$$
Elastic Stiffness Tensor
$$\mathbf{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$
Piezoelectric Strain Tensor

Figure 4.2. Tensors for evaluation of piezoelectric effects for crystals with 6mm symmetry.

charges that occurs when a strain or stress is applied to a crystal. In order for a uniform stress to induce the movement of the charges to produce an electric field, the crystal must not have a center of symmetry. Lack of a center of symmetry is the fundamental crystal characteristic that determines whether a crystal will be piezoelectric or not. As an example, a crystal from a system with no symmetry at all, the triclinic system will have the maximum of 18 independent piezoelectric constants. Additional crystal symmetries reduce the number of non-zero piezoelectric constants. The III-V nitrides can be grown in either a cubic (zincblende) or a hexagonal (wurtzite) crystal system. The most common type of nitride is the hexagonal type. The symmetry of the hexagonal nitrides system is denoted by 6mm, which indicates that it has a 6-fold rotation axis and two sets of mirror planes that contain the 6-fold axis.[12] The symmetry reduces the number of independent piezoelectric constants to three and the number of independent elastic constants to five. The elastic stiffness tensor and piezoelectric strain tensor for the hexagonal nitrides are given in Figure 4.2. The piezoelectric stress tensor has the same form as the piezoelectric strain tensor.

Strain in epitaxially grown semiconductors can be caused by either thermal expansion mismatch or lattice mismatch of the epitaxial layer and the substrate. In the initial growth of an epitaxial layer on a substrate of differing lattice constant, the epitaxial layer will grow with an in-plane lattice constant equal to that of the

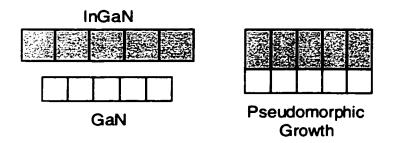


Figure 4.3. Illustration of the lattice dimension changes representative of pseudomorphic growth.

substrate. If the epitaxial layer's in-plane lattice constant is smaller than the substrate's, then the epitaxial layer will experience biaxial extensional strain in the growth plane. Conversely, if the epitaxial layer has a larger in-plane lattice constant than the substrate, the epitaxial layer will experience a biaxial compressional strain. To first order, the volume of the unit cell of the epitaxial layer will be the same as if the layer were grown with its natural lattice constant. Thus, extension in the growth plane will lead to compression in the growth direction, and compression in the growth plane will lead to extension in the growth direction. The above condition is termed pseudomorphic growth and is illustrated schematically in Figure 4.3. As the epitaxial growth is continued, the substrate's influence on the growth will weaken and dislocations will form to allow the epitaxial layer to grow with its bulk lattice constants. The formation of dislocations to reduce strain is termed relaxation, and relaxation limits the maximum thickness of pseudomorphic epitaxial layers.

The binary compounds, GaN, AlN, and InN form a compound semiconductor alloy system. AlN has the smallest a-plane lattice constant, followed by GaN, and finally InN with the largest. When thin, pseudomorphic layers of  $\operatorname{In_xGaN}^*$  or  $\operatorname{Al_xGaN}$  are grown on a thick layer of GaN oriented in the c-direction, the strain in the a-plane produces a piezoelectric field in the growth direction (the c-direction). The field can be derived by using the tensors given in Figure 4.2, equations (4.1), (4.2), and (4.3), and the relation between the polarization and field,  $F_3 = -P_3 / \varepsilon_r \varepsilon_o$ . The relation for the field is given in the literature[13-16] (a detailed derivation can be found in Appendix D) and is repeated here,

$$F_3 = -\frac{2d_{31}}{\varepsilon_{.}\varepsilon_{.}} \left( c_{11} + c_{12} - 2c_{13}^2 / c_{33} \right) S_1 \tag{4.4}$$

<sup>\*</sup> Ternary compounds in this dissertation will be indicated by the form  $In_xGaN$ , which will be taken as equivalent to  $In_xGa_{1-x}N$ .

where  $S_1$  is the biaxial strain (i.e.  $S_1=S_2$ ).

The sign of the terms in equation (4.4) are crucial to determining the direction of the field. First, the strain is defined as positive for an extensional strain and negative for compression. The sign of the piezoelectric constant is positive if the positive piezoelectric charge is induced in the positive direction by a positive strain.[11] For MOCVD-grown nitrides, the surfaces appear to be metal-terminated[17] and the growth direction is [0001] where the positive growth direction is defined, by convention, as pointing from the group-III element to the group-V element between basal planes.[17]

The magnitude of the piezoelectric field is also dependent on the growth direction of the InGaN layer on the GaN layer. The above equation (4.4) is valid for growth of the template and InGaN layer in the c-direction. Bykhovski et al. have made an analytical calculation for off-polar-axis growth.[13] Their calculation matches the lattice constants in the growth plane for any angle of growth. The results indicate that the largest piezoelectric effects are realized for growth in the c-direction, and the sign of the piezoelectric field changes sign at a certain angle, and finally, the polar piezoelectric field goes to zero for growth perpendicular to the polar axis. Figure 4.4 shows the relative piezoelectric polarization in the c-direction as a function of the angle between the c-axis and the growth direction. The calculations were made using a finite-element mechanical structure simulator, ABAQUS.<sup>†</sup> The crystal properties (see Appendix B) were entered into the simulation file and bar of GaN was subjected to a biaxial extensional stress of 10 GPa. In addition to calculating the strain and displacement of the crystal, if the piezoelectric properties of the crystal are included, the resulting potential and piezoelectric charge distribution can be simulated. The figure shows the same shape as the result of Bykhovski et al. Because of the large radius of the

<sup>&</sup>lt;sup>†</sup> ABAQUS<sup>TM</sup> is a registered trademark of Hibbitt, Karlsson & Sorensen, Inc., 1080 Main Street, Pawtucket, RI 02860-4847.

field emitter tips in this work, the emission is assumed to originate from planes nearly parallel or at only a slight angle to the (0001) plane, so that equation (4.4) can be used for the magnitude of the piezoelectric charge in this dissertation.

The strain-induced piezoelectric fields alter the electrical and optical properties of the nitrides with respect to their bulk properties. The piezoelectric properties and their effects on electrical and optical devices have been an active area of research for the past half decade. Bykhovski et al. have studied the effects of piezoelectric fields on the charge distribution and conduction characteristics of GaN-AlN-GaN structures and the piezoresistive effects in GaN.[13, 14, 18-20] Martin et al. have shown that piezoelectric effects must be considered when trying to determine the band offsets of nitride heterostructures.[15] Band-bending caused by piezoelectric fields has been suggested to explain the high amount free channel charge in un-doped nitride field-effect transistors.[21-30] Yu et al. have studied the piezoelectric effects on Schottky barrier heights.[31, 32] The effect of the piezoelectric fields on the optical properties of the nitride semiconductors are also an active topic of research.[16, 33-43] The next section will present a calculation of the effect of the piezoelectric field produced in a pseudomorphic layer of InGaN on the field emission from GaN FEAs.

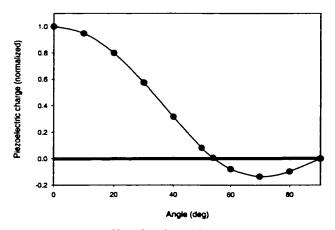


Figure 4.4. Normalized piezoelectric charge versus polar angle simulated using ABAQUS<sup>TM</sup> finite element program.

## (4.4) Surface Barrier Lowering in InGaN/GaN Field Emitter

A piezoelectric field in an epitaxial semiconductor produces a linear change in the potential of the conduction and valence bands. For a strained layer of InGaN grown on a thick GaN layer, the resulting band diagram is depicted in Figure 4.5. The a-plane lattice constant of InGaN is larger than that of GaN, thus the InGaN experiences a compressional strain. The positive direction in the figure is the growth direction, [0001]. The piezoelectric constants of the hexagonal nitrides have a negative sign, thus a positive strain produces a negative charge in the positive direction (see references given in Appendix B). Because the strain in this case is negative, the resulting charge at the InGaN/vacuum interface is positive. An equal amount of negative charge is induced at the GaN/InGaN interface. Thus, the piezoelectric field points in the negative direction,  $[000\overline{1}]$  in this case. The piezoelectric field produces a decreasing slope in the band diagram. Consequently,

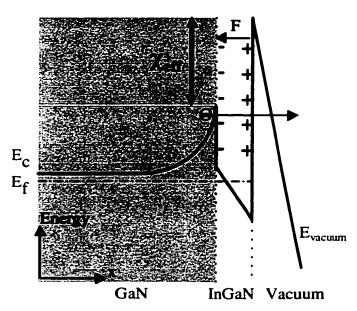


Figure 4.5. Schematic conduction band diagram of InGaN/GaN field emitter. Electrons travel ballistically across the InGaN layer and, thus, effectively tunnel from the maximum of the GaN conduction band edge at the GaN/InGaN interface. The vacuum level is shown for an applied bias.

the vacuum level at the surface of the InGaN is reduced relative to the vacuum level of the GaN. If band bending in the GaN and the filling of the InGaN conduction band by electrons from the GaN is ignored, the amount of potential drop is equal to the piezoelectric field multiplied by the thickness of the InGaN layer.

