Oxide coated silicon tip arrays for electron emission

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Oxide coated silicon tip arrays for electron emission

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School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2009

STATEMENT OF ORIGINALITY

I hereby certify that the content of this thesis is the result of work done by me and has not been submitted for a higher degree to any other University or Institution.

29/05/2009
Date

Bian Haijiao
Bian Haijiao (signature)

Acknowledgments

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SUMMARY

The study of cold cathode materials is currently an active topic of research due to widespread and important applications of these materials in products such as field emission displays and vacuum microelectronic devices. Of the wide range of readily available cold cathode materials, silicon (Si) tip arrays have attracted much attention owing to their compatible fabrication process with advanced integrated-circuit technology. However, an inherent high threshold electric field and poor emission stability limit their widespread use. In this dissertation, sputtered ferroelectric N-doped SrTiO_3 thin films have been proposed as a beneficial surface modification on Si tip arrays to improve the field emission behavior. Systematic and extensive analysis has been carried out to further understand their dependence on sputtering parameters as well as increasing the understanding of the underlying field emission enhancement mechanisms.

The N-doped SrTiO_3 thin films have been fabricated using a reactive RF sputtering technique. Field emission properties of Si tip arrays coated with these thin films have been investigated by varying the deposition gasses and thickness of the coatings. The microstructural evolution results indicate that the SrTiO_3 coatings exhibit a perovskite structure while deposited in different sputtering gasses of pure Ar, Ar + 20% O_2 and Ar + 50% N_2 . While a 6 nm thick film is amorphous in nature, the polycrystalline perovskite grains are seen to develop in a thicker film, with crystallinity improvements evident with an increasing film thickness. The study of the electronic structure using X-ray photoelectron spectroscopy (XPS) shows that the nitrogen has been successfully doped into the SrTiO_3 lattice. The field emission

Summary

characteristics of the SrTiO_3 deposited in a N incorporated gasses shows that the N addition significantly enhances the field emission properties of the coated Si tip arrays when compared with those deposited in other sputtering gasses. Results also indicate that the existence of O_2 in the sputtering gasses has a detrimental effect on the enhancement of the field emission properties. The electron emission characteristics were also shown to be dependent on the coating thickness. A 12 nm thick N-doped SrTiO_3 film was shown to be the optimum thickness for maximizing the field electron emission enhancements.

The emission behavior was then shown to be highly dependent on the nitrogen content of the N-doped SrTiO_3 coating. The threshold field was substantially lowered from 36.2 V/ μm for bare Si tip arrays to approximately 17.4 V/ μm for 12 nm thick coated Si field emitter arrays (FEA), deposited in a mixture gasses of Ar + 50% N_2 . In addition, the coating considerably improved the electron emission stability of Si tip array. Analysis of the emission data using the Fowler-Nordheim (F-N) plot suggests that the improvement in electron emission originates from a lowering of the effective work function. The proposed mechanism of bonding and band-forming provides a feasible mechanism for an N-enhanced threshold electric field in cold cathode emission because of the presence of the lone-pair-induced antibonding states above the Fermi level. Water contact angle measurements provided further evidence of the presence of the anti-bonding states induced by nitrogen doping, and subsequent validation of the proposed mechanism.

Extensive research has also been carried out into the effects of the sputtering parameters on field emission enhancement. The effects of substrate temperature and total sputtering pressure have been examined to optimize field emission properties. The films exhibit a perovskite structure at a high substrate temperature (600 °C) and a

Summary

high sputtering pressure (1.6 Pa) respectively. From the XRD and XPS results, the polycrystalline grain grows with an increasing substrate temperature and total sputtering pressure. When the substrate temperature and sputtering pressure are increased to 600 °C and 1.6 Pa respectively, the N-doped SrTiO₃ thin film exhibits well-developed perovskite microstructure and atomic nitrogen is doped into SrTiO₃ lattice. The enhanced field emission behavior thus originates from different states of doped nitrogen. Nitrogen substitution in the films reduces the effective work function of the silicon field emitter and therefore enhances the field emission properties according to the bonding and band-forming model.

The studies in this dissertation demonstrate the numerous benefits to field emission induced through the utilization of N-doped SrTiO₃ coated Si tip arrays. The field emission properties are shown to be closely correlated to the microstructure and electronic properties of SrTiO₃ thin films, which are influenced by nitrogen chemical bonding states.

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N-STO thin films deposited at different sputtering pressures.

LIST OF ABBREVIATIONS

η	Electronegativity
a.u.	Atomic unit
BBB	Band-band-barrier
CN	Coordination number
CMOS	Complementary Metal Oxide Semiconductor
CNTs	Carbon Nanotubes
Cs	Cesium
CVD	Chemical Vapor Deposition
DLC	Diamond like carbon
DOS	Density of states
E_F	Fermi energy
FEAs	Field Emission Arrays
FEDs	Field Emission Displays
F-N	Fowler-Nordheim
FNSL	Fowler-Nordheim Slope

List of abbreviations

FT-IR	Fourier Transform Infrared
NEA	Negative Electron Affinity
PEA	Positive Electron Affinity
PZT	Lead Zirconium Titanate
SEM	Scanning Electron Microscopy
Sr	Strontium
STO	Strontium titanate
Ti	Titanium
TO	Transverse Optical
VCA	video contact angle analysis
VBM	Valence-Band Maximum
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Motivation

Field emission technology is widely used in numerous aspects of modern society in fields ranging from everyday consumer products such as flat panel displays, to high-tech military and space applications. Due to their numerous attractive characteristics coupled with the emergence of vacuum microelectronics (VME), renewed research has been initiated into cold cathode field emission. By exploiting the merits of VME systems, in which a cold cathode is used as the active element, a broad range of new products and applications for field emission technology have been realized. As a result, field emission-based devices have gained immensely in popularity.

Compared with previously used vacuum tubes, which adopted thermionic cathodes, field emission devices offer unique advantages including the use of unheated “cold” cathodes under an electric field, rapid response to field variations, resistance to both temperature fluctuation and radiation, small size, modest power consumption and an inherent capability to integrate with solid-state electronics. The early history of electron field emission was traditionally encompassed within the

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discipline of surface science owing to the relationship between the emission current density and the electric field, which was first observed by Fowler and Nordheim in 1928.¹ Serious investigations into cold cathode materials became more wide spread in the late 1960s and early 1970s, when Spindt-type field emitter arrays (FEAs), were microfabricated in a gated configuration.² The advent of microfabrication technology resulted in an explosion of new research and the development of cold cathode materials such as Si FEAs,³ carbon-based films,⁴ carbon nanotubes (CNTs)⁵ and other one-dimensional nanomaterials.^{6,7}

Among the possible contenders, Si FEAs have arguably attracted the most attention owing to their ease of fabrication, primarily due to the available abundance of advanced semiconductor technology and the compatible fabrication process with advanced integrated-circuits. The resulting cold cathode materials have found uses in numerous important applications in consumer goods, military industries and space technology.^{6,8,9} However, an inherent high threshold electric field and poor emission stability limit the use of Si FEAs in many applications.

In order to design devices for a specific function, it is necessary to quantitatively understand the special character of micro-field-emission sources. Some important issues are usually addressed as follow: 1) current density-electric field characteristics; 2) emission fluctuation noise; 3) limits to the high currents that can be drawn; 4) energy distribution among the emitted electrons; 5) space-charge effects. In recent years, the search for tip arrays with low operating voltage or low work function, coupled with a high and stable emission current has been a major focus of vacuum microelectronics.

Apart from geometric modifications of the gated FEA, surface modification is a popular method lowering the operating electric field, which can improve field

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emission intensity and stability. Carbon-based materials,^{10, 11, 12} nitrides,^{13, 14} silicides,¹⁵ carbides,¹⁶ and refractory metals¹⁷ coated on Si tip arrays have recently been subject to intensive research and preliminary results have indicated promising enhancements of the emission properties of Si tip arrays. To further reduce the work function or threshold field, a number of investigations^{18,19} have been carried out that introduce dopant into the coatings of the emitter materials. Recently, silicon tip arrays modified by sol-gel $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST) ferroelectric thin films have demonstrated enhanced electron field emission characteristics, as shown by Kang^{20,21} and Zhu.²² The BST coated Si tip arrays exhibit a low threshold field and stable emission current. Such enhanced emission behavior is highly correlated with the microstructure and stoichiometric composition of the sol-gel coated BST thin films. In 1996, Okano et al.²³ discovered that nitrogen addition significantly reduced the effective work function of the CVD diamond thin film, and that the resulting threshold field was even lower than that when doped with boron and phosphorous.

While the sol-gel technique of Kang and Zhu has been demonstrated to be a very effective method of growing multi-element thin films with the ease of stoichiometric control, it requires a high post annealing temperature in order to achieve the ideal perovskite structure. This high-temperature process induces a solid-state interfacial reaction with the Si and diffusion into the film, which results in an interfacial layer that deteriorates the field emission performance. For the work of Okano et al., a detailed field emission mechanism for the improvements due to a nitrogen doped diamond film has not yet been established.

Therefore, in this work, a sputtering technique is firstly adopted to deposit ferroelectric thin film coatings with nitrogen doping on the Si tip arrays to improve its field emission behaviors. It is expected to obtain an oxide film with the much desired

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perovskite structure, at a relatively low temperature leading to a reduction in the amount of deterioration. I believe that the sputtering technique can provide more uniform coverage of the coatings on the Si tip arrays than sol-gel techniques. Nitrogen incorporated SrTiO_3 (STO) thin film is then proposed as a suitable cold cathode emitter to both improve the field emission characteristics of a Si FEA, as well as providing, for the first time, a basis for the proposal and development of a field emission mechanism to validate the field improvements induced by the nitrogen dopant.

These new exciting advances in field emission technology motivate the development of novel applications of ferroelectric thin films with nitrogen doping. The investigations presented in this dissertation provide important and ground breaking contributions pertaining to the understanding of the fundamental issues of doped ferroelectric thin films as well as furthering the ultimate realization of extensive potential applications for field emission devices.

1.2 Objectives

The goal of this dissertation is to address the fundamental and, to date, poorly understood principles regarding N-doped STO thin films coated on a Si FEA, using a reactive radio frequency (RF) sputtering technique. The primary objectives include:

- 1) To deposit N-doped STO thin films on a Si FEA using a reactive RF sputtering method.
- 2) To investigate and analyze the fundamental properties of the N-doped SrTiO_3 thin films, which include the microstructure, component analysis, chemical compound

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formation, and electronic structure. The effects of varying the sputtering parameters and film thickness are of interest to further the understanding of the sputtering process.

- 3) To extensively characterize the field emission properties including threshold field and emission current stability for Si tip arrays coated with N-doped SrTiO₃ thin films. Fowler-Nordheim (F-N) is adopted to analyze the acquired emission data. This is expected to give further understanding into the field emission principles and mechanisms of the ferroelectric thin film coated Si tip arrays.
- 4) To propose a field emission mechanism for the enhancements expected in the field characteristics from the Si FEA, as a result of the nitrogen doped STO thin film coating.

1.3 Major contributions

The major contributions achieved in this research work are summarized as follows:

- 1) Ferroelectric thin films are first successfully deposited on Si tip arrays for enhancement of field electron emission by physical vapor deposition. The N-doped STO thin films have been synthesized on Si tip arrays by a reactive RF sputtering technique which prevents the formation amorphous oxide layer between the silicon wafer and thin film in wet process. The sputtering parameters have also been optimized to dope nitrogen into the perovskite SrTiO₃ lattice.

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- 2) The microstructural features and component analysis have been extensively investigated by X-ray diffraction (XRD), Video contact angle analyzer (VCA), Ellipsometer spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. A strong dependence of the microstructure of the N-doped STO thin film on the deposition parameters has been found. The N-doped SrTiO_3 film has been shown to exhibit a good perovskite structure when deposited at a substrate temperature of 600°C and a sputtering pressure of 1.6 Pa, in an gasses mixture of Ar + 50% N_2 . The microstructure of the N-doped STO thin films also indicated a thickness dependency. The crystallinity of the perovskite structure was seen to improve with increasing of N-doped STO (N-STO) film thickness. Since a 6 nm thick N-STO film is amorphous in nature, the polycrystalline perovskite grains were seen to only develop in thicker films.
- 3) The chemical compound formation and electronic structure of the N-STO films have been intensely studied by X-ray photoelectron spectroscopy (XPS). It has been discovered that the Fermi level shifts up for the N-STO films with increases in the nitrogen partial pressure from 0% to 50%, and then reduces slightly with further increases to 100%. The initial upward shift of the Fermi level is proposed to be due to antibonding states located above Fermi level, which are induced by the lone-pair dipoles of doped nitrogen, and it is proposed that the downward shift of Fermi level with partial pressures in the range of 50% to 100% is associated with the production of H-like bonds at the surface due to nitrogen overdosing which conforms to the prediction of bond-band-barrier correlation.

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- 4) The field emission properties of the N-STO coated Si FEAs have been examined, which indicated considerable field emission improvements, when compared with the uncoated FEAs. The threshold field has been lowered substantially from 36.2 V/ μm for bare Si tip arrays to approximately 17.4 V/ μm for 12 nm thick N-STO coated Si tip arrays deposited at substrate temperature of 600 °C and a sputtering pressure of 1.6 Pa in a mixture gasses of Ar + 50% N₂. This was found to be the optimal nitrogen partial pressure to induce the maximum improvement of the field emission behavior. Furthermore, a U-shape dependence of the threshold field on the film thickness was discovered. The 12 nm N-doped SrTiO₃ coated Si tip arrays demonstrate the minimum threshold field, for a given set of temperature and partial pressure parameters. In addition, considerable improvements on the field emission stability of the Si tip arrays were observed. From analysis of the emission data using the F-N plot, it is proposed that the field emission is controlled by a tunneling mechanism and the improvements in field emission originate from a lowering of effective work function caused by the N-STO coating.
- 5) The field emission mechanisms of the N-STO coated Si tip arrays, under various sputtering conditions, have been discussed in the context of the bonding and band-forming model. From the discovered relationships to the sputtering parameters, a high crystallinity of perovskite structures in the surface region is observed as are an upwards-moved Fermi level induced by successful nitrogen addition. The proposed presence of anti-bonding states located above Fermi level is first verified by water contact angle measurements.