In reality, the band bending and filling of the InGaN conduction band must be considered to accurately calculate the band diagram of the GaN/InGaN layers. We chose to calculate the bands numerically using a band calculation program, BandProf.<sup>‡</sup> The BandProf program allows the input of material parameters such as band offsets, effective masses, and dopant energy levels. The values used for the material parameters of InN and GaN are given in Appendix B and the valence band offset between InN and GaN was taken as  $\Delta E_v = 0.46 \Delta E_g$ , which is an average of the offsets given in Ambacher.[44] Estimation of the material parameters for InGaN are made using Vegard's law (linear interpolation of the values of GaN and InN). In the BandProf program, the only way to introduce fixed charge is by the use of dopants. The piezoelectric charge is introduced into the description of the material by the use of two fictitious "dopants." Dopant A, is given an energy level 1.5 eV above the conduction band minimum (a donor), and thus, is always ionized with a positive charge. Dopant B, is given an energy level 1.5 eV below the valence band maximum (an acceptor), and thus, is ionized with a negative charge. Finally, a fictitious material was created to simulate vacuum. The conduction band of the fictitious material simulated the vacuum level and thus the conduction-band offset of the "vacuum" material with respect to GaN was set equal to the electron affinity of GaN.

The epitaxial layer structure to be studied is input to BandProf by specifying the layers in a text file. Each layer is specified by the composition of the

<sup>&</sup>lt;sup>‡</sup>W. R. Frensley, BandProf, © University of Texas at Dallas.

semiconductor, the thickness of the layer, and the doping type and amount, if any. At the InGaN/GaN interface, a small layer (two times the mesh size of 0.5 Å) is doped with dopant B to a volume charge density equivalent to the piezoelectric surface charge density. At the InGaN/vacuum interface, an equivalent charge is introduced by doping the surface with dopant A. To calculate the necessary piezoelectric charge, first the strain must be calculated. The strain is given by the lattice mismatch of the a-plane lattice constant,

$$S_{i} = \frac{a_{epi} - a_{sub}}{a_{epi}},\tag{4.5}$$

where  $a_{epi}$  is the lattice constant of the strained layer and  $a_{sub}$  is the lattice constant of relaxed substrate layer. Using Vegard's law to calculate the a-lattice constant for  $In_xGaN$ , the strain for an  $In_xGaN$  layer grown on a relaxed GaN layer can be calculated from

$$S_{1} = \frac{(a_{GaN} - a_{InN})x}{a_{GaN} + (a_{InN} - a_{GaN})x},$$
(4.6)

where x is the In mole fraction. A plot of equation (4.6) over range from x=0 to 1.0 is given in Figure 4.6. The strain varies from 0 to about -10% over that range of In

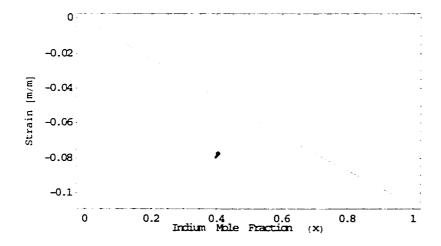


Figure 4.6. Strain in pseudomorphic  $In_xGaN$  layer as a function of In mole fraction, x.

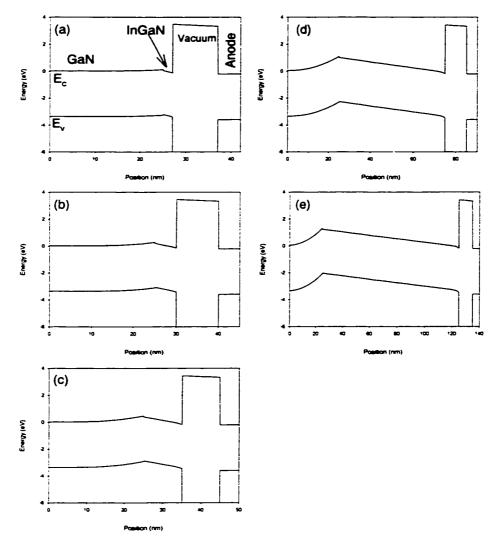


Figure 4.7. Calculated band diagram of InGaN/GaN field emitters. The growth direction is to the right. The InGaN layer can identified by the downward sloping region directly in front of the vacuum region. The In concentration is 5% and the InGaN thickness is varied from 5 to 100 nm (a)-(e). In this figure, the Fermi level is at 0 eV.

mole fraction. Now that the strain has been calculated, the field and charge can be calculated using equation (4.4), using Vegard's law to calculate the elastic and piezoelectric constants for the  $In_xGaN$ . The piezoelectric polarization charge ranges from  $5.8\times10^{12}$  cm<sup>-2</sup> for 5% In concentration to  $5.1\times10^{13}$  cm<sup>-2</sup> for 90% In

concentration. Note that these charge concentrations are in the same range as calculated for the Cs work function lowering  $(3.6 \times 10^{13} \text{ cm}^{-2})$  presented in section (4.2).

The band diagrams calculated by the BandProf simulations are similar to the schematic shown in Figure 4.4. A series of calculated band diagrams, for 5% In concentration and InGaN layer thickness from 5-100 nm, are shown in Figure 4.7. The field emission current from the GaN/InGaN structure could be calculated, in theory, by numerically integrating the transmission and supply functions based on the potentials given by BandProf, however, a physical argument leads to a simple interpretation of the effects of the InGaN layer. The main effect of the InGaN layer is to lower the vacuum level at the surface and raise the conduction band minimum at the InGaN/GaN interface. The energy difference between the surface vacuum level and the conduction band minimum at the GaN/InGaN interface can be seen to be equivalent to an effective electron affinity,  $\chi_{eff}$ . This effective electron affinity will be less than the electron affinity of GaN if the InGaN is strained and the piezoelectric field exists. In this approximation, the Fowler-Nordheim current-voltage relation given in Chapter 2 can be simply modified by replacing the electron affinity,  $\chi_{eff}$ 

$$I = AV^2 \exp\left(-\frac{B\chi_{eff}^{3/2}}{\beta V}\right). \tag{4.7}$$

BandProf simulations of the effect were calculated for In compositions ranging from 5% to 90% and InGaN layer thickness from 0 to 100 nm. The results of the calculations are given in Figure 4.8. The plot shows the effective electron affinity as a function of InGaN thickness with the In mole fraction as a parameter. The effect of increasing the InGaN thickness is to increase the length over which the piezoelectric field acts which increases the total electron affinity change. Increasing the In concentration increases the strain, which increases the piezoelectric field strength. The increased dipole strength increases the surface barrier lowering. The saturation of the effective electron affinity at increased InGaN thickness and In mole fraction is the result of the mobile charges transferred from the GaN accumulating at the InGaN/vacuum interface. The minimum value of the electron affinity is seen to be slightly less than 0, which indicates that it may be possible to produce a negative electron affinity with this method. The saturation of the effective electron affinity occurs at lower layer thickness with increasing In

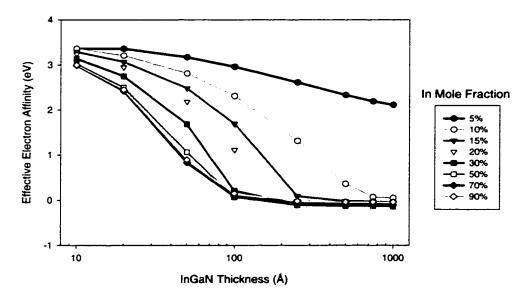


Figure 4.8. Calculated effective electron affinity of InGaN/GaN field emitters as a function of InGaN thickness with the In mole fraction as a parameter.

composition. For In concentrations above 10%, the lowering effect is strongest for InGaN thickness between 20 Å and 200 Å, and additional InGaN thickness does not greatly reduce the effective electron affinity.

Three effects limit the maximum reduction that can be achieved. These effects are strain relaxation, electron mean free path, and the depletion of the GaN layer. The first is the requirement that the InGaN film remains strained in order for the piezoelectric effect to exist. As the thickness of a strained layer increases, the film will relax through dislocations to relieve the strain. A critical thickness can be defined as the thickness where the film has relaxed so that it has its own bulk lattice constant. Simple calculations, such as those based on the Matthew-Blakeslee model, predict that only extremely thin strained InGaN layers can be grown (less than 100 Å).[16, 45] A simple estimation of the critical thickness can be given by the expression  $t_c = a_{sub}^2/2(\Delta a)$ , where  $t_c$  is the critical thickness,  $a_{sub}$  is the substrate a-plane lattice constant and  $\Delta a$  is the lattice mismatch. A plot of this function for InGaN on GaN is given in Figure 4.9, and shows that the critical thickness for In concentrations above 5% is limited to less than 30 nm. Experimental evidence

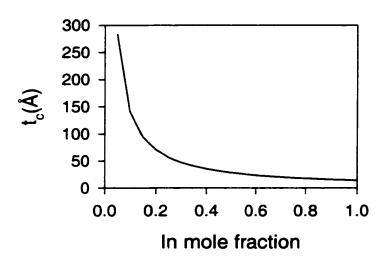


Figure 4.9. Simple estimation of the critical thickness of InGaN on GaN.