1.4 Organization

This dissertation proposes and emphasizes the merits of the adopting sputtered N-STO thin films on Si FEAs as field emission devices, as well as extensively furthering the understandings of their fundamental structure and field emission mechanism through analysis of the effects of various sputtering conditions. The dissertation is organized as follows:

This chapter provides the motivations for proposing and developing a further understanding of N-STO thin films for the field emission. The drawbacks of non sputtering methods have been outlined, as have the appealing potential attributes of N-doped coatings. The objectives and major contributions have been outlined, and the organization of the dissertation is presented.

Chapter 2 is devoted to discussions on the fundamental background and a related literature review with respect to the theory of field emission, the state of the art in cold cathode materials, principles of field emission from Si tip arrays without and with coatings and the potential field emission applications. The bond-band-barrier model, which is extensively used in this dissertation, is also introduced. The aim of this chapter is to provide a foundation of understanding for the emission processes and a solid principled basis for the analysis and proposed mechanisms of the experimentally observed characteristics, which are presented throughout this dissertation.

In **Chapter 3**, the experimental procedures used in this research work are presented. The procedures necessary for the preparation of the N-STO thin films, the characterization of their microstructure and components, the characterization of their photoelectron spectroscopy, and the characterization of their field emission properties

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are described in detail. This provides the experimental basis of the measurements used to develop the new understandings as well as forming the new conclusions and proposals of this dissertation.

Chapter 4 presents and analyzes various experimental results based on the microstructural features, component analysis, chemical compound formations and electronic properties of un-doped STO, Oxygen doped STO (O-STO) and N-STO coated Si FEAs, as well as their resulting field emission properties. Firstly, the effects of the deposition gasses on the field emission are presented. This includes an investigation of the microstructural evolution, component analysis, chemical compound and electronic properties of the doped STO coated Si tip arrays, and highlight of the merits of the N-STO coating. Following the verification of the superiority of the N-STO coating, the second section of the chapter provides a study on the effect of the N-STO coating thickness on the field emission and obtains the optimum film thickness for maximization of the field emission behavior enhancements.

Chapter 5 presents experimental results and discussion on the effect of the nitrogen content on the field electron emission from N-STO coated Si tip arrays. Firstly, the chapter introduces the characterization of sputtered N-STO thin films deposited at different nitrogen partial pressures, again including a study on the effects of the N content on the microstructure, chemical compound formation and electronic properties. The optimum nitrogen partial pressure in the sputtering gasses is obtained. The second section of the chapter provides a study of the field emission properties of N-STO coated Si tip arrays, an analysis of the emission data, and a discussion on the effect of the N content on the field emission mechanism. The bond-band-barrier

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correlation theory is used to propose a mechanism to explain reduction in the effective work function due to the nitrogen dopant.

Chapter 6 gives the experimental results and discussion of the effects of the substrate temperature and total sputtering pressure on the field electron emission from N-STO coated Si tip arrays. The first section introduces the characterization of the sputtered N-doped SrTiO₃ thin films deposited at different substrate temperatures and in different sputtering pressures, as before, including a study of the effects of the varying sputtering parameters on the resulting microstructure, chemical compound formation and electronic properties. The optimal temperature and pressure parameters are determined. The second section of the chapter then provides the study of field emission properties, the analysis of emission data, and the discussion on the effects of the substrate temperature and sputtering pressure on the field emission mechanism. The bond-band-barrier correlation theory is again used to propose mechanisms for the observed experimental data.

The conclusions of the dissertation are presented in **Chapter 7**, as are recommendations for interesting avenues of further research.

CHAPTER 2

LITERATURE REVIEW

In this chapter, the fundamental concepts and related literature are reviewed with respect to electron field emission mechanisms and their applications. The chapter provides an extensive fundamental basis for the work and proposals of this dissertation, as well reviewing the state of the art in field emission enhancement methods.

The chapter is organized as follows: The first section provides the background and underlying principles related to electron field emission theory, reviews the current state of cold cathode materials, of coated/uncoated Si array field emission as well as potential applications. The second section provides the introduction to the theory of bond-band-barrier (BBB) correlation, which is used to explain and propose mechanisms for much of the experimental findings of this dissertation. Conclusions of the review are presented in the final section of the chapter.

2.1 Electron field emission

The principles of electron field emission are outlined in this section. A brief history of field emission research is firstly presented, which is followed by a review of the fundamental aspects of field emission theory. The principles behind field emitter arrays (FEA) are then outlined, as these are also adopted as the emitters in this dissertation. A review of popular cold cathodes materials is then presented, of which silicon is used in this work. Film coatings are then reviewed and contrasted, with

SrTiO₃ being the coating chosen for the work of this dissertation. Finally, a short case study on one of the most popular practical applications of field emission technology is presented.

2.1.1 Introduction

Possibly the first reported discovery of field electron emission was by Wood²⁴ in 1897, through the study of the ‘arc’ between two platinum electrodes in a vacuum vessel. Late in 1922, Lilienfeld²⁵ made similar observations of this effect in a high vacuum X-ray tube with pointed cathode. An excellent historical account of early work is found in a review article by R. O. Jenkins.²⁶ It was noted by Wood that the small bulb-like chamber would be ‘of interest to those bent on getting a tube into the human body and lighting it from within’, which somewhat differs from the modern most popular application of flat screen displays. Classical emission theories at the time, which were based on thermionic principles, failed to sufficiently explain the experimental results, which indicated that field emission was independent of the temperature in the region. Furthermore, emission was evident at temperatures well below those believed required for the onset of thermionic emission.

Field emission is defined as electron emission from the surface of a condensed phase into a vacuum (or dielectric) due to the presence of a high electric field. Field-induced electron emission from a surface is primarily determined by the strength of the local electric field and the potential barrier to emission. In a metal, the barrier would correspond to the work function of the material. The other key aspect in the discussion of field emission is the concept of the local field, which differs from the applied macroscopic field. In the usual two-terminal experimental set-up, an anode at a potential V is separated by a distance D from a grounded cathode. The

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applied field is then V/D . The local field is enhanced relative to the applied field and this increase is characterized by the field enhancement factor or field magnification factor β . For tip-based emitters such as Spindt tips or carbon nanotubes, the enhancement factor usually depends on the geometric properties of the emitter tip, such as height and radius. In the field emission process, electrons with energies below the Fermi level tunnel through the potential barrier at the surface rather than escaping, as is the case for thermionic or photoemission. The high local electric field sufficiently narrows the barrier for the electrons to have a non-negligible tunneling probability during the field emission process. Thus there is a finite probability that electrons will be found outside the potential barrier at the surface. The efficiency of this emission process is of the order of tens of millions of times higher than other known emission processes. Due to an extremely high current density in field electron emission and the fact that no energy is consumed by the emission process, makes field emission suitable for an exceptionally wide range of practical possibilities and applications.

The difference between thermionic emission and field emission, and the transition between these two phenomena was initially described by Murphy and Good.²⁷ The mathematics behind the process was then explained by Fowler and Nordheim¹ in 1928 using a wave-mechanical formulation. The metrics of field electron emission from a metal (i.e. a material with an electron distribution described by Fermi–Dirac statistics) are described by the widely known Fowler–Nordheim equation.¹ In this seminal work, Fowler and Nordheim also consider the transition between thermionic and field emission. In their equation, the work function of the material and the field enhancement factor are key parameters. The work function is an intrinsic property of a material and is defined as the energy difference between the Fermi level and the

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vacuum level. Typically (for a metal) this value is 3.5 eV – 5 eV. The field enhancement factor is often termed the beta factor, and in simple terms, it is greater than unity for a non-planar solid/vacuum interface. A sharp pointed tip, for example, may have a beta factor of over 1000.²⁸

Currently, field electron emission is receiving an intense renewed research interest due to the emergence of vacuum microelectronics, a principally new branch of micro- and nano-electronics. When the first semiconductor transistors were invented by Shockley etc. in the 1950s,²⁹ and integrated circuits were subsequently developed in the 1960s,³⁰ it was generally accepted that the use of vacuum tubes had expired. However, with the emergence of vacuum microelectronic (VME) devices renewed interests have been generated to further exploit vacuum tubes for many new applications. Vacuum microelectronics is based on the employment of electrons in the vacuum at dimensions of active elements in tenths to hundredths of a micrometer. In practice, a field electron emitter is used as an active element in a VME system. By employing microscopic anode-to-cathode gaps, devices with a field emission cathode controlled by a voltage in the range of tens of volts can be constructed.

Small dimensional field electron emitters provide an opportunity for reducing the size of active elements down to a few tens of atomic dimensions (i.e. to 10^{-6} – 10^{-7} cm). Some recent experimental data indicates the existence of elective elements of a size on the atomic scale in such special materials as, for example, carbon nano-tubes.

Table 2-1 compares the characteristics of vacuum microelectronic devices with semiconductor devices and shows that a vacuum is a vastly superior transport medium compared to solids.

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Properties	Solid-State Devices	VME Devices
Current density	$10^4\text{--}10^5\text{ A/cm}^2$	$\sim 2 \times 10^3\text{ A/cm}^2$
Voltage	$>0.1\text{ V}$	$>10\text{ V}$
Structure	Solid/solid interface	Solid/vacuum
Electron transport		
Medium	Solid	Vacuum
Ballistic	$<0.1\text{ }\mu\text{m}$, Low temp.	100% Ballistic
Coherence	Length $<0.1\text{ }\mu\text{m}$ $t < 10^{-13}\text{ s}$ at RT	Length $\gg 0.1\text{ }\mu\text{m}$ $t \gg 10^{-13}\text{ s}$
Lens effect	Difficult	Easy
Noise	Random motion of carriers	
Thermal noise	Surface/interface effects	Comparable
Flicker noise	Fluctuation in generation/	Worse
Shot noise	recombination rates of carriers	Comparable
Electron energy	$<0.3\text{ eV}$	Several to 1000 eV
Cutoff frequency	$<20\text{ GHz}$ (Si) $<100\text{ GHz}$ (GaAs)	$<100\text{--}500\text{ GHz}$
Power	Small	Large
Radiation hardness	Poor	Excellent
Temperature sensitivity	$-30\text{--}+50^\circ\text{C}$	$<500^\circ\text{C}$
Fabrication/materials	Well established (Si), established (GaAs)	Not well established
Applications	Microprocessors, memory devices, optoelectronic devices, RF devices	Flat panel displays, microwave power tubes, electron/ion sources, e-beam lithography, e-beam memories, and excitation devices

Table 2-1 Characteristics of solid-state and vacuum microelectronic devices.³¹

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The advantages of VME devices as compared to the solid state electronics are as follows:

1. No dissipation of energy during electron transport through the medium, i.e. in a vacuum. That gives the vacuum micro-electronic devices advantages, especially for the high power/high frequencies classes.
2. VME devices are high speed due to the lack of inertia in the field emission process and a very small electron transport time in the vacuum gap, which permits designing of fast-acting high-frequency devices.
3. A marked non-linearity of the field emission current–voltage characteristics, which permits designing of frequency converters and multipliers.
4. No energy expenses on the act of electron emission to quantum origin of the tunneling process.
5. A high radiation tolerance and heat resistance of the emitters.

VMEs with cold cathode emitters are used extensively throughout the work of this dissertation.

2.1.2 Theory of electron field emission

This section introduces a background of the fundamental theory of field emission necessary to achieve the detailed understanding and effects of parameter changes, as developed throughout this dissertation.

2.1.2.1 Electron field emission from metals

As previously mentioned, electron field emission is a quantum-mechanism phenomenon in which electrons tunnel through a potential barrier at the surface of a solid as a result of the application of a large electric field. To achieve field emission,

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external electric fields in the order of 10^7 V/cm - 10^8 V/cm are required to generate appreciable electron currents. The presence of the electric field reduces the width of the potential barrier and therefore renders it permeable to electrons. This can be seen in Figure 2-1 which presents a diagram of the electron potential energy at the surface of a metal.³²

Figure 2-1 Diagram of the potential energy of electrons at the surface of a metal where, $e^2/4x$ is the image force potential, $-eEx$ is the external applied potential; ϕ is the work function and E is the electric field.³² Figure taken from Ref. 30.

The dashed line of Figure 2-1 shows the shape of the potential barrier in the absence of an external electric field. The height of the barrier is equal to the work function of the metal, ϕ , which is defined as the energy required to remove an

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electron from the Fermi level of the metal into the vacuum level. However, an abrupt potential change at the metal surface is not expected because the charge cloud does not terminate sharply. The potential near the surface is decreased by an image term V_{im}^{33} ,

$$V_{im} = -e^2 / 4x \quad (2-1)$$

where e is the elementary charge, for a V_{im} in volts and x in angstroms. The solid line in Figure 2-1 corresponds to the shape of the barrier in the presence of an external electric field. As can be seen, the high electric field narrows the potential barrier at the metal-vacuum interface sufficiently for the electrons to have a significant probability of tunneling from the solid in the vacuum. In the presence of an applied field, E , the potential at a metal surface has the term,^{31,33}

$$V(x) = -eEx - \frac{e^2}{4x} \quad (2-2)$$

In addition to the barrier becoming triangular in shape, the height of the barrier in the presence of the electric field is reduced, with the decrease given by,

$$\Delta\phi = \left(\frac{eE}{4\pi\epsilon_0} \right)^{1/2} \quad (2-3)$$

where ϵ_0 is the permittivity of vacuum. Knowing the shape of the energy barrier, the probability of an electron, with a given energy, tunneling through the barrier can be calculated. Integrating the probability function multiplied by an electron supply function in the available range of electron energies leads to an expression for the tunneling current density, J , as a function of the external electric field, E . The tunneling current density can be expressed by equation (2-4), which is often referred to as the F-N equation,³⁴

$$J = 1.42 \times 10^{-6} \frac{E^2}{\phi} \exp\left(\frac{10.4}{\phi^{1/2}}\right) \exp\left(\frac{-6.44 \times 10^7 \phi^{3/2}}{E}\right) \quad (2-4)$$

where J is in units of A/cm^2 , E is in units of V/cm and ϕ in units of eV . Plotting $\log(J/E^2)$ vs. $1/E$ results indicates a linear relationship with a slope proportional to the work function, ϕ , to the $3/2$ power. Although, equation (2-4) is derived under the assumption of an operating temperature of 0 K, it can be shown that the error induced by its use at more moderate temperatures (~ 300 K) is negligible.³³ And in the limiting case, of a potential barrier transparency of 1 (i.e., the barrier is fully eliminated by the external electric field), the maximum electron current density passing through a metal-vacuum interface can be expressed in the free electron model as $j = \frac{\pi \cdot e m_e E_F^2}{h^3} \cong 4.3 \cdot 10^9 E_F^2 [A/cm^2]$.³⁵ And the maximum current densities obtainable from good conductors in high vacuum are also limited in practice by resistive heating of the tip and shank.