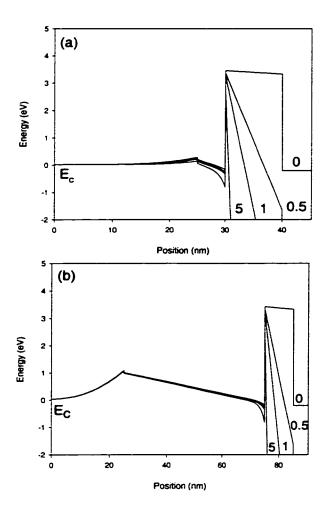


Figure 4.10. Effect of field penetration on the conduction band of the InGaN/GaN FEAs demonstrating the limitation of the effective electron affinity model. (a) 5% In, 50 Å InGaN. (b) 5% In, 500 Å. The numbers next to the profiles indicate the applied electric field in units of V/nm.

suggests that strained InGaN layers can be grown to larger thickness than the simple models suggest.[16, 46]

The second effect that can limit the effectiveness of the InGaN layer is scattering of the electrons in the layer. The above assumption of an effective electron affinity essentially relies on ballistic transport of the electrons through the InGaN. If the thickness of the InGaN layer is larger than the mean free path of

electrons in InGaN, the scattering of the electrons will lose energy until they reach the InGaN conduction band minimum. Because the electron affinity of InGaN is larger than the electron affinity of GaN, the scattered electrons will have a much lower probability of tunneling through the InGaN/vacuum barrier than electrons traveling ballistically through the InGaN. As the thickness of the InGaN increases, a greater fraction of the electrons will scatter in the InGaN layer, thus limiting the electron emission. Theoretical and Monte Carlo calculations of scattering in the nitride semiconductors indicate that the dominant scattering mechanism is polar optical phonon scattering. The Monte Carlo simulations of the channel regions of GaN FETs have shown that the electrons will thermalize to the conduction band in 200 to 400 Å. Ye et al. have measured a polar optical phonon emission time of 0.2 ps for GaN.[47] For an electron velocity of 10<sup>7</sup> cm/s, the resulting relaxation length is 200 Å, which shows reasonable agreement with the theory. The above data are taken from studies of hot electron relaxation in GaN and provided a best current estimate for the mean free path, as a literature search yielded no references to similar studies for InGaN.

The final effect that can limit the validity of our model is the barrier caused by the large depletion in the GaN layer as a result of the piezoelectric effect in the InGaN, for thick InGaN layers. This upward bending of the bands can be clearly seen in Figure 4.7. Under operation, the field penetration of the applied electric field can cause increased band bending near the surface. For thin layers (<100 Å) the field can penetrate sufficiently to decrease the barrier and allow electron transport. This is illustrated in Figure 4.10, where BandProf simulations with a bias applied to the anode (but no current flow) are shown. For 50 Å of In<sub>0.5</sub>GaN (Figure 4.10(a)), the field penetration causes the bands to bend sufficiently to allow the application of the effective electron affinity model. For a thicker InGaN layer

<sup>§</sup> J. Singh, private communication, 1999.

(500 Å), the field can not penetrate sufficiently to cause appreciable band bending at the barrier and the effective electron affinity model should not be applicable. BandProf simulations are limited to zero current flow, and dynamic effects may have an effect not indicated here.

#### (4.5) InGaN/GaN Field Emitter Results

InGaN/GaN field emitter arrays were grown and fabricated as discussed for the integrated-anode GaN field emitter arrays presented in Chapter 3. The InGaN layers were grown on the GaN pyramids immediately after the GaN pyramid growth and were not intentionally doped. The thickness of the InGaN layer on the pyramids is difficult to measure. The thicknesses reported herein are estimated based on growth time and the enhanced growth rate of the pyramids versus planar films. The growth rate of InGaN on the sidewalls was grossly estimated to be four times the planar growth rate. Consequently, the absolute values of the thickness are not known, but the relative thickness of the InGaN layers can be assumed based on the growth times.

The first set of emitters grown to test the electron affinity lowering effect included a GaN FEA control, and two InGaN/GaN FEAs, one with InGaN thickness of 100 nm and the other with InGaN thickness of 200 nm. The In mole fraction was 15% as measured by x-ray diffraction on a planar InGaN region of the sample, provided by Giacinta Parish. The GaN field emitter exhibited a turn-on of about 175 V, emitters from the 100-nm InGaN sample showed a turn-on ranging from 63-123 V. The 200-nm emitter showed the highest turn-on of about 220-225 V. Each of the arrays had 5 tips and the anode-cathode separation was 2.8 µm for the 100-nm InGaN sample and 2.5 µm for the 200-nm InGaN sample and the control. Processing difficulties caused by large non-uniformity of the planar GaN template layers lead to geometrical differences in the FEA pyramids and, thus, the magnitude of the electron affinity reduction could not be accurately determined.

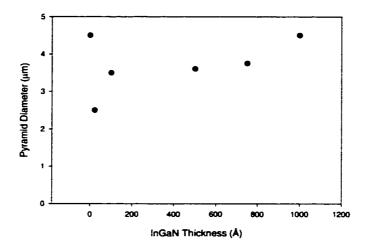


Figure 4.11. Variation of the pyramid base width for samples of differing InGaN layer thickness.

Qualitatively, the reduction of the turn-on voltage for the 100-nm sample was encouraging. At a thickness of 1000 Å, the theoretical effective electron affinity for 15% In is -0.4 eV. Although the turn-on of 63 V from this sample was the lowest turn-on voltage for a nitride-based FEA measured, the turn-on expected for such small effective electron affinity would be much lower. This thickness is somewhat above the calculated values of the mean free electron path discussed above, so that it may be suggested that scattering effects would increase the turn-on voltage. A second set of InGaN/GaN FEAs with more thickness points and less processing variation was fabricated to further investigate the effect.

In the second set of InGaN field emitters, InGaN layers of 20, 100, 500, 750, and 1000 Å were grown. The growth conditions of the MOCVD system had changed since the above-reported growth, and the In mole fraction was about 3-5% as measured by x-ray diffraction analysis, provided by Amber Abare, of a planar region on the 1000 Å sample. Thickness fringes in the x-ray measurements indicated a thickness of the planar film of 274 Å, which was very close to the target planar region thickness for the 1000 Å sample. This indicated that at least the control over the planar growth rate of the InGaN was very good. In contrast, the

variation of the pyramid sizes was not as good as for past arrays. Over a single sample, the base width of the pyramids was observed to vary by as much as 20%. To determine the sample-to-sample variation, the base width of pyramids from the center of each sample was measured. The variation is shown in Figure 4.11, where the base width of the pyramids is plotted versus the target InGaN thickness (essentially, this is versus growth time). The variation of the base width among the samples is also about 20%. Other than the control sample, the base width increases with growth time although at a greater rate than would be expected from the target InGaN thicknesses. The pyramids from each sample were complete as observed in the SEM.

Current-voltage characteristics of the InGaN/GaN field emitters were performed using the same measurement techniques described in Chapter 3. From the emission current measurements, given in Figure 4.12, the turn-on voltage was measured and the Fowler-Nordheim plots (F-N plots) were constructed (see Figure 4.13). All of the emission characteristics reported in this section came from arrays that showed a linear F-N plot with a negative slope, and reverse leakage current at least three orders of magnitude below the forward current. From the

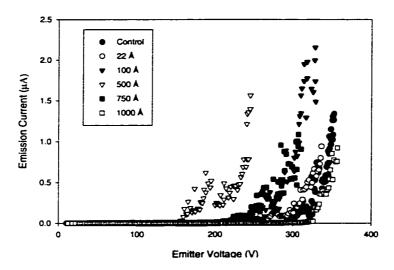


Figure 4.12. Current-voltage characteristics of In<sub>0.05</sub>GaN/GaN FEAs.

slope of the F-N plots, the either the field enhancement or effective electron affinity could be calculated using the equations given in Chapter 2. The field enhancement factor of the control device was estimated by assuming that the electron affinity of the control was 3.5 eV. To check the reasonableness of this assumption, the geometry of the integrated anodes were observed by SEM observation.

The two most important geometrical parameters were the tip sharpness and the anode-cathode separation. Since the tips were all grown to completion, the radius of all of the tips was assumed to be 90 nm. The fitted field enhancement factor of the control sample was  $67,000 \text{ cm}^{-1}$  and using the concentric sphere model, the resulting k factor is 1.77 which is in the acceptable range for the model. The field enhancement factors calculated from the InGaN samples using their individual anode-cathode separations and the same k factor extracted from the control sample, yields only a 7% variation among the FEAs (see Table 4.1). Because the emission current depends exponentially on the field enhancement factor, this variation may cause a large change in the current voltage characteristic; however, the variation in anode-cathode separation was random from device to device so that no trend could be clearly observed from the geometrical data.

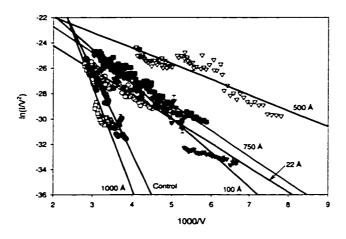


Figure 4.13. Fowler-Nordheim plots of emission data given in Figure 4.12.

Table 4.1. Measured Anode-Cathode Separations and Theoretical Field Enhancement Factors (k=1.77).

InGaN Thickness (Å)	Anode-Cathode Separation (µm)	Field Enhancement, β (cm <sup>-1</sup> ) 67,000 64,590		
0	1.38			
22	3.20			
100	2.71			
500	1.77	66,139		
750	1.98	65,765		
1000	0.73	71,665		

The same field enhancement factor as the control is assumed to apply to the InGaN/GaN FEAs. The effective electron affinity of each of the InGaN/GaN FEAs was then calculated from the slope of the F-N plots using the common field enhancement factor. Table 4.2 contains the turn-on voltages, slope and intercept of the fits to the F-N plots, and the calculated effective electron affinities and emission areas. The goodness of the fit is given by the adjusted  $R^2$  figure, also given in Table 4.2, with a value closer to one indicating a better fit. Figure 4.14 is a plot of the experimentally determined effective electron affinity versus InGaN thickness, shown along with the calculated theoretical effective electron affinities from Figure 4.8. Except for the point at 20 Å, the experimental points seem to follow the trend of the 5%-10% In calculations up to an InGaN thickness of 500 Å. From 500 Å to 1000 Å, the effective electron affinity increased, possibly from the aforementioned relaxation or scattering in the thicker layers. The minimum effective electron affinity achieved in this set of samples was the 1.04 eV from the sample with 500 Å of InGaN. The reduction of the effective electron affinity by 2.46 eV relative to the electron affinity of GaN represents a 70% reduction. The observation of lowering at InGaN thicknesses up to 500 Å does not agree with the above-mentioned limitations concerning the field penetration and the energy barrier

Table 4.2. Measured and Calculated Data from InGaN/GaN FEAs.

InGaN Thickness (Å)	Turn-on Voltage (V)	F-N Intercept	F-N Slope	$R_{adj}^2$	β (cm <sup>-1</sup> )	Emission Area (cm²)	Xeff (eV)
0	290	-7.3±0.8	-6300±200	0.91	67000±2000	3×10 <sup>-8</sup> ±2×10 <sup>-8</sup>	3.5
22	214	-20.2±0.4	-1970±90	0.86		4×10 <sup>-15</sup> ±2×10 <sup>-15</sup>	1.61±0.02
100	210	-16.8±0.3	-2590±60	0.95		2.5×10 <sup>-13</sup> ±0.7×10 <sup>-13</sup>	1.93±0.01
500	146	-20.3±0.5	-1030±90	0.69		5×10 <sup>-16</sup> ±3×10 <sup>-16</sup>	1.04±0.04
750	200	-18.5±0.3	-2070±70	0.94		2.5×10 <sup>-14</sup> ±0.8×10 <sup>-14</sup>	1.66±0.01
1000	313	-4.5±2.1	-7700±700	0.80		6×10 <sup>-7</sup> ±13×10 <sup>-7</sup>	3.9±0.2

The electron affinity for the control is assumed 3.5 eV, and the field enhancement factor,  $\beta$ , is calculated from the equation for the F-N slope. This field enhancement is assumed for all of the InGaN samples to calculate the effective electron affinities.

in the GaN. This disagreement is not understood at this time, but may be attributable to incomplete knowledge of the InGaN thickness and unknown surface states.

The turn-on voltages of the InGaN/GaN field emitters were also measured from the current-voltage characteristics of the FEAs. Figure 4.15 shows the experimentally measured turn-on voltages and theoretical calculations of the turn-on voltage of field emitters with the theoretical effective electron affinities calculated for In percentage of 5 and 10%. The trend of the experimental turn-on voltages follows the 5% In theoretical calculation up to an InGaN thickness of 500 Å and then begins to increase. Interestingly, the turn-on voltage measured for the 1000 Å InGaN FEA is very close to the theoretically calculated turn-on voltages expected for emission from relaxed, bulk InGaN of 5 or 10% In composition.

In order to avoid array-damaging vacuum arcs, the InGaN/GaN FEAs were typically measured up to currents of 1-2  $\mu$ A. If the current increase above this

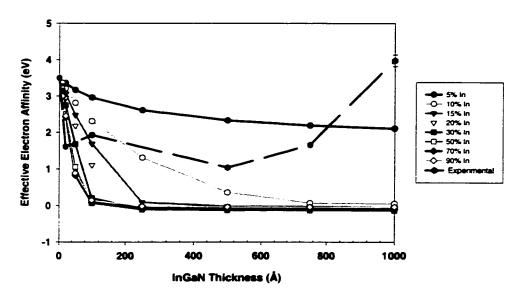


Figure 4.14. Experimental effective electron affinity of the InGaN/GaN FEAs (dashed line with hexagonal symbols) compared the theoretical effective electron affinities.

limit, the measurements of the arrays were often terminated by a destructive arc. A few of the arrays were tested using the curve tracer to determine the maximum current before failure. In all of the destructive tests, the device failed as a short. An array with 100 Å of InGaN showed maximum emission current of 9.8 μA from a 10-tip array at 372 V. The arrays with the smallest turn-on voltage, the 500 Å InGaN, showed the highest current capacity. Figure 4.16 shows a screen shot of the curve tracer showing a maximum current of about 19 μA at 310 V from a 10-tip array. The FEAs with 750 Å of InGaN display a maximum current of 1.9 μA at 334 V from a 10-tip array and 3.6 μA at 344.5 V from a 40-tip array. Finally, a 10-tip array with 1000 Å of InGaN showed a maximum current of 1.8 μA at 417.5 V. From the current-voltage pairs given above, the power being delivered to the anode at the maximum current can be calculated. For the low turn-on, high current samples with thin InGaN, the anode power at breakdown was 3.65 mW (100 Å) and 5.89 mW (500 Å). For the thicker InGaN samples, the anode power at breakdown was lower, 0.64 mW (750 Å) and 0.75 mW (1000 Å). If the breakdown

of these samples were being initiated by the destruction of the anode, it would be expected that the anode power would be about the same. This difference between the thin InGaN samples, where most of the electrons are assumed to travel ballistically through the undoped InGaN, and the thick InGaN samples, where the electrons will have a higher chance of scattering, suggests that the InGaN layer may have a role in determining the maximum current capability of the InGaN/GaN FEAs. More research will be necessary to test this hypothesis.

Finally, we present some preliminary measurements of the current instability of the InGaN/GaN FEAs. The applied voltage to the array was set so that the current was approximately 1  $\mu$ A. Then the current was monitored for one minute. The instability of the current was estimated by the standard deviation of the current divided by the average current for the measurement duration. For the control sample the variation of the current was 12.5%, for the 20-Å sample the variation was 11%, and for the 100-Å InGaN sample the variation was 5%. Of the samples listed here, the 20-Å sample had the lowest effective electron affinity and should have demonstrated the lowest noise. Thus, these preliminary measurements do not support the simple noise model discussed in Chapter 2 (equation (2.31)) but

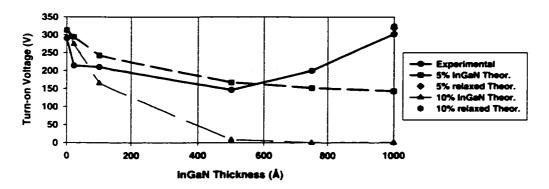


Figure 4.15. Experimental turn-on voltage (solid) and the theoretical turn-on voltages (dashed) calculated for 5 and 10% In composition InGaN/GaN FEAs. Also plotted on the right side, are two points calculated assuming the 5 and 10% InGaN layers are relaxed.

the scarcity of the data does not allow any conclusion to be drawn. InGaN/GaN FEA (20-Å InGaN) was tested at a constant current overnight. The current was set to 1 µA (367 V applied bias) and the current was monitored at one reading per minute. The emission current versus time is shown in Figure 4.17. The figure shows that the current gradually decreased with time but undetermined events would cause a sudden increase in the emission current. The current would then decrease again. After 14.3 hours of emission, a sudden increase in current to the limit of the range of the picoammeter was observed and the device was later discovered to be shorted. The pressure was not monitored during the measurement but the pressure of the vacuum system was the same after the test as before it. The voltage reading of the power supply was also monitored and showed no change more than 0.3 V during the test. The gradual decay of emission current has been observed in lifetime tests by other researchers and is often attributed to reaction of the surface with residual gas atoms.[48-50] The sudden rise in current could be attributed to a number of events: changes in pressure, ion bombardment of the cathode, or spikes in the power supply voltage to list a few.

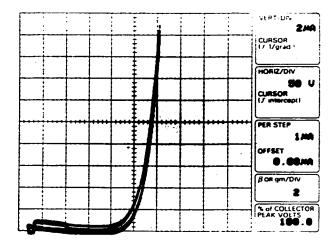


Figure 4.16. Picture of curve tracer screen with highest emission current observed for InGaN/GaN FEAs with 500 Å InGaN.

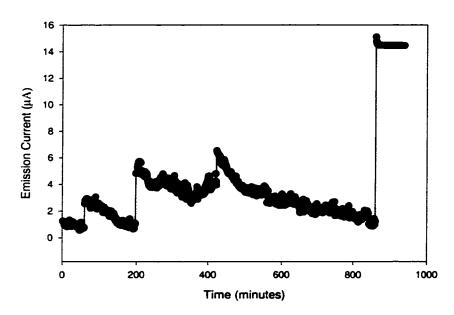


Figure 4.17. InGaN/GaN FEA lifetime test.