2.1.2.2 Electron field emission from semiconductors

The theory of electron field emission from semiconductors can be derived in a largely analogous manner to that of the theory for metals. However, special factors which are not considered in metal field emission cannot be neglected with semiconductors, due to the state of their surface and the fact that an external field applied to a semiconductor may penetrate the surface to a significant distance.³³

The electrons or holes concentrated at the surface can be supplied by donor and acceptor impurity atoms. This results in the formation of an electric double layer, with a sharply defined surface charge, and a volume charge of opposite polarity, decaying slowly towards the interior as shown in Figure 2-2. The potential of this layer introduces resistance to the interior charge carriers attempting to approach the

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surface. This can be considered as analogous to the work-function increment in adsorption for metal field emission. The relationship between the contact potential ϕ' and the layer thickness l (Figure 2-2) is shown as,³³

$$l = (k\phi' / 2\pi Ne)^{\frac{1}{2}} \quad (2-5)$$

where k is the dielectric constant, and N is the density of the impurity ions in the exhaustion layer. In most semiconductors, l has values in the order of 10^{-6} cm or more.

Figure 2-2 Schematic diagram of the energy levels near the surface of an n -type semiconductor with surface acceptor states, where l is the layer thickness and ϕ' is the contact potential due to adsorption.³³ Figure taken from Ref. 31.

When an external electric field penetrates into the interior of an n -type semiconductor, and neglecting the surface states, $\log(J/E^2)$ is shown to be a linear function of $1/E$, which was also the case for metals, presented in the previous section. However, the work function, ϕ , in the F-N equation, is substituted with a quantity $\chi - \delta$, where χ is the electron affinity, defined as the energy required to remove an

electron from the bottom of the conduction band of the semiconductor into the vacuum energy level, and δ denotes the band bending below the Fermi level, as shown in Figure 2-3. Electron field emission from semiconductors has been recently subject to extensive theoretical investigations, which take into account added complexities due to electron scattering, surface state density, temperature, and tip curvature.^{36,37,38}

Figure 2-3 Diagram of the potential energy of electrons at the surface of an *n*-type semiconductor with field penetration into the semiconductor interior.³²

Figure taken from Ref. 30.

2.1.3 Field emitter arrays

The concept of a field emitter arrays (FEA) was firstly introduced in the early 1960s when Shoulders proposed the use of devices based on microfabricated field emission sources. The concept was put into practice by Spindt and his co-workers by 1968.³⁹ The Spindt-type emitters came to denote metal FEAs fabricated via evaporation of the material through a shrinking aperture. Not surprisingly, due to its

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widespread use by the integrated circuit industry, silicon was the primary material from which FEAs would come to be fabricated, which was demonstrated by Thomas et al.⁴⁰ in 1972. These arrays were ungated, i.e. they did not incorporate an integrated gate electrode. A method of incorporating the gate was soon proposed by Smith et al.⁴¹ In the 1980s Gray introduced the concept of an integrated microfabricated vacuum transistor based on gated silicon FEAs, fabricated the gated FEAs using etching and oxidation sharpening techniques, and reported their electrical characteristics.^{42,43,44,45} Historically, microstructured tips have played a central role in field emission technology, initially produced from molybdenum and subsequently other materials.

Since the work of this dissertation also adopts usage of silicon based FEAs, this section provides a brief description of the underlying physical mechanism for field emission and a review of the developments that have taken place over the past number of decades in microfabricated field-emitters. The principles of field emission from bare Si tip arrays are introduced in this section. In order to achieve an improvement of the field emission, coatings are employed as surface modifications on the Si tip arrays and this section also details the related field emission mechanisms. The field emission measurements from bare Si tip arrays are used extensively throughout this dissertation for benchmark comparison of the improvements induced by the novel N doped coatings deposited by a sputtering technique, as well as for thorough quantification and comparison of the intensive characterization and analysis carried out in this dissertation.

2.1.3.1 Field emission of bare Si tip arrays

As previously stated, the principle of field emission is based on the application of a very high electric field to extract electrons from the surface of a metal or a highly

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doped semiconductor. Generally the field is in the order of 10^7 - 10^8 V/cm. In practical terms, this means approximately 1000kV for an anode-cathode separation (vacuum gap) of 1 mm for a parallel flat electrode configuration. However, electrons may be extracted at a substantially lower applied field if the cathode surface has a high point (tip) or a protrusion as depicted in Figure 2-4. This is because the physical geometry of the tips provides a field enhancement and the lines of force converging at the sharp point. If E_t is the electrical field at the tip apex, V is a applied voltage, d is a distance between the tip and anode, and β is a geometrical enhancement factor, E_t can be deduced as,⁴⁶

$$E_t = \beta(V/d) \quad (2-6)$$

A large β can therefore result in a high electric field, E_t , at the tip apex.

Figure 2-4 Illustration of electron field emission from a (Si) tip.⁴⁶ Figure taken from Ref. 46.

The current generated by the field emission can be described by the F-N equation, as expressed previously in equation (2-4). It can be seen that the electron emission current is strongly dependent on (i) work function, ϕ of the emitter surface

and (ii) the geometrical enhancement factor, β . The work function value is affected by the electronic properties of the emitter surface. It is clear that materials that exhibit a low work function can produce higher emission currents in a specific field. However, not all materials with a low work function are suitable as field emission cathodes. For example, the work function of cesium is only 1.8 eV but it is difficult to obtain a stable emission current and long lifetime from cesium cathodes. The value of β depends on the geometrical parameters of a tip and can be expressed as,^{47,48}

$$\beta = h/r \quad (h \gg r) \quad (2-7)$$

where h is the height of the tip and r is the emitter-tip radius. Therefore, it is important to make the tips as sharp as possible in order to reduce the field required for electron emission. This has been long realized by the advanced semiconductor industry which commonly adopts conventional photolithographic patterning, silicon anisotropic etching, oxidation for tip sharpening and buffered oxide etching, to obtain sharp tips.

2.1.3.2 Fowler-Nordheim equation for a single-cell gated FEA

Figure 2-5 Schematic diagram of a cell in a gated FEA. The emitter height is denoted,

h , the gate aperture diameter, d , and the tip radius of curvature, r .

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Figure 2-5 presents a schematic diagram of a cell in a microfabricated gated FEA. The emitter has the form of a sharp tip to exploit the advantages of the well-known enhancements of electric field at surfaces exhibiting high curvature.

If a voltage, V_g , is applied to the gate electrode, the electric field, E , at the tip is given by,

$$E = \beta \times V_g \quad (2-8)$$

where as before, β is the field enhancement/conversion factor. If E is in units of $V\ cm^{-1}$ and V_g is in units of V , β is in units of cm^{-1} . If the area from which emission of electrons takes place is denoted as α , and equation (2-8) is substituted for E in the F-N equation (2-4), the following expression can be obtained,³⁴

$$I = J \times \alpha = A \times V_g^2 \exp(-B/V_g) \quad (2-9)$$

where,

$$A = 1.42 \times 10^{-6} \times \alpha \beta^2 / \phi \times \exp(10.4/\phi^{1/2}), \quad (2-10)$$

and,

$$B = 6.44 \times 10^7 \times \phi^{3/2} / \beta. \quad (2-11)$$

In equation (2-9), I is in units of A , α is in units of cm^2 , β is in units of cm^{-1} , ϕ is in units of eV and V_g in units of V . Plotting experimental values of electron emission current vs. gate voltage in the so-called F-N coordinates, $(\log(I/V_g^2))$ vs. $1/V_g$, is a common way of analyzing the electrical performance data for gated FEAs, and are often adopted in the work of this dissertation. As can be seen from equation (2-9), a linear relationship should be evident over a large portion of the emission region. The constants A and B in equation (2-9) provide a means of comparing the performances of FEAs with different geometrical parameters, emitter materials, etc. over a wide range of emission currents. The A and B values can be extracted from a

least-square fit of the experimental data, with A related to the intercept and B to the slope of the linear approximation of the F-N coordinates.

2.1.3.3 Field enhancement and work function effects

Figure 2-6 Plots of emission current density as a function of gate voltage for: (a) a fixed value of $\phi = 4 \text{ eV}$ and varying values of β ; (b) a fixed value of $\beta = 4 \times 10^5 \text{ cm}^{-1}$ and varying values of ϕ .³² Figure taken from Ref. 30.

As is evident from the F-N equation, electron emission current is highly dependant on the field enhancement factor and work function. As an example, Figure 2-6 (a) shows plots of the emission current, J , calculated from equation (2-9), as a function of the gate voltage V_g for a fixed value of $\phi = 4 \text{ eV}$ and β varying from

$3 \times 10^5 \text{ cm}^{-1}$ to $6 \times 10^5 \text{ cm}^{-1}$. Figure 2-6 (b) shows plots of J vs. V_g for a fixed value of $\beta = 4 \times 10^5 \text{ cm}^{-1}$ and varying ϕ from 2 eV to 5 eV.

The plots show that increasing β or lowering ϕ causes significant increases in the emission current density for a given gate voltage. For example, increasing β by 25% from 4×10^5 to $5 \times 10^5 \text{ cm}^{-1}$ at a gate voltage of 100 V (Figure 2-6 (a)) results in an increase in the emission current density, from approximately 2×10^5 to $4 \times 10^6 \text{ A cm}^{-2}$. An even more dramatic effect is observed by decreasing the work function. For a gate voltage of 100V, decreasing ϕ from 4 eV to 3 eV (Figure 2-6 (b)) results in a more than two orders of magnitude increase in the emission current density, i.e. from 2×10^5 to over $1 \times 10^8 \text{ A cm}^{-2}$.

While the work function value ϕ is affected by the electronic properties of the emitter surface, the values β depend on geometrical parameters of the device structure, such as the gate opening diameter, d , tip radius of curvature, r , emitter height, h , and position of the tip with respect to the center of the gate thickness, c . These parameters are marked in Figure 2-5. To analyze the effects of device geometry on the device performance, the electric field values at the emitter tip can be calculated as functions of these parameters, using finite-element field calculation methods. It has been shown^{49,50,51,52} that the tip radius of curvature and the gate aperture diameter significantly influence β , i.e. β increases rapidly as r and d decrease. A less significant effect is produced by altering h ^{53,54} and c ,⁵⁰ relative to the center of the gate metal layer thickness. It can be shown that centering the tip vertically in the gate metal, corresponding to $c = 0$, produces the highest value of β .

2.1.3.4 Field emission from coated Si tip arrays

Practical applications of Si tip arrays are highly restricted owing to their high threshold electric field and unstable emission current. Research into tip arrays with

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low operating voltage and capable of generating high and stable emission currents has been a major focus of the vacuum microelectronics research community. Applying a thin coating of a suitable material is a common method of field emission enhancement. Coatings, in fact, play a dual role in improving the emission process, which may be considered as follows: (a) to decrease the effective work function and correspondingly enhance the emission behavior, (b) to act as a protective layer against absorption and ion bombardment for the sharp conductive core. Furthermore, if the coating has a high thermal conductivity, overheating of the core will be minimized since the coating can conduct heat away from the tip and act as a radiator.

In order to obtain enhancement and stability of the electron field emission from Si tip arrays, a large number of coatings have been used, with promising enhancement results presented. These coatings include diamond and related materials, nitrides, silicides, and carbide refractory metals. It is widely accepted that field emission from Si tip arrays coated with a wide band gap thin film, is a three-step process, comprising the supply of electrons to the thin film at the Si/film interface, their transportation through the bulk to the film surface, and their subsequent emission into vacuum as shown in Figure 2-7.^{31,55} There have been a number of mechanistic models proposed to account for the improved emission characteristics induced by a coating. The models are not necessarily mutually exclusive, because each addresses a particular aspect of the overall field emission process. As this dissertation analyzes the effects and mechanisms of a coating enhanced Si FEA, a detailed review of the current mechanistic models follows. This provides more understanding as to the principles behind the field enhancements induced by coatings, which are central to the contributions and focus of this dissertation. Section 2.2 introduces the recently

proposed bond-band-barrier model, which is applied to explain the observed characteristics of the N-STO thin film Si FEAs proposed in this dissertation.

Figure 2-7 Band diagram representations of the quasi tunneling process associated with (a) a surface positive electron affinity (PEA) and (b) an effective negative electron affinity (NEA), where E_v is the valence band, E_c is the conduction band, E_F is the Fermi energy, and U is the energy difference from E_F to the maximum electron energy level.⁵⁵ Figure taken from Ref. 53.

(a) Low or negative electron affinity

Si tip arrays coated with diamond films show an enhancement in field emission compared with that from bare Si tip arrays. The original work on field emission from diamond surfaces was motivated by the discovery of its low or negative electron affinity.⁵⁶ It was proposed that electrons are injected into the conduction band of the low/negative electron affinity material, in which there is a small barrier that needs to be overcome for electron emission to occur. Recently, some wide band-gap materials, such as carbon nitride, boron nitride, and aluminum nitride were found to possess the

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attractive NEA property and were applied as effective coatings on tip arrays to improve emission behavior.^{12,13,14}

Electron affinity was defined previously in section 2.1.2.2, and at the surface, is simply the difference between the vacuum level and the conduction band minimum. The electron affinity is not dependent on the Fermi level of the wide band-gap material but is closely related to both the fundamental atomic structure of the material and the surface dipoles created by surface terminations such as steps, reconstructions, and adsorbate.⁵⁷ While atomic arrangements are an intrinsic property of a material, the surface dipoles can readily be altered and manipulated to affect the electron affinity.

Figure 2-8 Band schemes of a semiconductor surface with (a) PEA, (b) true NEA (b), and (c) effective NEA.³¹ Figure taken from Ref. 29.

For most insulators and semiconductors, the conduction band minimum is below the vacuum level and the electron affinity is positive as shown in Figure 2-8 (a). Electrons in the conduction band are bound to the material by an energy equal in magnitude to the electron affinity. In some rare cases, surface conditions can be obtained in which the conduction band minimum is above the vacuum level, as shown

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in Figure 2-8 (b), and the electron affinity is thus negative. In such conditions, the electrons in the conduction band are not bound to the sample but can escape from the surface; however the electrons are still bound to the vicinity of the surface by coulomb forces. The effective NEA model shown in Figure 2-8 (c) can be described as a combination of PEA and depleted band bending at the surface of the material. This band bending can result in the vacuum energy level occurring at energy below the minimum of the conduction band. The magnitude of the effective NEA is determined by, $\chi_{eff} = \phi_{BB} - \chi$, where ϕ_{BB} is band bending and χ is the positive electron affinity.

The low or even negative electron affinity property of a surface may represent an aspect of the explanation for thin film enhanced field emission, but it does not adequately explain the whole process. As shown in Figure 2-7, for electron field emission to occur, and more importantly to be sustained, there must be a continuous supply of electrons and a sustainable transport mechanism for the electrons to reach the surface. The energy levels of these electrons relative to the vacuum level are critical in determining the threshold field required for emission. A low electron affinity or even an effective NEA surface is useful in reducing the barrier for electron emission only when the energy levels of some occupied states or bands, including surface states, are positioned sufficiently close to the conduction band minimum.

(b) The defect/ impurity theory

As seen from the previous description, electrons at the surface can be readily emitted when the thin coating film has a low or even negative electron affinity. Prior to this occurrence however, a sufficient electron supply must be present at the surface of the thin film. The thin film coating is usually a semiconductor or insulator with a

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wide band gap, therefore either the bulk or the surface of the thin film must be made conductive in order to sustain the emission process.

The defect/impurity theory addresses the process of electron transport in thin films and suggests that structural defects and impurities can form energy states within the band gap of thin films.^{58,59} When the defect density is sufficiently high, the electronic states of various defects can interact and form energy bands. If these bands are wide enough or closely spaced, an electron hopping mechanism within the bands, similar to the Poole–Frenkel conduction mechanism or the Hill type conduction,⁶⁰ could easily provide a steady flow of electrons to the surface and sustain stable electron emission. The electrons can either be excited into the conduction band or the unoccupied surface states from these defect/impurity bands to be emitted directly or emitted by tunneling directly from the defect/impurity bands. The defects/impurities essentially raise the Fermi level by acting as donors of electrons and thus reduce the tunneling barrier. This theory is supported by overwhelming experimental data indicating that defective or lower quality diamonds have better emission properties. It also appears to explain why emission characteristics are enhanced in many “doped” diamonds, not necessarily because of the electrical doping effect, but rather by the creation of defects in the doping process. However, the exact nature of the defects responsible for this process has not been identified, and the very existence of many defect/impurity energy bands and their locations within the diamond band gap have not yet been accurately confirmed or linked to field emission. Recently, interesting work has been carried out into determining the origin of the emitting electrons using field emission energy distributions.^{61,62}

(c) Other conduction channels

Besides the hypothesis that defects/impurities in wide band-gap materials act as conduction channels, graphite phase and/or grain boundaries have also been suggested as other conduction channels in diamond films by Athwal⁶³ and Kim⁶⁴. It is suggested that a field-induced hot electron emission process can be induced from an isolated conductive particle (i.e. graphite) inclusion in an insulator matrix (i.e. diamond), where an antenna effect results in field concentrations on a “floating” conductive particle. Cui⁶⁵ has concluded from a photoelectron sub-band gap emission study that the diamond phase provides a thermally and mechanically stable matrix with a comparatively low work function, and graphite provides the transport medium for electrons to reach the surface and be emitted. Grain boundaries have also been suggested to function as conduction channels.

(d) Back-contact interface mechanism

One of the prominent parameters governing field emission is the potential barrier height at the back-contact interface. For an undoped wide band-gap insulator, the Fermi level is commonly assumed to be at the centre of the band gap. The electrons at the Fermi level of the Si tips will see a potential barrier height equal to $E_g/2$ (Figure 2-7). The emission current is limited by the tunneling of electrons through a potential barrier height of $E_g/2$ into the conduction band of thin film, and not by electron emission from the thin film surface into vacuum, even if the thin film has a low electron affinity. For very thin films coated on sharp Si tips, the injected electrons could directly reach the thin film surface and be emitted into vacuum. This can be illustrated as follows:

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(a)

(b)

Figure 2-9 A model based on the α -C:H:N acting as a space charge interlayer on the n^{++} -Si, with (a) no applied field top and (b) an applied voltage of 10 V between the anode and n^{++} -Si.⁶⁶ Figure taken from Ref. 66.

Electrons, following injection, may become heated at the surface as a result of being accelerated by a penetrating field that is high in the coating due to local enhancement. Little energy loss occurs since the electron mean-free path may be compatible with the thickness of the coating. A low surface potential barrier results in tunneling out into vacuum. This electron injection role is supported by the observation that a roughened interface between a nickel contact and nitrogen-doped diamond improves electron emission due to local field enhancement effects at the interface that facilitate tunneling through the Schottky barrier.⁶⁷ This model emphasizes the

importance of the back contact, and indicates that it may also be associated with the rate limiting process for field emission.

Silva and his coworkers⁶⁸ proposed another model that electron injection is facilitated by band bending at the interface. In this model, shown in Figure 2-9,⁶⁶ a fully depleted and doped interlayer is shown to sustain a larger electric field than the applied macroscopic field due to space charge effects as a consequence of having to satisfy the Poisson relationship in the interlayer. Electrons in the conduction band gain energy and become “hot” due to higher internal field which lowers the barrier at the film/vacuum interface. It is worth noting that the tunneling current density at the interface as a function of applied field follows a numerical formula similar to the F-N equation, consequently it is difficult in practice to differentiate between this interface barrier mechanism and the surface barrier mechanism from current-voltage data alone. Additionally, it is difficult to identify the highly defective barrier structure at the interface of the Si.

(e) Sharp morphological features model

Among the various proposed models, the simplest and most obvious explanation cites classic field emission theory by noting that there is a local field enhancement on sharp morphological features protruding on the thin film surface. For example, surfaces of chemical vapor deposition (CVD) diamond film coatings are typically full of facets and ridges. These rough crystallographic features can function as conventional field emitters, in which electrons tunnel into the vacuum at the protruding small features, facilitated by the enhanced local electric field. While this could provide a working and contributing mechanism, it addresses neither the source of electrons in the wide band gap thin film nor the issue of effective electron transportation to the surface of the thin film.

(f) Other models

Other proposed models include dielectric breakdown that provides conductive channels in diamond,⁶⁹ surface arcing that results in the formation of tips and protrusions thus providing additional geometric field enhancement,⁷⁰ space charge limited conduction current through the bulk of thin film,⁷¹ and surface conduction enhanced electron emission.⁷²

2.1.4 Cold cathode materials

Owing to their numerous attractive characteristics and wide spread application in consumer goods, military industries and space technologies, many novel cold cathode materials have been developed over the past decades. These include diamond and related films, carbon nanotubes, quasi one dimensional nanomaterial, thin films and coatings which will be described in this section. Cold cathode materials are a primary focus of the research present in this dissertation.

2.1.4.1 Carbon based materials

Diamond was proposed as a cold cathode material for photocathode in 1979.⁷³ A little more than 10 years ago, obtaining field electron emission from diamond was unheard of, due to the high cost of natural and high-pressure synthesized diamond crystals they were not a viable option for use in fabricating commercial devices. However, in the late 1980s, researchers succeeded in synthesizing low-pressure diamond films inexpensively, and many researchers^{74,75,76} soon realized the potential application of diamond films in the area of field electron emission because of their appealing properties such as a NEA, high thermal conductivity, large intrinsic breakdown field and chemical inertness, which are essential properties for cold cathode field-emitters. Currently, although quasi one-dimensional nanomaterials such

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as carbon nanotubes are generally considered superior candidates for cold cathode materials, field emission from diamond and related films maintains strong research support due to the unique properties of diamond. Even though the properties of diamond and related films have been extensively investigated, experimental data available on these properties tends to be rather scattered since they are very much dependent on the film growth conditions. Table 2-2 gives a summary of the properties of various diamond surfaces that are important for the understanding of the field emission phenomenon from this material. Another carbon-based material, carbon nanotubes (CNT), is also an attractive candidate and satisfies a broad range of requirements for field emission applications.⁷⁷

Figure 2-10 SEM micrographs of (a) randomly orientated CNTs and (b) aligned CNTs.^{78,79} Figure taken from Ref. 78.

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Table 2-3 lists some important findings from the field emission characteristics from CNTs, reported thus far in the literature. Figure 2-10 shows the scanning electron microscopy (SEM) of randomly oriented CNTs and aligned CNTs.^{78,79} The tips of the CNTs have a diameter in range of 1 nm – 30 nm and the length can be > 1 μm , consequently the aspect ratio is very high. The geometrical field enhancement factor, β , of the CNTs is larger than 1000, making them naturally attractive as field emitters. High field concentrations can then be locally induced at the tips of the nanotubes, allowing electrons to be emitted at low voltages. Moreover, CNT arrays may be grown using simple deposition techniques which make them attractive candidates cold cathodes applications.

Type	Parameters		Substrate	Note
	Eg (eV)	χ (eV) Φ (eV)		
Bare	5.47	0.38 4.97	(1 1 1)-(2x1)	Type II diamond, measured data [80]
Full coverage of H	5.47	-1.27 3.52	(1 1 1)-(1x1)	Type II diamond, measured data [80]
C-O-Cs	5.47	-0.85 1.25	N/A	Diamond (1 0 0) surface, calculated data [81]

Table 2-2 Typical values of energy band-gap, electron affinity, and work function for various diamond surfaces: bare, full coverage of H and terminated by C-O-Cs bonding configuration (Ref. 46)

Key parameter	Typical	Best	Reference
Current density of CNT films	100 mA/cm ² -1 A/cm ²	3 A/cm ²	82
Current density of a single CNT (A/cm ²)	10 ⁵	10 ⁷	83,84,85
Turn-on field (V/ μ m)	1.0	0.6	82, 86
Threshold field (V/ μ m)	6	5	82, 86
Emission site density (cm ⁻²)	$\sim$ 10 ⁵	10 ⁸	87,88

Table 2-3 Typical CNT field emission properties and their maximum values (Ref. 46)

2.1.4.2 Quasi one-dimensional nanomaterials

CNTs has been actively researched, in the past several years there has been a rapidly growing interest in investigating other novel nanomaterials as potential cold cathodes. These include wide and narrow band-gap semiconductor nanowires and metallic nanowires. It has been shown that the field emission properties of such nanowires are comparable to those of CNTs. In addition, it is possible to prepare a thin film of nanowires with a unique electronic property, i.e. either semiconducting or metallic, unlike CNT films, in which both semiconducting and metallic CNTs can co-exist. Furthermore, aligned nanowires may be prepared and synthesized at room temperature.

Figure 2-11 SEM images of: (a) needle-shaped SiC nanowires, (b) ultra-sharp (2 nm in diameter) needle-shaped SiC nanowires, (c) SiC nanotrees and (d) SiC nanojunctions.^{89,92} Figure taken from Ref. 89.

A large number of techniques have been developed for the preparation of quasi one-dimensional nanomaterials. Table 2-4 lists a summary of the nanomaterials and their preparation methods reported by various research groups. Besides chemical

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vapor deposition (CVD), three other promising methods include: (i) thermal evaporation or physical vapor deposition (PVD)^{90,105,106} (ii) direct heating^{92,104,105} and (iii) room temperature gas–solid interaction.^{7,107,108} Other interesting nanowires and nanofibers have also been prepared.^{91,114} One of the advantages of nanowires over CNTs is that they may be grown into different morphological structures, which can be useful for low-field emission. This can be seen from Figure 2-11, where SiC nanowires of different shape are shown. In particular, the needle-shaped SiC and the SiC nanotrees have sharp nanotips which enhance field emission, as outlined previously.

Field emission characterization of novel quasi one-dimension nanomaterials has been mostly depicted by recording I–V performance and emission site distribution. Table 2-5 lists various findings on threshold fields used for obtaining the density of emission current and maximum current densities. It is evident that most of the high-performing emitters are from wide band-gap semiconducting nanomaterials. It is also noticeable that there is no explicit and obvious difference between the field emission properties of nanowires, and that of nanotubes or nanobelts.