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## **Chapter Five**

#### Conclusion

## (5.1) Summary of Accomplishments

The major accomplishments of our work for this dissertation have been the design, fabrication, and testing of the first GaN and InGaN/GaN field emitter arrays. We have demonstrated the first field emission measurements from selectively grown GaN pyramids. The largest currents drawn from these arrays were approximately  $81~\mu A$  at 1100~V. The low field emission currents and high turn-on voltages of these arrays were the result of the use of an external anode to apply the field to the emitter array. The high operating voltages of the emitters often lead to their destruction by vacuum arcs. The operating voltage of the field emitter arrays could be decreased by decreasing the separation of the anode and the cathode.

The operating voltage of the GaN field emitters arrays were lowered by integrating the anode structure on-wafer with the field emitter arrays. Using standard lithography techniques, the anode was fabricated as an air bridge over the field emitter arrays. The air-bridge anode technique allowed the placement of the anode over the emitter array controllably in the range of 1 to 5  $\mu$ m. The turn-on voltages of the emitter arrays with the integrated anodes were decreased to a range of 176-435 V for anode-cathode spacing ranging from 0.4-2.35  $\mu$ m respectively. Emission current from these arrays typically was limited to 1-2  $\mu$ A and failure of these devices was most often attributed to failure of the integrated anode.

Taking advantage of the piezoelectric fields present in strained layers of hexagonal nitride semiconductors, we developed a novel technique to lower the surface barrier of the field emitters, and thereby reduce their turn-on voltage further. By placing a strained layer of InGaN on the GaN pyramids, a piezoelectric

dipole could be grown into the crystal at surface of the field emitters. For the case of InGaN on GaN, the dipole has a sign such that it reduces the surface barrier. Analysis of the band diagram of the InGaN/GaN heterostructure with the Fowler-Nordheim solution of the field emission problem allowed us to propose an effective electron affinity for the field emitters. Calculations of the effective electron affinity of the InGaN/GaN structure as a function of In composition and InGaN thickness were performed. The theory suggests that at sufficient In composition and InGaN thickness, the effective electron affinity can be significantly reduced from the electron affinity of GaN (3.5 eV), even becoming negative. Negative electron affinity implies that the electrons would experience no barrier to emission and large emission currents could result. The effect of the piezoelectric surface barrier is limited by three factors: relaxation of the InGaN as the thickness increases which leads to no piezoelectric field, electron scattering in the InGaN layer making the assumption of an effective electron affinity invalid, and, finally, the energy barrier created by the depletion layer in the GaN caused by the presence of the InGaN well at the surface.

InGaN/GaN field emitter arrays were grown and then fabricated together to ensure the same emitter geometry in order to test the magnitude of barrier lowering. A constant In composition (~5%) was used and the thickness of the InGaN layer was varied from 20-1000 Å. At an InGaN thickness of about 500 Å, the effective electron affinity extracted from the experimental emission data is approximately 1.0 eV. This represents a 70% reduction in the surface barrier height compared to the control sample (a GaN FEA). The corresponding experimental turn-on voltage of the 500-Å emitter was 150 V, which was 50% of the turn-on voltage of the control. At larger thicknesses of InGaN, the effective electron affinity and turn-on voltage of the emitters increased, suggesting that the effects of relaxation or increased electron scattering in the InGaN layer were being observed.

### (5.2) Suggestions for Future Work

Three main areas of future work for nitride-based cold cathodes can be suggested to follow from the work in this dissertation. The first involves the further miniaturization of the GaN field emitter array structures so that more testing of the suitability of GaN and its alloys for use in field emitter arrays can be ascertained. The second involves the further study of the piezoelectric surface barrier lowering effect. The final suggestion for further work involves using the piezoelectric fields in a GaN/AlGaN/InGaN heterostructure to produce a planar cold cathode with a band diagram similar to the planar-doped barrier electron emitters presented previously by Dr. W.-N. Jiang.

- 1. Further lowering of the turn-on voltage could be attained by using the InGaN/GaN field emitter arrays in a Spindt cathode structure (see Figure 1.1 of Chapter 1). In the Spindt-cathode structure, the distance between the tip and the extracting electrode can be in the sub-micron range. With such a small gap, turn-on voltage may be reduced to below 20 V, thus allowing biasing and control of the field emitters by cost-effective CMOS driver circuits. By lowering the voltage, the risk of emitter damage is much reduced, thus allowing more device testing such as lifetime, sensitivity to pressure and gas, and noise testing. Finally, the Spindt structure is a three-terminal device thus allowing modulation of the emission current and more useful potential applications than the two-terminal diode presented here.
- 2. Further investigation of the piezoelectric surface barrier lowering effect is warranted. Studies of field emitters with high In composition and optimized thickness could have effective electron affinities near zero. This may produce very low turn-on voltages. The study of the current-voltage characteristics of field emitters with electron affinities below 1 eV may provide insight into the physics of field emission from surfaces with very small energy barriers, where the Fowler-Nordheim formalism fails due to the approximations made in determining the

transmission probability. The improving development of nitride growth by molecular beam epitaxy (MBE), may allow the growth of InGaN layers with higher In composition and better uniformity than presently possible by MOCVD growth.

3. The most exciting prospect for nitride cold cathodes may be in the application of the piezoelectric fields to engineering a band diagram of the nitride materials to be similar to that of the planar-doped barrier electron emitters (PDBEEs) developed by Dr. Wei-Nan Jiang in the AlGaAs/GaAs material system.[1] In the AlGaAs/GaAs PDBEE, a planar-doped p-type layer is used to create a triangular barrier. This triangular barrier is used to launch hot electrons over the surface barrier of the emission region. For the AlGaAs/GaAs PDBEE, two major problems exist. One, the band gap of the AlGaAs/GaAs layers are small enough that parasitic tunneling currents lowered the efficiency of the devices. Two, the surface of the GaAs had to be coated with Cs in order lower the barrier and increase the efficiency of the emitter. Dr. Jiang conlcuded that PDBEEs would be more efficient if a higher band gap material were used.

Planar doping of nitride materials has not been demonstrated and p-type doping of the nitrides is difficult. Thus, another method to produce the triangular barrier of a PDBEE is necessary in the nitrides. The application of the piezoelectric fields to create a triangular barrier is suggested by the piezoelectric surface barrier lowering method. We showed in Chapter 4 that if an InGaN layer is grown on GaN, a piezoelectric field of negative sign develops. The piezoelectric field for a layer of AlGaN on GaN will point in the opposite direction due to the opposite sign of the strain. The suggested band diagram of a nitride-based piezoelectric-barrier electron emitter (PBEE) is compared to the band diagram for the PDBEE in Figure 5.1. The similarity of the two structures is evident in the figure. Whereas the surface of the PDBEE must be cesiated to lower the vacuum level, the magnitude of the piezoelectric fields may make cesiation unnecessary in the PBEE. The effectiveness of this structure will be highly dependent on the material quality and

uniformity of the AlGaN and InGaN layers, and will require that the layers have low defect density and precise thickness uniformity. The benefits of a planar cold cathode compared to a field emitter-based cold cathode, such as low sensitivity to

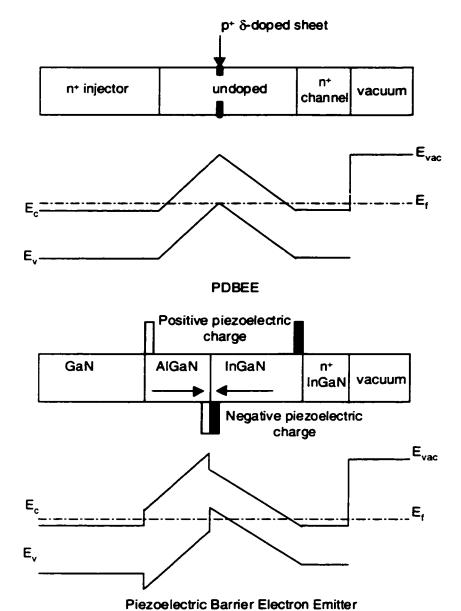


Figure 5.1. Comparison of the band diagrams of the PDBEE and the suggested piezoelectric planar electron emitter. The PDBEE band diagram is taken from [1].

pressure, long lifetime, and low operating voltage, make this a device idea worthy of investigation.