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Type	Materials	Method	Substrate, temperature (°C)	Reference
Wide band-gap	SiC nanowire	Direct heating of SiC particles + catalyst	SiC, 1700	92
	SiC nanowire	Vapour–solid	CNT, 1400	93
	SiC nanotip	ECR CVD	Si, 200	94
	SiC	nanorod HFCVD	Si, 1100	95
	SiCN nanorod	ECR CVD + MW CVD	Si, 650–1100	96
	BCN nanofiber	CVD	Ni, 600–650	97
	AlN nanowire	Vapour–liquid–solid	1100	98
	AlN nanotube	DC arc discharge	N/A	99
	ZnO nanowire	Evaporation	Si, 550	100
	ZnO nanoneedle	Vapour deposition	Si, 500	101
	ZnO nanopin	Vapour transport	Si, 600–700	102
	GaN nanorod	Epitaxy	Sapphire, 478	103
	MoO ₃ nanobelt	Vapourization	Si, 500–550	104
	MoO ₃ nanowire	Vapourization + oxidation	Si, 1100	105,106
Narrow band-gap	Cu ₂ S nanowire	Gas–solid	Cu, RT	107
	CuO nanobelt	Liquid phase	Cu, RT	108
	CuO nanorod	Direct heating of substrate	Cu, 400	109
	CuO nanofiber	Direct heating of substrate	Cu, 500	110
	MoS ₂ nanoflower	High-temperature reduction	Mo, 950–1000	
Metallic	Mo nanowire	Vapourization + reduction in H ₂	Si, 1100	105
	W nanowire	Vapourization + reduction in H ₂	Si, 1100	
	W nanowire	CVD	Si, 850	111
	MoO ₂ nanowire	Vapourization in O ₂	Si, 1100	105
	WO ₂ nanowire	Vapourization in O ₂	Si, 1100	

Table 2-4 Preparation and syndissertation of various nanomaterials (Ref. 46)

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Type	Materials	Orientation	Various threshold field	Maximum current density	Reference
Wide band-gap	SiC nanowire	Aligned	2.5 MV/m (10 mA/cm ²)	19 mA/cm ²	94
	SiC nanorod	Random	20 MV/m (10 mA/cm ²) 30 MV/m (10 mA/cm ²)	N/A	95
	SiC nanotip	Aligned	0.35 MV/m (10 mA/cm ²)	3.0 mA/cm ²	94
	SiC nanowire	Aligned	5.0 MV/m (10 mA/cm ²) 8.5 MV/m (10 mA/cm ²)	90 mA/cm ²	112
	SiCN nanorod	Aligned	10 MV/m (10 mA/cm ²)	4.5 mA/cm ²	96
	BCN nanofiber	Aligned	5~6 MV/m (10 mA/cm ²)	20~80 mA/cm ²	97
	AlN nanowire	Random	1 MV/m (1 mA/cm ²)	2.4 mA/cm ²	98
	AlN nanotube	Random	N/A	N/A	99
	ZnO nanotip	Partially aligned	1.92 MV/m (0.1 mA/cm ²) 5.9 MV/m (1 mA/cm ²)	2 mA/cm ²	102
	ZnO nanowire	Aligned	6 MV/m (0.1 mA/cm ²) 11 MV/m (1 mA/cm ²)	~2 mA/cm ²	100
	ZnO nanoneedle	Aligned	5 MV/m (0.1 mA/cm ²)	2.4 mA/cm ²	101
	ZnO nanowire	Aligned	18 MV/m (0.01 mA/cm ²) 24 MV/m (0.1 mA/cm ²)	10 mA/cm ²	113
	GaN nanorod	Aligned	0.5 MV/m (1 mA/cm ²)	54 mA/cm ²	103
	MoO ₃ nanobelt	Random	8.7 MV/m (10 mA/cm ²) 12.9 MV/m (10 mA/cm ²)	1000 mA/cm ²	104
	MoO ₃ nanowire	Aligned	3.5 MV/m (10 mA/cm ²) 7.65 MV/m (10 mA/cm ²)	13 mA/cm ²	105
Narrow band-gap	Cu ₂ S nanowire	Aligned	6.5 MV/m (1 mA/cm ²)	0.6 mA/cm ²	107
	CuO Nanobelt	Aligned	10.5 MV/m (1 mA/cm ²)	1.2 mA/cm ²	108
	CuO nanorod	Aligned	6~7 MV/m (10 mA/cm ²)	0.2 mA/cm ²	109
	CuO nanofiber	Aligned	6~7 MV/m (10 mA/cm ²)	9 mA/cm ²	
	MoS ₂ nanoflower	Partially aligned	4.5 MV/m (10 mA/cm ²) 7.6 MV/m (10 mA/cm ²)	50 mA/cm ²	110
Metallic	Mo nanowire	Aligned	2.2 MV/m (10 mA/cm ²) 6.24 MV/m (10 mA/cm ²)	30 mA/cm ²	105
	MoO ₂ nanowire	Aligned	2.4 MV/m (10 mA/cm ²) 5.6 MV/m (10 mA/cm ²)	35 mA/cm ²	
	Graphite nanofiber	Aligned	2.5 MV/m (1 mA/cm ²)	50 mA/cm ²	114
	W nanowire	Aligned	5 MV/m (0.1 mA/cm ²)	0.2 mA/cm ²	111

Table 2-5 Various nanomaterials and their field emission properties (Ref. 46)

2.1.4.3 Thin films and coatings

Thin films of wide band-gap materials, such as nitrides, and those having excellent hardness, such as carbides, have been extensively investigated either as plate emitter materials or coatings on microtip arrays. A review of the major film types is presented here.

(a) Nitride films

Several types of nitrides have been studied as candidates for cold cathode materials, including carbon nitride^{115,116,117}, boron nitride^{13,118,119,120,121,122,123,124}, aluminum nitride^{125,126} and gallium nitride.¹²⁷ Amorphous carbon nitride films may be produced by plasma enhanced CVD using C_2H_2 and N_2 gases without substrate heating.¹¹⁸ They have optical band-gaps in the region of 1.5 eV - 2.6 eV. Their electrical resistivity may be lower, typically in the range of 104 V/cm – 1011 V/cm, and their thermal stability may be higher, 600 °C – 900 °C when compared to those of diamond like carbon (DLC).

Chi et al.¹¹⁹ investigated the field emission properties of a-carbon nitride coating on a silicon field-emitter array and discovered that the coating could reduce the turn-on voltage of the emitter arrays. Other independent studies^{116,117} showed that a low field emission may be obtained from an a-CN films. This low field emission phenomenon was attributed to possible NEA, although one theoretical derivation related the observed phenomenon to field emission from the states in the narrow region around the Fermi level.¹¹⁵

Cubic boron nitride (c-BN) films have many properties similar to diamond films, including NEA¹²⁸, chemical inertness, and mechanical robustness. This type of film may be produced by a number of methods including electrophoresis¹²⁸ and plasma-assisted CVD.¹²³ These films are nanostructured consisting of c-BN

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nanocrystallites of hexagonal grains of a few nm in size. The energy band-gap may be as wide as 6.0 eV and the electrical resistivity may be around 10^2 V/cm.¹²³ Sugino et al. found that a coating of c-BN on silicon FEA could reduce the turn-on field from 20 V/mm to 6 V/mm. McCarson et al.¹²² found that the emission current from c-BN-coated Mo tip arrays in a given field increased by as much as two orders of magnitude. Their FEED measurements showed that the energy of the emitted electrons was linearly related to the applied potential, indicating the possible generation of hot electrons in the film. Further calculations based on the FEED data revealed that the electrons were emitted from the conduction-band minimum of the c-BN coating. The research also succeeded in fabricating low field, high current planar emitters using c-BN films.¹²¹ Busta and Pryor showed that if laser annealing was applied to the BN thin film, a current density $>1\text{A/cm}^2$ could be observed.¹²⁰ c-BN coatings were also applied to CNT films and enhanced field emission was observed.¹²⁴

Like some other wide band-gap semiconductors, aluminum nitride (AlN) presents another promising candidate material for use as a cold cathode since it exhibits NEA.^{129,130,131} Sowers et al.¹²⁵ designed a gated device structure to test the field emission from AlN films. It consisted of an aluminum gate electrode separated from the AlN films by a layer of SiO_2 , and a pattern of aperture holes was etched to form an array of triodes. Field emission currents in the range of 10nA – 100nA from a single triode were measured with gate voltages as low as 20 V – 100 V. Subsequently, Wang et al. studied the field emission performance of AlN nano-coatings on silicon FEAs, and achieved a reduction of 400 V in the applied voltage.

(b) Carbide films

Since carbide materials are resistant to ion sputtering, they can operate under poor vacuum conditions as well as in the presence of oxygen. They have also attracted much attention in the field of cold cathode research. Zirconium carbide (ZrC) has been studied as an ultra-thin coating for W and Mo emitters.¹³² The low work function of ZrO allows for a 30% reduction in the field to obtain a given emission current. ZrC coatings on tip arrays can reduce the issues associated with high-current operation when ion bombardment on the emitting surface becomes significant.¹³² An NdC coating on Nb field-emitter arrays was also studied.¹³³

(c) Oxide thin films

Ferroelectric materials have interesting properties such as low electron affinity, moderate band gap, and an induced internal polarization electric field that can be beneficial for electron emission. Kang et al.^{134,135} developed techniques to coat silicon field-emitters with the well-known ferroelectric material, $(\text{Ba}_{0.67}\text{Sr}_{0.33})\text{TiO}_3$ (BST). This thin film coating was found to significantly improve emission characteristics from silicon tips, where experimental results indicated turn-on fields ranging from 4 V/mm to 10 V/mm as compared to 70 V/mm for uncoated arrays. However, experimental results indicate that the emission current from BST film surface differs from the so-called ferroelectric electron emission (FEE).

It is known that FEE is an unconventional electron emission effect^{136,137}, which is generated by a deviation of spontaneous polarization from the equilibrium state under pyroelectric, piezoelectric effects, or polarization reversal. In contrast, the emission current from BST thin films demonstrates a steady state current, which is similar to the classical types of electron emission from solids. Furthermore, the

emission behavior is found to be highly correlated with their structure^{134,135} and stoichiometric composition.²² Thus, while promising characteristics were observed from oxide thin films, the emission mechanism is poorly understood and should be further investigated in order to control and optimize the emission characteristics. For that reason, a SrTiO₃ (STO) thin film is deposited for field enhancement in this dissertation.

2.1.5 An application of cold cathode materials

Field emission is based on the physical phenomenon of quantum tunneling, in which electrons are emitted from the surface of the material into a vacuum under the influence of an electric field. Compared to the currently used thermionic emission from hot filaments, field emission from cold cathodes occurs at room temperature. In addition, coupled with VME, it offers some attractive characteristics, including small size, modest power consumption, instantaneous response to field variation, resistance to temperature fluctuation and radiation, and an exponential current-voltage relationship in which a small variation of voltage can result in a large change of emission current.

Based on the above attractive properties, there has been a very significant growth in interest and activities in vacuum microelectronics, and considerable progress has been made in field emission devices over the past decades. Field emission devices are frequently deployed in domestic and military industries. Some devices (e.g., field emission displays (FEDs)) benefit from having a large number of independently addressable sources operating in parallel. Some devices (e.g., high voltage or microwave power tubes) utilize the high speed of electrons and/or the high electric field of a vacuum. Some devices (e.g., x-ray source) require a high kinetic

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energy that only free electrons can achieve. Other devices (e.g., instruments used in nuclear reactors and space applications) take advantage of the vacuum microelectronics, where electrons propagate through vacuum and are therefore immune to radiation and high temperatures.

FEDs are a classical example of a prominent consumer application of cold cathode materials, due to their widespread commercial use in flat panel displays. FEDs have several advantages over other technologies including low power consumption, higher brightness, wider viewing angle and fast response time. It is predicted that FEDs will soon replace existing cathode ray tube (CRT) displays, and compete with popular technologies such as liquid crystal displays, plasma discharge panel displays and organic light emitting displays. The principle of operation of an FED is similar to a cathode ray tube display in the sense that the display image comes from the cathodoluminescence of phosphor materials.

Figure 2-12 Architecture of a Spindt cathode-based flat panel display.⁴⁴ Figure taken from Ref. 46.

Figure 2-12 shows the architecture of a Spindt cathode-based flat panel display. The primary difference between this and the CRT display is how the electrons are generated and delivered to excite the phosphor coated anode. Instead of

one or three electron guns in the CRT display, miniaturization allows every pixel to have its own electron source, which is independently addressed, and hundreds of emitters are made to define a single pixel line by line scanning of electron beams is not required as is the case for CRTs. In FEDs, for example, the suitable selection of cold cathode materials is critical to achieve a low threshold electric field and stable emission current.

2.2 Bond-band-barrier (BBB) correlation theory

The previous section presented an extensive review of the background theory and related literature pertaining to field emission theory which is central to the work of this dissertation. An exposition of current methods of field enhancement was shown, as were the state of the art proposed models and mechanisms (section 2.1.3.4), which are frequently adopted to explain the experimental results. As previously presented, nitride compounds display intriguing properties, and are thus proposed for field emission enhancement in this dissertation. Inclusion of N in synthetic diamond films has been demonstrated to significantly reduce the threshold of cold cathode emission of diamond thin films.²³ Remarkably, a lower threshold field of electron emission of nitrogenated carbon films has been observed than that of carbon films doped with boron and phosphorous. Even though the performance of nitride compounds has been intensively investigated and widely used, a deep understanding of the correlation between the local atomic-bonding, or the energy band structures and the observed or predicted properties of such compounds remains elusive to the research community.^{138,139,140} Concerns about the correlation between the chemical bond and valence density of states and their effects on the materials performance are therefore addressed in this section. In this section, the recently developed bond-band-barrier

(BBB) correlation mechanism originated for oxidation¹⁴¹ is introduced. A major contribution of this dissertation is then to expand this model and subsequently propose a BBB based model for the field emission enhancement mechanism from N-doped STO coated Si FEAs.

2.2.1 Oxide quasi-tetrahedron formation

Figure 2-13 The primary oxide quasi-tetrahedron. Each of the two ions B, labeled 1, donate one electron each to the central oxygen atom to form Goldschmidt-contraction ionic bonds. The atoms B labeled 2 are then the lone-pair-induced metal dipoles with an expansion of size and an elevation of energy states.

This model extends the H_2O molecular structure to a solid surface with chemisorbed oxygen by replacing the H atom with a host atom of an arbitrary element B, as illustrated in Figure 2-13. This model considers two primary factors. Firstly, the atomic radius is not considered constant but varies with changes in not only its atomic valence, but also, its coordination number (CN). Secondly, the sp orbitals of oxygen

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hybridize and a quasi-tetrahedron forms. The bond angles and the bond lengths are not constant but vary within fixed bounds. Therefore, an oxygen atom can react with atoms of an arbitrary element B, in any gaseous, liquid or solid states, through two bonding electron pairs and two non-bonding lone pairs.

Oxygen interacts with the atoms of element B (Figure 2-13) and hybridizes its sp orbitals to form four directional orbitals. The oxygen atom captures two electrons from element B atoms resulting in the 2s and 2p levels of oxygen being fully occupied with eight electrons, which will subsequently repopulate in the four directional orbitals. Therefore, two of the four hybridized orbitals are occupied by shared electron pairs (bonding orbitals). The remaining two orbitals are occupied by the lone electron pairs of oxygen (non-bonding orbitals). It may be necessary to point out that the sp orbitals of oxygen hybridize independently without the involvement of orbitals of atoms of other elements, but the hybrid orbitals may be occupied by electrons of surround atoms. Therefore, both the process of the orbital being occupied and the actual occupancy of the hybridized orbital are significant, as the orbital can be occupied by both sharing or non-sharing electron pairs. In a bonding orbital, the extent of electron sharing, or the nature of the bond, depends on the difference in electronegativity (η) between the oxygen atom and the element B. Due to the high η value, oxygen captures an electron from B (labeled 1 and 2) to form the Goldschmidt-contraction ionic bonds at the surface. Formation of the nonbonding lone pairs, however, is independent of the nature of the arbitrary element B. The lone pairs are likely to polarize atom B (labeled 3) and the B atom becomes a B^{dipole} with a resultant expansion of size and elevation of energy of the polarized electrons that occupy the anti-bonding energy levels.

2.2.2 Valence density of states (DOS)

Figure 2-14 O induced valence DOS features of bonding, nonbonding, anti-bonding and holes.¹⁴² The arrows represent the process of charge transportation. The non-bonding (lone pair) states of O^{2-} are located below E_F . The anti-bonding (lone-pair-induced dipole) states are located above or close to E_F . Upon being overdosed with oxygen, H-like bonds form at the surface. The arrow from the anti-bonding sub-band to the bond states corresponds to the process of H-like bond formation.

Because of the OB_4 tetrahedron formation, the energy-band of the B host solid is modified with four additional valence DOS features. As illustrated in Figure 2-14, the difference in the DOS between an oxide compound and its parent B solid leads to the bonding ($<E_F$), nonbonding ($\leq E_F$), holes ($\leq E_F$) and antibonding ($>E_F$) states.^{140,141} The bonding states are at a slightly lower energy while the nonbonding states are of equivalent energy to that of the original p -levels of an isolated O atom, as nonbonding states neither increase nor decrease the system energy. Electrons of the dipoles occupy the empty states well above E_F as they gain energy upon polarization. Dipole formation enhances the charge density of the surface atomic layers and hence reduces

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the work function of the system.¹⁴³ Alterations in the atomic sizes and valences modify the potential barrier or the morphology of the surface. From this perspective, oxygen additives not only act as acceptors to produce holes at the valence band edge but also act as donors with additionally localized nonbonding and antibonding states. With the full occupancy of the p -orbital of oxygen, the sp orbitals of the O^{2-} hybridize, which results in the formation of four additional DOS features, as illustrated in Figure 2-14.

The BBB mechanism can be summarized as,

- ❖ Electronic vacancies are produced right below E_F , generating a gap between the conduction band and the valence band of the metal. Electron transportation can also expand the original band-gap of a semiconductor from E_{g0} to E_{g1} .
- ❖ The non-bonding (lone pair) states of O^{2-} are located below E_F without an apparent energy change, which is in principle comparable to the 2p-level of an isolated atom of oxygen.
- ❖ The energy of the bonding states are equivalent to that of the originally occupied 2p-energy levels of the isolated oxygen.
- ❖ The anti-bonding (lone-pair-induced dipole) states are located above or close to E_F . The oxygen-induced dipole reduces the work function from Φ_0 to Φ_1 .
- ❖ Upon being overdosed with oxygen, H-like bonds form at the surface. The overdosed oxygen receives electrons from the dipoles and the B^{dipole} becomes $B^{+\text{dipole}}$. The arrow from the anti-bonding states above E_F to the deeper bonding sub-band represents the process of H-like bond formation. This process results in a lowering of the system energy.

CHAPTER 3

EXPERIMENTAL PROCEDURES

This chapter introduces the practical aspects of the work performed in this dissertation, outlining the experimental procedures carried out in detail. The main experiments necessary for this work comprise fabrication and characterization. The fabrication procedure was required to produce the Si tip arrays, onto which ferroelectric SrTiO₃ thin films were then deposited through the RF magnetron sputtering technique. In terms of characterization, the micro and electronic structures of the fabricated thin films, as well as the electron field emission properties of SrTiO₃ thin film coated Si tip arrays, have been systematically investigated. In this chapter, the following detailed experimental procedures are described:

- a) Preparation of the SrTiO₃ thin films by the RF magnetron sputtering technique.
- b) Characterization of the SrTiO₃ thin films using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, video contact angle analysis (VCA), ellipsometry, and X-ray photoelectron spectroscopy (XPS).
- c) Characterization of the electron field emission properties.

Such fabrication and characterization experiments are essential in the development of electron field emission applications.

3.1 Fabrication of SrTiO₃ thin films on silicon tips

The Si tip arrays were fabricated by the Micro Fabrication Lab in NTU. The fabrication process is presented in this section. The SrTiO₃ thin films were then deposited on the Si tip arrays using the RF magnetron sputtering system. The sputter technique is adopted for the deposition of the thin films due to its good homogeneity, ease of chemical composition control, ease of process integration with standard semiconductor manufacturing technology and comparatively lower cost than other techniques.

3.1.1 Fabrication of silicon tips

The device fabrication process is illustrated in Figure 3-1. Silicon tips were fabricated on (100) n-type silicon wafers with a resistivity of 2-5 Ω/cm . The initial step required 0.3 μm thick silicon dioxide to be thermally grown on the silicon wafer. This was followed by a conventional photolithographic patterning with circular dots of 4 μm diameter, from which silicon dioxide circular “dots” were obtained after buffered oxide etching. The silicon wafers were then wet etched by an anisotropic KOH solution (KOH: H₂O: IPA=24:63:13) at 80 $^{\circ}\text{C}$, followed by an isotropic acid mixture (HNO₃: CH₃COOH: HF=25:10:3) at 20 $^{\circ}\text{C}$. To reduce the tip radius, tip sharpening treatment was performed by dry oxidation at 950 $^{\circ}\text{C}$ which resulted in the reduction of the tip radius to ~ 30 nm with a tip height of 2 μm . Following the sharpening, the distance between the tips was observed to be ~ 8 μm with a tip density of 1.56×10^6 tips/ cm^2 . The SiO₂ layer was then etched away. Finally, SrTiO₃ thin films were coated on the fabricated Si tip arrays by the RF sputtering process for further research. The following section details the sputtering procedures carried out for the work of this dissertation.

Figure 3-1. The fabrication process of SrTiO₃ thin film coated silicon tips.

3.1.2 Film deposition by RF sputtering

In this dissertation, an extensive investigation was carried out into the deposition of SrTiO₃ thin films on a silicon substrate using a conventional RF-sputtering technique. This was performed to increase the electron emission and improve the field characteristics and optimize perovskite grain growth. Prior to deposition, the fabricated wafers were first cleaned through a sequential rinsing with de-ionized water, iso-propanol, and acetone, and then blown dry by N₂. The native oxide layer was then removed by 1:10 de-ionized water diluted hydrofluoric acid (HF). Wafers cleaned in this manner allow for good quality thin films to be deposited.

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During the sputtering process, a sintered and stoichiometric SrTiO₃ target of 99.95% purity was used, which was typically rotated at 20 rpm to obtain a uniform deposition.

This dissertation studies and characterizes various sputtered thin films to highlight the merits of adopting the proposed N-STO coating. As well as depositing undoped and oxygen doped STO films, nitrogen doped STO thin films are deposited at differing nitrogen partial pressure, total deposition pressure, substrate temperature, and of varying film thickness. To deposit the differently doped films, the gas gasses used were pure Ar, a mixture of Ar and N₂ gasses and a mixture of Ar and O₂ gasses with the ratio of Ar. For this process, the stainless chamber of the system was evacuated to a base pressure of less than 5×10^{-6} mbar.

To vary the nitrogen partial pressure, five differing nitrogen concentrations, 10%, 25%, 50%, 75% and 100% were selected for the reactive sputtering process and the growth pressure was controlled at approximately 1.6 Pa. The mixing gas flows were adjusted using two MKS mass flow controllers (MFC) to maintain the 10%, 25%, 50% , 75% and 100% nitrogen concentrations respectively. Figure 3-2 illustrates the calibrated curves of the sputtering rate versus the total deposition pressure. The sputtering rate was calibrated by measuring the thickness of thin films deposited at room temperature using a Sloan Dektak 8000 surface profile. The effect of temperature variation was studied by heating up the substrate to 400 °C, 500 °C, 550 °C and 600 °C respectively by the PID controlled halogen lamps before the deposition process. The RF output power was 200 W.

Film thickness was altered by varying the deposition time from 45min, 1h 30min, 3h, and 4h 30min resulting in the formation of films with a thickness of approximately 6 nm, 12 nm, 24 nm and 36 nm respectively. The deposition parameters of the sputtering processes are summarized in Table 3-1.

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Figure 3-2. Sputtering rate calibrated curves.

N-doped SrTiO ₃ thin films deposition parameters					
RF input power	200W				
Total deposition pressure	1.6 Pa	0.9 Pa	0.5 Pa	0.3 Pa	
Substrate temperature	600 °C	550 °C	500 °C	400 °C	
Nitrogen partial pressure	10%	25%	50%	75%	100%
Thickness	6 nm	12 nm	24 nm	36 nm	

Table 3-1. The sputtering parameters for depositing SrTiO₃ thin films on the silicon wafer & tips

3.2 Characterization of SrTiO₃ thin films

Following the fabrication and deposition procedures outlined in the previous section, extensive and systematic analysis of the resulting effects on electron emission as well as intensive characterization of the resulting thin films was then carried out. The procedures undertaken, for the work of this dissertation, to analyze such properties are presented in this section.

3.2.1 Structural studies of the SrTiO₃ thin films

The microstructural evolution of the sputtered N-STO thin films was investigated using a Rigaku X-ray diffractometer with a thin film attachment cum Ultima⁺ wide-angle goniometer (40kV, 40mA). A Cu K α radiation source (1.54 Å) was used for phase identification. The scanning sweep range was from 20° to 70° in 2 θ with a sweep rate of 2 degrees/min. A small glancing angle, fixed at 2°, was used to ensure that the diffraction intensity came primarily from the measured thin films.

The chemical bonding configuration of the thin films was evaluated by using Fourier transform infrared (FT-IR) spectroscopy in the reflection mode at room temperature using a Perkin-Elmer Spectrum 2000 in the wavelength range of 1500-400cm⁻¹. The FT-IR spectrometer operated with a spectral resolution of 2 cm⁻¹ and a frequency accuracy of 0.5 cm⁻¹.

The Spectroscopic Ellipsometric (SE) spectra of the N-doped SrTiO₃ films on silicon substrate were measured by a J.A.Woollam Variable Angle Spectroscopic Ellipsometer (VASE) in the wavelength range of 270-800 nm at 2 nm intervals. The incident angle of the incidence was 70°.

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The water contact angle between N-doped SrTiO₃ coatings with water drop was measured by DataPhysics OCA 20 video contact analyzer (VCA) with a $\pm 0.1^\circ$ measuring accuracy of the video system

X-ray photoelectron spectroscopy (XPS) characterization was carried out to investigate the chemical compound formation and electronic properties, using a VG ESCALAB 220i-XL instrument with a monochromatic Al K α X-ray source (1486.6 eV). All XPS measurements were obtained at a take-off angle of 90° with respect to the sample surface plane. The pass energy of the analyzer was set to 20 eV to achieve high energy resolution. The base pressure in the analysis chamber was set to less than 1×10^{-10} mbar. To minimize the charging effects, a low energy electron flood gun, in conjunction with a transmitting fine mesh proximity screen, was used. The measurement quantification was carried out using the relative sensitivity factors taking into consideration both the X-ray cross-section and the transmission function of the spectrometer. The binding energy was referenced to the C 1s line at a binding energy of 285.0 eV. After a Shirley-type background subtraction, an XPS spectral deconvolution was obtained by a curve fitting procedure based on Lorentzians broadened by a Gaussian, due to the instrumental resolution, using the manufacturer's standard software. The component peak shape and full widths at half maximum for a particular peak envelope were kept constant during the curve fitting.

These microstructural experimental procedures form the basis of further the understanding of the perovskite structure, dopant incorporation, optical bandgap, surface energy, as well as the chemical bond states of the thin film coated Si FEAs.

3.2.2 Characterization of field emission properties

Prior to the acquisition of field emission measurements, the surface morphologies of the coated and the uncoated Si tips were examined by a JEOL JSM-5600 scanning electron microscope (SEM). A plane Si wafer was used as the cathode to ensure that no field emission current could be measured within the sensitivity of the instrumentation, with an applied electric field lower than $100 \text{ V}/\mu\text{m}$. This is far higher than the actual electrical field being measured and is to ensure that no parasitic field emission currents occur during the measuring process.

Figure 3-3 A schematic diagram of the electron field emission characterization apparatus

Field emission characterization was carried out in a diode configuration in a vacuum chamber at 1×10^{-6} mbar, as shown in Figure 3-3. A stainless steel base was used to make electrical contact with the Si tip arrays and, as an anode, an indium tin oxide (ITO) glass with a sheet resistance of $10 \text{ } \Omega/\square$ was placed $50 \mu\text{m}$ above the cathode via a Teflon spacer. The diameter of the opened Teflon hole was 6.0 mm . The computer-controlled measurement system was integrated with a Keithley 248 high

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voltage supply and a Keithley 487 picoammeter/voltage source.

Figure 3-4 The multi-cycling J-E measurements on bare Si tip arrays

Surface cleaning of the N-STO coated Si FEAs was performed under a low emission current of 1 μA by applying a voltage to the FEAs before measurement. The multiple cycling of voltage was applied to sample till the field emission current was stable. The emission measurements were then recorded at room temperature after a stabilized emission current was achieved. The data was collected from the final 5 cycles. Here, the multi-cycle J-E measurement on bare silicon tip are shown in Figure 3-4 as a sample. So, the field emission data are confident to be repeatable and reliable. The field emission stability characterization was also carried out in an electric field which could induce an initial emission current density of several $\mu\text{A}/\text{cm}^2$ for each sample. The applied electrical field was then kept constant during the measurement. Field emission current data was recorded at 2 second intervals. The field emission properties of the N-STO coated Si tip arrays were then confirmed by the F-N plot and light generation on a phosphorous anode of ITO glass.