## (5.3) References

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## Appendix A

## Exact Transmission Function for the Triangular Barrier

In this appendix, we will consider the exact solution and the WKB approximation for the triangular barrier with no image force correction. The potential profile for the triangular barrier is sketched in Figure A.1. The relevant energies are given by

- C is the work function of the cathode
- $\phi_{ma}$  is the work function of the anode
- W is the electron energy referenced to the Fermi level

In sections I and III, the wave function and its derivatives are given by the

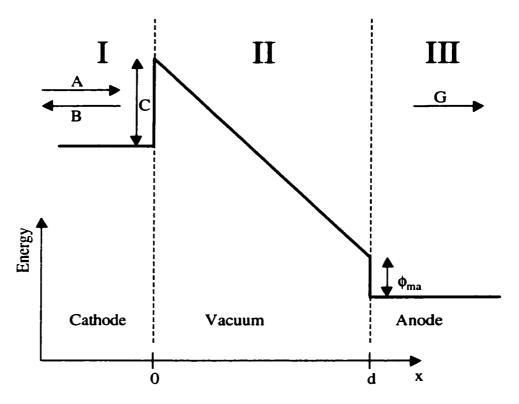


Figure A.1. Potential energy diagram of triangular barrier for the problem of electron tunneling through vacuum between two metals.

well known traveling wave solutions for a constant potential,

$$\psi_{I} = Ae^{-ik_{I}x} + Be^{+ik_{I}x}$$

$$\psi'_{I} = -Aik_{I}e^{-ik_{I}x} + Bik_{I}e^{+ik_{I}x}$$

$$\psi''_{I} = -Ak_{I}^{2}e^{-ik_{I}x} - Bk_{I}^{2}e^{+ik_{I}x}$$

$$k_{I}^{2} = 2mW / \hbar^{2}$$
(A.1)

and

$$\psi_{III} = Ge^{-ik_{III}(x-d)} + He^{+ik_{III}(x-d)} 
\psi'_{III} = -Gik_{III}e^{-ik_{III}(x-d)} + Hik_{III}e^{+ik_{III}(x-d)} 
\psi''_{III} = -Gk_{III}^{2}e^{-ik_{III}(x-d)} - Hk_{III}^{2}e^{+ik_{III}(x-d)} 
k_{III}^{2} = (2m/\hbar^{2})(W - C + qFd + \phi_{ma})$$
(A.2)

In a tunneling calculation, the particles coming from section III and traveling to the left are ignored and, thus, H=0.

For 0 < x < d, the Schrödinger equation is

$$\frac{d^2 \psi_{II}^2}{dx^2} + \kappa^2 (W - C + qFx) \psi_{II} = 0$$

$$\kappa^2 = \left(2m/\hbar^2\right) \tag{A.3}$$

and the solution of this equation is less well known than the traveling-wave solutions of a constant potential. To solve this equation we can make a change of

variables, 
$$y = (\kappa^2 qF)^{1/3} \left( -\frac{C - W}{qF} + x \right)$$
. The resulting equation is

$$\frac{d\psi_{II}^2}{dv^2} + y\psi_{II} = 0. {(A.4)}$$

From standard mathematical references, we find that the solution of this equation is given by[1]

$$\psi_{II}(y) = M \operatorname{Ai}((-1)^{1/3} y) + N \operatorname{Bi}((-1)^{1/3} y)$$
 (A.5)

where Ai(z) and Bi(z) are the Airy functions and M and N are constants. The first derivative of the wave function is given by

$$\psi'_{II}(y) = (-1)^{1/3} (\kappa^2 q F)^{1/3} (M \operatorname{Ai}'(y) + N \operatorname{Bi}'(y))$$
 (A.6)

where the prime indicates the derivative with respect to x.

Now the wave function and the slope of the wave function must match at the interfaces. At the left interface, x=0,

$$\psi_{I}(0) = A + B$$

$$\psi'_{I}(0) = -Aik_{I} + Bik_{I}$$
(A.7)

and

$$\psi_{II}(0) = M \operatorname{Ai}(z_{1}) + N \operatorname{Bi}(z_{1})$$

$$\psi'_{II}(0) = (-1)^{1/3} (\kappa^{2} q F)^{1/3} [M \operatorname{Ai}'(z_{1}) + N \operatorname{Bi}'(z_{1})]. \tag{A.8}$$

$$z_{1} = (-1)^{1/3} (\kappa^{2} q F)^{1/3} \left( -\frac{C - W}{q F} \right)$$

Matching  $\psi_I(0) = \psi_{II}(0)$  and  $\psi_I'(0) = \psi_{II}'(0)$  gives two equations

$$A + B = M \operatorname{Ai}(z_1) + N \operatorname{Bi}(z_1)$$

$$ik_1(B - A) = (-1)^{1/3} (\kappa^2 q F)^{1/3} [M \operatorname{Ai}'(z_1) + N \operatorname{Bi}'(z_1)]$$
(A.9)

Now we must match the functions at the right interface, x=d.

$$\psi_{II}(d) = M \operatorname{Ai}(z_{2}) + N \operatorname{Bi}(z_{2})$$

$$\psi'_{II}(d) = (-1)^{1/3} (\kappa^{2} q F)^{1/3} [M \operatorname{Ai}'(z_{2}) + N \operatorname{Bi}'(z_{2})]$$

$$z_{2} = (-1)^{1/3} (\kappa^{2} q F)^{1/3} \left( d - \frac{C - W}{q F} \right)$$
(A.10)

and

$$\psi_{III}(d) = G$$

$$\psi'_{III}(d) = -Gik_{III}$$
(A.11)

Thus, setting  $\psi_{II}(d) = \psi_{III}(d)$  and  $\psi'_{II}(d) = \psi'_{III}(d)$  gives two equations

$$M \operatorname{Ai}(z_{2}) + N \operatorname{Bi}(z_{2}) = G$$

$$(-1)^{1/3} (\kappa^{2} q F)^{1/3} [M \operatorname{Ai}'(z_{2}) + N \operatorname{Bi}'(z_{2})] = -Gik_{yy}$$
(A.12)

We now have four equations in five unknowns, which does not have a unique solution. Nevertheless, the quantity we seek, the transmission probability, is given by  $(k_{III}/k_I)|G/A|^2$  and we can solve for this quantity. The expressions necessary to calculate  $(k_{III}/k_I)|G/A|^2$  are given below.

$$\frac{G}{A} = \frac{2(a\tau - b\xi)}{b\delta(\zeta - g) + a\delta(w - v) + \tau(g - \zeta) + \xi(v - w)}$$

$$a = \text{Bi}(z_2)$$

$$b = \text{Ai}(z_2)$$

$$g = \text{Bi}(z_1)$$

$$w = \text{Ai}(z_1)$$

$$\zeta = (1/ik_1)(-1)^{1/3}(\kappa^2 qF)^{1/3} \text{Bi}'(z_1)$$

$$v = (1/ik_1)(-1)^{1/3}(\kappa^2 qF)^{1/3} \text{Ai}'(z_1)$$

$$\xi = (-1)^{1/3}(\kappa^2 qF)^{1/3} \text{Bi}'(z_2)$$

$$\tau = (-1)^{1/3}(\kappa^2 qF)^{1/3} \text{Ai}'(z_2)$$

$$\delta = -ik_{III}$$
(A.13)

A plot of  $(k_{III}/k_I)|G/A|^2$  generated using the Mathematica© program appears in Figure A.2. Mathematica has the Airy functions and their first

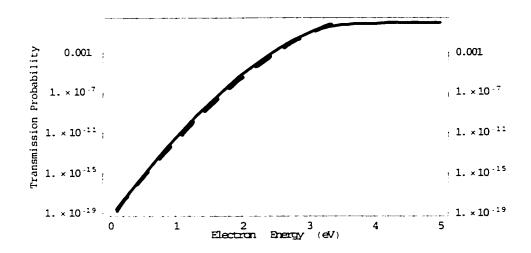


Figure A.2. Plot of the exact (solid) and WKB approximation (dashed) transmission probabilities for the triangular barrier problem. (F=10 $^9$  V/m, C=3.5 eV,  $\phi_{ma}$ =4.5 eV, d=1 mm)

derivatives built-in, so plotting this complex function is a simple matter.[2] Also plotted in the figure is the WKB approximation given in Chapter 2 for comparison. Figure A.3 shows a plot of the ratio of the WKB solution to the exact solution. Over the range of energies from the Fermi level up to the barrier top, the WKB approximation is essentially indistinguishable from the exact solution. It should be noted that the exact solution retains its validity at the apex of the barrier and above the barrier, but for problems in which the energies of the electrons are below the barrier, the WKB approximation provides a more tractable and yet accurate solution.

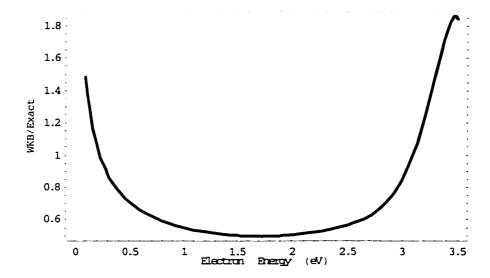


Figure A.3. Ratio of WKB approximation to exact solution for energies below the barrier.

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# Appendix B

# Physical Constants of Wurtzite GaN and InN

Table B.1. Selected Physical Constants.