CHAPTER 4

FIELD EMISSION FROM N-DOPED ARRAYS

Despite the considerable interest in Si FEAs in recent years and the abundance of Si-based fabrication technology, inherent material properties such as a high work function (ϕ), low electric conductivity and poor stability limit their wide spread application.^{144,145,146} As outlined previously in Chapter 2, emission efficiency and stability can be substantially enhanced by coating with materials of lower ϕ , smaller electron affinity or high field enhancement factor (β) on the silicon surface. The NEA properties of carbon-based surface modification^{147, 148} and the merits of ferroelectric materials such as sol-gel $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST)^{20,21,22,149} have been shown to induce promising field emission improvements. Recent work has shown comparable improvements when another ferroelectric material, nitrogen-incorporated SrTiO_3 (STO), was deposited on Si FEAs using a sputtering process.¹⁵⁰ Optimizing the film in terms of its dopant levels and thickness can significantly reduce the effective work function of the Si FEAs.

These field emission enhancements are believed to have originated from a change in the energy-band structure of the Si FEAs,¹⁴⁹ which is sensitive to the microstructure and deposition gasses of the STO films. However, the specific reasoning behind the

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work function reduction and the affects of various sputtering gasses on N-incorporated STO is a new research area and many fundamental questions remain open. A systematic study is therefore necessary to explore and verify the properties and mechanism of field emission of STO coated Si tip arrays.

In this chapter, the microstructural properties, component analysis, chemical compound formation and electronic properties of STO thin films are described in detail, as are the field emission properties of STO coated Si tip arrays. Discussions of the field emission mechanism are also presented. The field emission properties are investigated by varying the deposition gasses and thickness of STO coatings. The field emission characteristics are studied by using the home-designed automatic field emission characterization system.

This chapter is outlined as follows: Experimental procedures are initially summarized, followed by a presentation on the effects of various depositions gasses on the field emission of STO Si FEAs. It includes an investigation of the microstructural evolution, component analysis, chemical compound and electronic properties of the STO thin films. The chapter then addresses the effect of varying the STO coating thickness on the field emission properties and the optimal coating thickness for maximum enhancement of the field emission behaviors is discovered.

4.1 Experimental details

STO films were deposited on the Si tip arrays using an RF magnetron sputtering system (Leybold UNIVEX450B). The Si tip arrays were fabricated using conventional microfabrication technologies. Before sputtering, the native-oxide layer on Si FEAs was removed by dipping in a buffered hydrofluoric acid solution. The STO deposition was performed at 600 °C from a 3-inch stoichiometric SrTiO₃

ceramic target (99.9% purity). To isolate the influence of the sputtering gasses, the RF power and total deposition pressure were maintained at 200 W and 1.6 Pa, respectively, over the course of the entire experimental process. Three gas gasses were used in this work, i.e. pure Ar, a mixture of Ar and N₂ gasses with the ratio of Ar: N₂ = 1:1, and a mixture of Ar and O₂ gasses with the ratio of Ar: O₂ = 4:1. To optimize the thickness of the N- incorporated coating, deposition times of 45min, 1h30min, 3h, and 4h30min were used under the same deposition conditions. This resulted in film thicknesses of 6 nm, 12 nm, 24 nm and 36 nm respectively. XRD, FT-IR, XPS, ellipsometer spectroscopy and water contact angle measurements were then acquired, as outlined in the previous chapter.

4.2 Microstructure and component analysis

This section presents microstructural analysis of the STO thin films to increase the understanding of properties such as the crystalline structure and chemical bond states, under varying thickness and different sputtering gas mixtures. The work outlined in this section provides, for the first time, a comprehensive study of the microstructural properties of the newly proposed N-incorporated STO films, as well as systematic comparison with undoped and oxygen doped STO films.

4.2.1 X-ray diffraction

To examine the crystalline structure of the film, an X-ray diffractometer (XRD) measurements were carried out using the Rigaku system with Cu K α (1.54 Å) radiation source. The scanning angle range was from 20° to 70° in 2 θ with a scan rate of 2 degrees/min. A small glazing angle fixed at 2° was used to ensure that the diffraction intensity came primarily from the thin films. The ICDD (International

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Centre for Diffraction Data) files then were used for the analysis of all XRD results. The microstructural evolution of the sputtered STO films was examined by varying the film thickness and sputtering gasses. The resulting XRD patterns are shown in Figure 4-1 and Figure 4-2, respectively.

Figure 4-1 shows the XRD patterns of stoichiometric STO films with thicknesses of 6 nm, 12 nm, 24 nm and 36 nm deposited in an Ar-50%N₂ gasses at a substrate temperature of 600°C. As is evident from the presented result, the diffraction patterns display a strong dependency of the microstructural evolution on the film thickness and deposition gasses. It is observed that there are no obvious diffraction peaks of perovskite structure in the STO films with thickness of 6 nm and 12 nm. The 6 nm STO film shows peaks mainly due to the silicon substrate, as a result of the film being excessively thin that X-ray beam penetrate through and are diffracted at the silicon surface. It is hypothesized that these films are still at the nucleus formation stage and the formatted nuclei are likely to be nano-structured with a very fine size. With the film thickness increasing to 24 nm, the peaks of the STO perovskite phase appear in the XRD pattern. The (220) peak of the STO perovskite phase at 66.7° becomes clearly evident and its intensity increases with an increase in the thickness of the films. This indicates that the polycrystalline perovskite grains in the films have begun to grow with the (220) crystal face and develop proportionally with an increasing thickness. With a further thickness increase to 36 nm, the film exhibits higher crystallinity, and other perovskite diffraction patterns also become evident, such as (110) and (211).

Figure 4-1. XRD patterns of sputtered STO films of various thickness, deposited at 600 °C in an Ar-50% N_2 gasses.

Due to the 12 nm STO film being too thin to be detected in the XRD pattern, 36 nm thick films were deposited at different gasses conditions to illustrate the influences of differing sputtering gases on the structural evolution of the films. The XRD patterns for the STO samples deposited in different gasses are depicted in Figure 4-2. These indicate that single-phase STO is present in all specimens.^{151,152} However, the intensity of (110) peak for STO deposited in gas mixtures of Ar + N_2 or Ar + O_2 are found to be weaker when compared to the intensity peak deposited in pure Ar gas. This N- or O-induced structural alteration may be due to the generation of numerous O vacancies or defects. Because the nitrogen substitutions create oxygen vacancies to maintain the charge balance in the crystal lattice,¹⁵³ the N incorporation of the STO

may distort the perovskite structure of the films, resulting in the suppression of the polycrystalline-perovskite grain growth. The re-sputtering process may then cause defects in the O-rich gasses. However, insufficient direct evidence is provided by the XRD of nitrogen incorporation in the ultra-thin STO films.

Figure 4-2. XRD patterns of 36 nm thick STO films on Si deposited at 600 °C in different gasses.

4.2.2 FT-IR analysis

While the XRD patterns provide useful information regarding the effect of film thickness on the diffraction peaks of perovskite structure, compelling evidence of nitrogen incorporation into the STO films remains elusive. Therefore, FT-IR analysis was performed to specify the chemical bonds and compositional distribution in the

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N-STO films. Figure 4-3 shows a comparison of the FT-IR transmittance spectra of the N-STO and STO thin films. The added absorption peak is observed in the N-STO films, when compared with that of the STO film, at 1070 cm^{-1} is attributed to $\text{Ti}\equiv\text{N}$ stretch.¹⁵⁴ The presence of $\text{Ti}\equiv\text{N}$ stretch vibration is convincing evidence of nitrogen substitution in the STO perovskite lattice. The second peak at 480 cm^{-1} is as a result of the longitudinal optic (LO) phonon mode of STO perovskite.¹⁵⁵

Figure 4-3. A comparison of the FT-IR transmittance spectra of STO films with and without N incorporation.

The influence of a varying film thickness on the FT-IR absorption spectra is illustrated in Figure 4-4, in which a strong dependence is clearly evident. With an increasing film thickness, the absorption peak at 480 cm^{-1} , from the LO phonon

modes, becomes sharper and narrower, with the 36 nm thick STO film having the sharpest absorption peaks. From these observations, as confirmed from the previous XRD patterns, this film is believed to have the highest crystallinity.

Figure 4-4. The FT-IR transmittance spectra of N-STO films as a function of the film thickness.

4.2.3 Ellipsometer spectroscopy

The optical bandgap of STO as a function of the sputtering gasses was also investigated, using the ellipsometer spectra. Figure 4-5 shows the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) derived from the ellipsometer spectra, where α is the absorption coefficient. Assuming a direct transition between the valence band and the conduction band, the bandgap energy, E_g , of the STO film can be estimated by applying the Tauc relation,

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (4-1)$$

where C is a constant. Using the results displayed in Figure 4-5, the optical bandgap of the STO films deposited in pure argon, mixed gasses of Ar + N₂, and mixed gasses of Ar + O₂ is calculated at 4.29 eV, 3.86 eV, and 4.34 eV, respectively.

Figure 4-5. $(\alpha h\nu)^2$ versus photon energy, $h\nu$, for the STO films deposited in different gasses.

As can be seen from these results, the nitrogen incorporation can induce a significant decrease in the bandgap of the STO film by modifying the electronic structure.¹⁵³ Nitrogen ions replace oxygen atoms in the STO lattice and thus the corresponding N-induced antibonding states are located above the valence-band edge. This additional lone pair state below E_F decreases the bandgap of the N-STO. The STO deposited in the gas mixture of Ar + O₂ induces a slightly larger bandgap because of its poorer crystallinity.¹⁵⁶

4.2.4 Water contact angle analysis

Nitrogen incorporation into STO films may also be associated with changes of their physical properties, such as the surface energy which can quantify the disruption of the chemical bonds occurring when a surface is created. The surface energy of the films was characterized by contact angle measurements of the wetting behavior of pure water droplets on the film surface. Figure 4-6 shows a 3 μ L water droplet on the surface of STO, N-STO and O-STO thin films, with corresponding water contact angle measurements of 54.2°, 60.6° and 39.5°, respectively.

It is widely accepted that a higher water contact angle means a lower surface energy of test surface. Therefore, from these measurements, it can be concluded that the surface energy of the N-STO thin film is the lowest of the three samples.

Figure 4-6. Water contact angle images of SrTiO₃ thin films deposited in different gas gasses of: (a) pure Ar; (b) Ar + 50% N₂ and (c) Ar + 20% O₂.

4.2.5 X-ray photoelectron spectroscopy (XPS) characterization

The nitrogen chemical bond states are investigated from an XPS survey spectrum of the 12 nm thick sputtered N-STO thin film deposited at 600 °C, in the gasses mixture of Ar + 50% N₂. The results of the survey are shown in Figure 4-7, and are seen to compare well with the bulk SrTiO₃'s standard spectrum¹⁵⁷, with the expected

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addition of a nitrogen peak. No other impurity elements, except for carbon C 1s at 285 eV, are evident, indicating that the thin film is composed of Sr, Ti, O and N.

Figure 4-7. XPS survey spectrum of an N-incorporated SrTiO_3 thin film with thickness of 12 nm deposited in the mixture gasses of Ar + 50% N_2 .

A quantitative analysis of the XPS data is obtained using high resolution spectra of Sr 3d, Ti 2p, O 1s and N 1s. For a homogeneous sample, the number of photoelectrons per second in a given spectra peak is given by:¹⁵⁸

$$I = nf\sigma\theta\lambda AT \quad (4-1)$$

where n is the number of atoms of the element per cm^3 of the sample, f is the X-ray flux in photons/ cm^2 -s, σ is the photoelectric cross-section for the atomic orbital of interest in cm^2 , θ is an angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron, γ is the efficiency in the photoelectric process for the formation of photoelectrons of normal

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photoelectron energy, λ is the mean free path of the photoelectrons in the sample, A is the area of the sample from which the photoelectrons are detected, and T is the detection efficiency for the electrons emitted from the sample. The number of atoms of the element per cm^3 of the sample can be expressed as,

$$n = I / f\sigma\theta\lambda AT \quad (4-2)$$

which can be simplified to,

$$n = I / S \quad (4-3)$$

where the denominator of equation (4-3) can be defined as the atomic sensitivity factor, S , and where I is the peak area of the element. A general expression for determining the atomic fraction of any constituent in a sample, C_x , can be written,

$$C_x = (I_x / S_x) / (\sum I_i / S_i) \quad (4-4)$$

Based on equation (4-4), atomic percentages of Sr, Ti, O and N in the STO films deposited in different sputtering gasses are obtained from the XPS high-resolution spectra, as shown in Table 4-1. It can be observed that the ratio of O/Ti (last column) in the STO deposited in a pure Ar and an oxygen rich gasses is less than 3, which is potentially due to oxygen vacancies in the thin films. It is also noticeable that the ratio of O/Ti in the SrTiO_3 deposited in the oxygen rich gasses is less than that deposited in the pure Ar gasses. This absence of oxygen in the SrTiO_3 lattice deposited in the oxygen rich gasses is confirmed by the XRD results. In XRD results, the film deposited in oxygen contained sputtering gas shows the poor crystallinity due to the small grains size. Consistently, it is revealed in the later XPS study that there are large amount of absorbed oxygen presented accordingly, which is believed due to small grain size and large grain-boundary interface. As estimated in XPS, such film is oxygen-deficient with oxygen atomic concentration about 53.6%.

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	Sr (at%)	Ti (at%)	O (at%)	N (at%)	O/Ti
N rich SrTiO ₃	11.7	19.9	65.0	3.4	3.27
O rich SrTiO ₃	20.5	25.9	53.6	-	2.07
SrTiO ₃	17.2	22.0	60.8	-	2.77

Table 4-1. Atomic percentages of Sr, Ti, O and N in SrTiO₃ thin films, obtained from the XPS high-resolution spectra.

Figure 4-8 N 1s XPS spectra of the N-STO and STO thin films.