Physical Property		GaN					InN	
Elastic stiffness constants (GPa)	[1,13,19]	[2]	[15]	[5]	[6]	[7]	[2]	[15]
c <sub>11</sub>	296±18	391	367	374	390±15	377	271	223
c <sub>12</sub>	130±11	143	135	106	145±20	160	124	115
c <sub>13</sub>	i58±6	108	103	70	106±20	114	94	92
C33	267±18	399	405	379	398±20	209	200	224
C+4	24.1±2	103	95	101	105±10	81.4	46	48
C <sub>66</sub>	83	124	116	134	123±10	109	74	54
a-plane lattice constant (Å)	3.160-3.190[1] 3.17[2] <b>3.189</b> [4,9] 3.160[8]						3.5446[1] 3.548[4,9]	3.53[2] 3.545[8]
c-plane lattice constant (Å)	5.125-5.190 5.185[9]	[1]	5.13[2]		5.125[8]		5.7034[1] 5.703[8]	5.54[2] 5.760[9]
Band gap (eV)	3.44[1]		3.4[4]		3.39[9]		1.89[1,9]	1.9[4]
Electron affinity (eV)	3.3[12]	2.1-4.		3.5[17		.2[20]	4.3[18]	
Electron effective mass	0.22[1,8]		0.2[4,9]				<b>0.11</b> [1,9] 0.115 [8]	
Hole effective mass	0.8[1]		1.1[4]					
Dielectric constant								
ε(0)	10.4 (Ellĉ) 9.5[9]	[1]	9.5 ( <b>E</b> J	<b>.ĉ</b> ) [1]	8.9[9]		15.3[8]	
ε(∞)	5.8 ( <b>E</b> ll <b>ĉ</b> )[	1]	5.35 ( <b>E</b> .	L <b>ĉ</b> )[1]	5.35[9]		9.3 [1]	
Density (g/cm <sup>3</sup> )	6.095[16]		6.150[8]				6.81[1,13]	6.810[8]

Table B.2. Piezoelectric Constants.

Piezoelectric Constants			GaN			In	N
Stress constants (C/m <sup>2</sup> )	[3]	[11]	[11]	[14]		[14]	
e <sub>31</sub>	-0.217	-0.33	-0.36	-0.49		-0.57	I
e <sub>33</sub>	0.434	0.65	1.0	0.73		0.97	
e <sub>15</sub>	-0.217	-0.33	-0.3				
Strain constants (cm/V)	[3] <sup>†</sup>	[11]‡	[11]5	[14]		[14]	
$d_{31} (\times 10^{-10})$	-0.703	-1.1	-1.3	-1.4	-1.7 [5]	-3.3	-1.1 [5]
$d_{33}(\times 10^{-10})$	1.47	2.2	3.2	2.6	-2.0[10]	8.0	]
$d_{15}(\times 10^{-10})$	-2.11	-3.2	-2.9	-4.8	I	-12	

All values are given at T=300K; bold font specifies values used throughout this dissertation.

<sup>&</sup>lt;sup>†</sup>Calculated from data in [3] and using the elastic constants given in bold in Table B.1.

<sup>\*</sup>Calculated from data in [11] and using the elastic constants given in bold in Table B.1.

<sup>&</sup>lt;sup>§</sup>Calculated from data in [11] and using the elastic constants given in bold in Table B.1.

<sup>\*\*</sup>Calculated from data in [14] and using the elastic constants given in bold in Table B.1. In addition, the assumption that  $e_{15}=e_{31}$  has been made.

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# Appendix C

# Example Process Sheet for FEA with an Integrated Anode

P	roces	s Deta	ails of	S	ubstrate#
ı	Templa	te			
••	Α.		µm inGaN/GaN on Sapphire	e	InGaN thickness
			pcara care on capp	•	In concentration
11.	Regro	wth Ma	sk		
			Samples		
			Toluene 6 min (1 min Ultra	so	und (US))
			Acetone 3 min (1 min US)		. "
		3.	Acetone 3 min (30 sec US)	)	
			Methanol 3 min (1 min US)	)	
			Methanol 3 min (30 s US)		
		6.	Dehydration Bake (DHB) 1	20	°C oven 10 minutes
	В.		PECVD (PlasmaTherm Sys		
		1.	300 mTorr, 80 W, 250 °C p	ola	ten, 100 sccm CF <sub>4</sub> O <sub>2</sub>
			30 minute clean		
	C.		it PECVD SiO2 Regrowth m		
		1.	9m44s 900 mT, 1300 sccn	n, I	N₂O 100 sccm, SiH₄, 22 W
	_		Results: n=, thicknes		
	D.			) (	plasma enhance chemical vapor
		deposit			
			DHB samples 15 min		
			HMDS/4110 Photoresist	<b>.</b> .	rates (OD) had alone (UD) ( 4 cm)
					pake (SB) hot plate (HP) (~1 μm)
		4.	• • • • • • • • • • • • • • • • • • • •		Expose: 30s Develop: 15s, 1:4 400K:H <sub>2</sub> O
		_	(400K is developer)	-1-	n. 45a 4.4 (dade field manifes) (con
		Э.	vacuum contact)	510	p: 45s 1:4 (dark field, positive) (use
		6	Hardbake (HB) resist 120 °	·	UD 4 min
					nr (100) mTorr, 100 W, Low Freq. (LF) Technics
		7.	PE II-A Plasma System	)U(	THIOH, 100 W, LOW Fleq. (EF) Technics
		A	Etch SiO <sub>2</sub> 1:10 buffered HF	=·  -	I-O min (~2000 Å/min)
			5 min deionized water (DI)		
					5 °C HP 25 mins/ 3 min acetone/ 3 min
			methanol/ N <sub>2</sub> blow dry		
		11.	UV Ozone Clean (after 5 m	nin	system preclean) 5 min
					1:20 bHF:DI dip 5 s / DI rinse
П	Regrov		amids by MOCVD	_	
			ie Mesa (layer 2_2)		
•		Remov			
	,		HF Etch 100% buffered HF	- 5	min.
	В.		n evaporate SiO₂ 2000 Å to i		
			tch Lithography		· · · · · · · · · · · · · · · · · · ·
			<del>-</del> • •		

- 1. DHB 10 min
- 2. Spin HMDS/4330 4 krpm 40 s (~3 μm)
- 3. SB 1min
- 4. EBR Exposure: 1 min Develop: 20s 1:4
- 5. Image Expose: 19s Develop: 1 min (layer 2\_2) (light field, positive)
- 6. O<sub>2</sub> plasma descum 20 s
- C. Mesa Etch (RIE #5) Cl<sub>2</sub> RIE
  - 1. 5 mTorr, 10 sccm Cl<sub>2</sub>, 200 W (0 sccm He)
  - 2. Etch Rate ~1250 A/min
- D. Results Dektak stylus profilometry show GaN thickness \_\_\_\_ μm
- E. Strip resist. 1165/Acetone/Methanol/H<sub>2</sub>O (3 minutes each)
- F. Remove SiO<sub>2</sub> 100% buffered HF 60s
- G. Check pyramids in SEM to see if damaged from etch.

#### V. Cathode Contact Pads and Airbridge Supports (layer 2\_3)

- A. Lithography
  - 1. DHB 10 min
  - 2. HMDS/ 4330 (use ammonia oven to image reverse)
  - 3. Spin 5 krpm 40s
  - 4. SB 1 min
  - 5. EBR Expose: 1 min. Develop 30s 1:4 400k:DI
  - 6. Image Exposure: 18 s
  - 7. Image Reversal Bake 45 minutes in ammonia oven 90°C
  - 8. Flood Exposure: 1 min w/ filter
  - 9. Develop: 1:4; 4 min.
  - 10. O<sub>2</sub> descum: 20 s
- B. Metalisation
  - 1. E-beam Evaporation
  - 2. 200 Å Ti
  - 3. 6000 Å of Au
- C. Lift-off
  - 1. Acetone, room temperature
  - 2. intermittent hand agitation
  - 3. brief ultrasound
  - 4. Clean sample 10 min 1165/H<sub>2</sub>O dip/ 1min Acetone/ 1min Methanol/H<sub>2</sub>O rinse (1 min)
- D. Anneal (optional for large contacts)
  - 1. Rapid Thermal Annealer (RTA)
  - 2. No ambient
  - 3. 700 °C for 15 s
- VI. Airbridge Definition
  - A. Bridge support (sacrificial resist; PMGI SF15)
    - 1. DHB 10 min.
    - 2. spin 5 krpm 40 s SF15 (give ~2.2 μm according to chart in cleanroom)
    - 3. SB 2 min 200°C HP; 30s cool down
    - 4. spin 5krpm 40 s SF15
    - 5. SB2 min 200°C HP; 30s cool down
    - 6. EBR-X-acto knife scrape
  - B. Pattern Bridge Posts (layer 2\_4)
    - 1. Spin 4330 6k 40s

- 2. SB 1min
- 3. EBR Expose: 1min Dev:30s 1:4 400k:H<sub>2</sub>O
- 4. Image Expose:15s Develop: 40s
- 5. O<sub>2</sub> plasma descum 30 s
- 6. Deep UV (DUV) flood 3500 mJ/cm2 develop SAL 101 45s
  - a) lamp 14mW/cm<sup>2</sup>
  - b) ~300s exposure
- 7. DUV again for 60 s for overexposure
- 8. 45 s develop SAL 101
- 9. 120 s DUV
- 10. 40 s dev SAL 101
- 11. O<sub>2</sub> Plasma descum 5 min 300mT/100W/LF
- 12. Remove 4330: 60s Acetone/60 s Isopronol/60 s DI soak
- 13. O<sub>2</sub> Plasma descum 40 s
- 14. Heat 95 °C HP 1 min; Reflow SF15 19min/200°C HP
- C. Bridge Definition (layer 2\_5)
  - 1. Tri-layer photoresist: OCG 825+OCG 825+4110
  - 2. Spin 5krpm 40 s OCG 825
  - 3. SB 1min 95°C HP
  - 4. Flood expose: 5s
  - 5. Spin 5krpm 40s OCG 825
  - 6. SB 1min
  - 7. Flood expose: 5s
  - 8. Spin 4110 5krpm 40s
  - 9. SB 1min
  - 10. EBR Expose: 1m30s Develop: 1m30s 1:5 400k:DI
  - 11. Image Expose: 20s Develop: 2m5s
  - 12. O<sub>2</sub> Plasma descum 20 s
- D. Bridge Metalisation
  - 1. E-beam evaporation
  - 2. 200 Å Ni (for sticking and Schottky contact)
  - 3. 1.5021 µm Au for rigidity
- E. Bridge liftoff
  - 1. Acetone room temp.
  - 2. Hand agitation and short burst of ultrasound.
  - 3. Left in Acetone for several hours.
- F. Remove Bridge Support
  - 1. 5 hours 1165 100°C HP (covered petri dish)
  - 2. Use a stir bar to agitate 11653. Acetone/Methanol clean

  - 4. bHF dip (1:10) 5 s
- Microposit® 1165 photoresist stripper and Microposit® SAL 101 developer are products of Shipley Corporation, 455 Forest Street, Marlborough, MA 01752.
- AZ 4110 and AZ 4330 photoresists, and AZ 400K developer are products of Clariant Corporation, 70 Meister Avenue, Somerville, NJ 08876.

Nano<sup>TM</sup> PMGI SF 15 is a deep UV photoresist and is a product of MicroChem Corp., 1254 Chestnut Street, Newton, MA 02464.

OCG 825 photoresist is a product of Olin Microelectronic Materials, 501 Merritt 7, Norwalk, CT 06856.

## Appendix D

# Derivation of Piezoelectric Polarization in the c-direction for Dihexagonal Polar Crystal Class (Class 26, $C_{6v}$ , 6mm)

The aim of this appendix is to derive the equation for the piezoelectric polarization in the c-direction in terms of the strain in the a-plane for the wurtzite-type ( $\alpha$ -phase) crystals. This class of crystals is known as the hemimorphic hemihedral class according to Voigt and the dihexagonal polar class (class number 26) according to Miers[1]. A more common and logical method of specifying the crystal system based on using symbols for the crystal symmetries is the use of the Schönflies or Hermann-Mauguin symbols. In the Schönflies system, the wurtzite crystals are denoted by  $C_{6\nu}$ , which refers to the six-fold cyclic axis that has six parallel planes of symmetry. The Hermann-Mauguin symbol is 6mm, which designates the same six-fold axis and distinguishes the two different types of mirror planes that are parallel to the six-fold axis. For this class of crystals, the complexity of the elastic stiffness tensor and piezoelectric constant tensors is reduced from the general anisotropic case because of the symmetry of the crystal. The relevant tensors are given below.

$$c = \begin{bmatrix} c_{11} & c_{12} & c_{13} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{13} & 0 & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix}$$
elastic stiffness tensor[2]
$$(D.1)$$

$$d = \begin{bmatrix} 0 & 0 & 0 & 0 & \frac{1}{2}(c_{11} - c_{12}) \end{bmatrix}$$

$$d = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$
piezoelectric strain tensor[3]
(D.2)

We begin with the equation for polarization in terms of the strain[4],

$$P_3 = e_{31}S_1 + e_{32}S_2 + e_{33}S_3 + e_{34}S_4 + e_{35}S_5 + e_{36}S_6,$$
 (D.3)

where  $P_3$  is the polarization in the z-direction,  $e_{ij}$  are the components of the piezoelectric stress tensor, and  $S_i$  are the components of the strain. The piezoelectric stress tensor, e, has the same symmetry as the piezoelectric strain tensor, d, given in equation (D.2). Thus, equation (D.3) simplifies to

$$P_3 = 2e_{31}S_1 + e_{33}S_3. ag{D.4}$$

By convention, the results are expressed in terms of the piezoelectric strain coefficients so we must calculate the piezoelectric strain constants from the piezoelectric stress constants. The piezoelectric strain and stress constants are related through the elastic constants,  $c_{ij}$ , by[5]

$$e_{mh} = \sum_{i=1}^{6} d_{mi} c_{ih}^{E}$$
 (D.5)

where the non-zero c and d coefficients are given above in equation (D.1) and equation (D.2). The superscript of the elastic constants refers to the elastic constants at a constant electric field. The equations for  $e_{31}$  and  $e_{33}$  are given by

$$\begin{array}{l}
e_{31} = d_{31}c_{11} + d_{31}c_{12} + d_{33}c_{13} \\
e_{33} = d_{31}c_{13} + d_{31}c_{13} + d_{33}c_{33}
\end{array} \right}.$$
(D.6)

Inserting these expressions into equation (D.4) gives

$$P_{z} = 2(d_{31}c_{11} + d_{31}c_{12} + d_{33}c_{13})S_{1} + (2d_{31}c_{13} + d_{33}c_{33})S_{3}$$
 (D.7)

which expresses the polarization in terms of the elastic constants, piezoelectric strain constants, and the applied strain.

The strain in the z-direction is related to the strain in the x-direction by Poisson's ratio,  $\sigma$ , which is defined by

$$S_3 = \frac{-S_1}{\sigma} \tag{D.8}$$

Stress and strain are related through the elastic constants. Stress is given as a function of strain by

$$\mathbf{T} = \mathbf{c} \cdot \mathbf{S} \tag{D.9}$$

where T is the stress tensor and S is the strain tensor. Poisson's ratio is calculated using the condition that there is no stress in the z-direction, i.e.  $T_3 = 0$ . Using equation (D.9) to calculate the z-directed stress in terms of the strain gives

$$T_3 = c_{13}S_1 + c_{13}S_2 + c_{33}S_3 . {(D.10)}$$

Using the condition of biaxial strain of equal magnitude in the x- and y-directions, i.e.  $S_1=S_2$ , and equating this to zero gives

$$T_3 = 2c_{13}S_1 + c_{33}S_3 = 0 (D.11)$$

which is solved to yield

$$S_3 = \frac{-2c_{13}S_1}{c_{33}} \tag{D.12}$$

and thus,

$$\sigma = \frac{c_{33}}{2c_{13}} \tag{D.13}$$

for Poisson's ratio.

Plugging equations (D.8) and (D.13) into equation (D.7) gives

$$P_3 = 2(d_{31}c_{11} + d_{31}c_{12} + d_{33}c_{13})S_1 - \left(\frac{2d_{31}c_{13}}{\sigma} + \frac{d_{33}c_{33}}{\sigma}\right)S_1$$
 (D.14)

$$P_{3} = \left(2d_{31}c_{11} + 2d_{31}c_{12} + 2d_{33}c_{13} - \frac{2d_{31}c_{13}}{\sigma} - \frac{d_{33}c_{33}}{\sigma}\right)S_{1}$$
 (D.15)

$$P_3 = \left(2d_{31}c_{11} + 2d_{31}c_{12} + 2d_{33}c_{13} - \frac{4d_{31}c_{13}^2}{c_{33}} - \frac{2d_{33}c_{33}c_{13}}{c_{33}}\right)S_1 \qquad (D.16)$$

$$P_{3} = 2d_{31} \left( c_{11} + c_{12} - \frac{2c_{13}^{2}}{c_{33}} \right) S_{1}$$
 (D.17)

Equation (D.17) is the important result and expresses the c-directed polarization in terms of the strain in the a-plane, the  $d_{3l}$  piezoelectric constant, and the relevant elastic stiffness coefficients. This equation applies for material grown parallel to the c-axis.

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## Index

A	H
air-bridge83, 85, 87 Airy functions138	hemimorphic hemihedral crystal class151 Hermann-Mauguin symbols151
B	L
band diagram 35-36	lifetime48, 51, 53
C	M
cathode-ray tube       1         cesium       5         cold cathodes       2         critical thickness       112	Malter effect
D	negative electron affinity4
damage86, 90 dihexagonal polar crystal class151	nitride semiconductors12 Nottingham effect52
dislocations103	0
E	optoelectronic cathode4
effective electron affinity	P
	photocathode
ferroelectric cathodes4	piezoelectric strain constants
field emission	planar cold cathodes5
field emission microscope32	planar cold cathodes2 planar-doped barrier electron emitter4, 134
field emitter	<i>p-n</i> junction cathodes4 pseudomorphic growth103
flat panel display15	S
Fowler-Nordheim equation	sample holder75
Fowler-Nordheim plot78, 117	Schönflies
<i>G</i>	selective area growth66-69, 71, 73, 74
GaN FEAs external anode72	self-limited growth       70         Spindt cathode       14, 133         supply function       32, 36, 38, 40-42
integrated anode83, 87, 91	• • •

1	V
test chamber75	vacuum microelectronics13
thermal conductivity	vacuum tube17
thermionic cathode1-2	vacuum tubes15
transmission function 32, 36, 38, 40-42	) •
triangular barrier 137	; <b>w</b>
tunnel emitter4	
tunneling	WKB approximation39, 40, 50, 141
TWT 10	