From Table 4-1, it is clear that approximately 3.4% of nitrogen atoms are doped into the STO thin film. In order to investigate the nitrogen chemical status and confirm whether the nitrogen atoms have been successfully incorporated into the STO lattice, the N 1s core levels were measured and the results are shown in Figure 4-8. It is noted that the sample deposited in an Ar + 50% N₂ mixture, shows a peak of the binding energy at approximately 396 eV, assigned to the atomic β -N state.¹⁵⁹ The

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exclusive atomic β -N peak (396 eV) indicates that the nitrogen incorporated in the STO film is mainly atomic nitrogen. Asahi *et al.*¹⁵⁹ proposed that the atomic β -N peak around 396 eV was assigned to substitutional N, which would indicate here that oxygen atoms have been replaced by nitrogen atoms in the STO perovskite lattice.

A high resolution O 1s spectra obtained from 12 nm thick STO films deposited in various sputtering gasses, is given in Figure 4-9. A good fitting is obtained to the spectrum, as indicated in the figure, and plotted in dashed lines. It is surprising that all O 1s spectra can be fitted within two peaks at binding energies of approximately 530 eV and 532.2 eV. The lower binding energy at 530 eV, denoted by O₍₁₎, can be attributed to the oxygen in the lattice, and the higher binding energy at 532.2 eV, denoted by O₍₂₎, is reported in the literature to be caused by adsorbed oxygen species and hydroxyl ions.^{160,161,162,163} Furthermore, the O₍₂₎ peak is broader than that of O₍₁₎, suggesting that the former contains at least two components (adsorbed oxygen and a hydroxyl group). It has been reported that the levels of adsorbed oxygen increases with an increase in the number of oxygen vacancies.^{160,161,162,163}

The change in oxygen vacancy concentration can be estimated from the variation of the intensity ratio of the two fitted O1s peaks. From the O 1s spectra, it can be observed that the intensity ratio of the O₍₂₎ to O₍₁₎ peaks, varies with the deposition gasses. Since the samples were measured in the same oxygen atmosphere, it is reasonable to attribute the varying O₍₂₎/O₍₁₎ intensity ratio to the change in oxygen vacancy concentration in the STO thin films. This leads to the conclusion that the oxygen vacancy concentration in the O-STO film is the highest of the three samples, which correlates with the XRD results presented previously in section 4.2.1. It is well known that oxygen vacancies donate electrons, resulting in n-type conductivity in the films according to the following defect equation,

However, in the N-STO film, the N^{3-} substitutes O^{2-} in the STO lattice, resulting in p-type conductivity in the film. The electrons donated by the oxygen vacancy and the electron hole induced by the doped N, will induce an oxygen binding energy shift which is clearly depicted in Figure 4-9.

Figure 4-9. XPS O 1s core level spectra obtained from the 12-nm-thick N-incorporated SrTiO₃ thin film deposited at different sputtering gasses.

Figure 4-10 shows the XPS Ti 2p core-level spectra obtained from the 12 nm STO films deposited in pure Ar, Ar + 20% O₂ and Ar + 50% N₂ mixture gasses. All fitted Ti 2p spectra display two wide peaks of Ti 2p_{3/2} and Ti 2p_{1/2} with binding energies of 458.8 eV and 464.5 eV respectively, which are assigned to Ti-O bonds. No significant change is obvious in the peak shape of the Ti 2p and partially oxidized Ti³⁺ were not detected, which indicates that Ti is present in a Ti⁴⁺ state in all the films. This

illustrates that the atomic nitrogen incorporation into the STO lattice does not alter its perovskite structure, which is consistent with results from the XRD pattern. However, Figure 4-10 shows a binding energy shift of the Ti $2p_{3/2}$ peak in the N-STO sample, can be attributed to the polarization of Ti induced by doped N, which will be discussed in section 4.3.1.3 later.

Figure 4-10 XPS Ti 2p core level spectra obtained from the 12 nm N-STO films deposited in different sputtering gasses.

4.3 Field emission properties

The previous section presented detailed microstructural analysis of STO films of various thicknesses and comprising various dopants. Results showed both the presence of perovskite grains as well as the incorporation of N into the STO lattice without altering its structure. The expected field emission enhancements due to these

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observations are experimentally verified in this section, with further theoretical justification provided.

In this section, the effects of the sputtering gasses and coating thickness on the field emission properties of Si tip arrays are investigated respectively. For each changing parameter, the emission current density-electric field (J - E) characteristics are initially studied, which is followed by a discussion of the field emission stability. The J - E data is then analyzed using the F-N plot and the effective work function of the STO coated Si tips is estimated. Finally, for each investigation, the field emission mechanism is discussed.

4.3.1 Sputtering gasses effect

The effect of the sputtering gasses on the field emission properties of the Si tip arrays coated with SrTiO₃ thin films is presented in this section.

4.3.1.1 The J-E characteristics

In the field emission property tests, the applied electric field was increased until the emission current exhibited some saturation which is an important point in the analysis of the Fowler-Nordheim curves. And the tests of all samples were repeated more than 20 times at same conditions until the field emission current became stable. And then we choose the last 5 times data to plot the J - E curve. Here, we selected one of five plots for each sample to show their field emission behaviors.

Figure 4-11 shows a plot of the emission-current density versus electric field (J - E) for Si FEAs with 12 nm thick sputtered STO coatings deposited in pure argon, Ar + 50% N₂, and Ar + 20% O₂ under the same testing conditions. The merits of coating

the FEAs with materials of lower work function are clearly evident as field-emission

Figure 4-11 The field emission current density of Si FEAs with various 12 nm thick STO coatings. All coatings are deposited at a substrate temperature of 600 °C and a deposition pressure of 1.6 Pa to yield the optimal emission performance.

properties are remarkably improved. The electron-field-emission threshold field (E_{thr}) is defined as the macroscopic field at which a current density of $10^{-2} \mu A/cm^2$ is obtained, which corresponds to a signal-to-noise ratio of 1000:1. From this definition, it can be observed that the threshold electric field of the Si tip arrays is drastically reduced from 36.2 V/μm for the bare Si tip arrays, to 17.4 V/μm for tips with 12 nm thick N-STO coatings. The measurements highlight that all coatings demonstrate a reduced E_{thr} when compared to the uncoated array. The broad threshold range

indicates that the field-emission properties of silicon-tip arrays depend highly upon the surface STO coatings.

Figure 4-12 The variation in the threshold electric field of STO films deposited in different gasses of pure Ar, mixture of Ar + O₂ and Ar + N₂. All coatings are deposited at a substrate temperature of 600 °C and a deposition pressure of 1.6 Pa.

For the arrays coated with 12 nm thick STO in the mixture of Ar + 50% N₂, the threshold field is reduced to approximately 17.4 V/μm, when compared to that deposited in pure an Ar gasses. This unequivocally shows that nitrogen incorporation can enhance the field emission behavior of STO coated silicon tips. It is interesting to note that E_{thr} for the O-STO coating exceeds that of the STO coating. The threshold electric field in this gasses is measured at approximately 26.4 V/μm. This indicates

that nitrogen and oxygen have somewhat differing influences on the enhanced the field-emission properties of STO films.

The variation in E_{thr} for the different STO films is shown in Figure 4-12. A subtle correlation can be observed between the field-emission properties and the optical bandgap of films which was shown previously in Figure 4-5. From comparison of these figures, it is evident that the STO film of a relatively small bandgap has a threshold field lower than a film with a large bandgap. The threshold field for the N-STO film with $E_g = 3.86$ eV, has a threshold field of 17.4 V/ μm , whereas that of the O-STO film with $E_g = 4.34$ eV, is 26.4 V/ μm .

4.3.1.2 Field emission stability

The influence of the sputtering gasses on emission current stability of the STO coated Si FEAs is investigated in this section, and the results highlight that the STO-modified Si arrays also demonstrate an improved stability for field emission. The emission currents of the uncoated FEA, as well as that from FEAs with a 12 nm thick STO, 12 nm thick O-STO and 12 nm thick N-STO film were examined as a function of time. The duration of the experiment was 1800 seconds with a measurement time interval of 2 seconds. The resulting emission currents are shown in Figure 4-13. The initial current was maintained at approximately 1 μA for all samples using a computer-controlled data acquisition system. During the measurement, the emission current from the bare Si arrays exhibited a remarkable deterioration after 800s as well as severe fluctuation over the course of the trial. The amplitude of the emitted current from the bare silicon tips was reduced to 0.01 μA after 30 minutes, representing two orders in magnitude decrease from the initial current. From

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comparison with the coated emission stability, dramatic improvements are evident as the initial amplitude of 1 μA is maintained throughout the entire experiment.

Figure 4-13. The field emission current stability of both uncoated Si FEAs and those with various coatings deposited in different sputtering gasses. The emission current on the y axis is shown on a log scale.

The coefficient of variation is used to measure the degree of dispersion of the average current. The corresponding average electrical current $\langle I \rangle$, standard deviation ΔI and the coefficient of variation, ($CV = \Delta I / \langle I \rangle$), are listed in Table 4-2. These are commonly used metrics to evaluate the quality of the emission current.

Figure 4-14. The variation of CVs of bare and coated silicon-tip arrays deposited in different gasses of pure Ar, mixture of Ar + O₂ and Ar + N₂. All coatings are deposited at a substrate temperature of 600 °C and a deposition pressure of 1.6 Pa.

A large difference is present between the coefficients of variation of the bare Si FEA than that of STO-coated arrays. Those with a 12 nm thick STO film display the smallest fluctuation of 25.62%, compared to that of the bare Si arrays a with fluctuation of 81.96%. This illustrates that STO coated arrays display improved current stability characteristics and proves the advantages of using thin films to improve field emission. The emission stability is also influenced by the deposition gasses. Silicon tips coated with N-STO display smaller fluctuation (28.63%) compared with the tips coated with O-STO (38.31%). A comparison of the emission current fluctuations for the Si tip arrays under study is shown in Figure 4-14. In

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correlation with the previous microstructural findings shown in Figure 4-2, the results demonstrate that a coating with good perovskite structure improves the field emission current stability. Furthermore, it is discovered that the nitrogen rich deposition gasses not only lowers the threshold electric field, but also enhances the emission current stability of the silicon tip arrays when compared with those deposited in the oxygen rich gasses.

4.3.1.3 Analysis of emission data

The emission current density-electric field (J - E) characteristics were previously investigated by varying sputtering gasses of the STO coatings in section 4.3.1.1. The results were analyzed according to the F-N formula.^{31,33} As introduced in Chapter 2, the field enhancement factor (β),^{13,164} and the effective work function (ϕ),^{10,20,165,166} can be obtained from the slope of the F-N plot.

(a) Field enhancement factor

As before, the F-N equation is expressed as,

$$I = A \times V^2 \exp(-B/V) \quad (4-6)$$

where,

$$A = 1.42 \times 10^{-6} \times \frac{\alpha \times \beta^2}{d^2 \times \phi} \times \exp\left(\frac{10.4}{\phi^{1/2}}\right) \quad (4-7)$$

and,

$$B = 6.44 \times 10^7 \times d \times \phi^{3/2} / \beta. \quad (4-8)$$

In equations (4-6), (4-7) and (4-8), I is field emission current in units of A, V is the applied voltage in units of V, d is distance between the anode and cathode in units of cm, α is the area from which the emission of electrons takes place in units of cm²,

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ϕ is effective work function in units of eV, and β is the field enhancement factor. The electric field at the tip apex can be substantially enhanced with a field enhancement factor β as shown previously in equation (2-6).

As demonstrated in Figure 4-15, the F-N plot exhibits an approximately linear relationship of differing slope at higher voltages. This linear relationship suggests that the electron emission is controlled by tunneling through a potential barrier. The field enhancement factor β of the Si tip arrays can thus be deduced using equation (4-8). Assuming the tunneling barrier height of Si to be 4.1 eV (corresponding to the work function of *n*-type silicon with 2 Ω /cm resistivity), the enhancement factor β can be estimated as 110 from the F-N slope (*FNSL*) in Figure 4-15.

Figure 4-15. F-N plots of the field emission from bare Si tip arrays and those coated with N- incorporated SrTiO₃, deposited in different gasses.

Conversely, the value of β could also be estimated using the curvature of the Si tip as the following equation,^{47,48}

$$\beta = h/r \quad (4-9)$$

where r is the emitter-tip radius, and h is the tip height. Taking $h = 2 \mu\text{m}$, $r = 30 \text{ nm}$ for a Si tip from the scanning-electron micrographs (SEM) shown in Figure 4-16, the value of β is estimated at approximately 68. This can be regarded as being sufficiently close to the FNSL based estimate.

(b) Effective work function

The effective work functions of the various coated and uncoated Si FEAs are estimated here. Here, it is necessary to make some comments to clarify the term “effective work function” in our study. The formal implementation of FN equation requires either the work function or the emitter geometry to be known. We use the term of “effective work function” to characterize the shift of the J-E curve whether to lower electric field or higher electric field regions, as compared to the uncoated Si tip arrays. It should be also noted that physically the “effective work function” of the diamond coated field emitters is not simply the barrier height at the solid/vacuum interface, as it is for “real” work functions of metals or semiconductors. The “effective work function” depends on the dielectric constant, the effective electron mass, etc. Therefore using the term “effective work function” may be useful for comparison of results obtained from different coatings for field emitters compared with uncoated ones. From a typical SEM image of a single bare silicon tip, such as that shown in Figure 4-16 (a), it is shown that the Si tip was controlled at a height of approximately $2 \mu\text{m}$ and that the tip-to-tip separation was $8 \mu\text{m}$. The Si tip coated with a 12 nm thick STO film, shown in Figure 4-16 (b), demonstrates that the sharpness of the silicon tip with coating is comparable to that of the uncoated tip. These figures highlight that the sputtering process can provide a very uniform coating

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on the silicon tips without detrimental effects on the tip sharpness. It is therefore reasonable to assume that the STO-coated Si tips and the bare silicon tips possess the same field enhancement factor β . As a result of this intuition, the effective work function of the STO-coated tips can be calculated from the ratio of the $FNSL$ to the uncoated silicon tip as¹⁶⁶

$$\phi_{SrTiO_3} = \phi_{Si} (FNSL_{SrTiO_3} / FNSL_{Si})^{2/3} \quad (4-10)$$

According to the $FNSL$ (deduced from Figure 4-15) and the Si work function of 4.1 eV, the values of the effective work function are estimated at 2.44 eV, 2.09 eV, and 3.54 eV for STO, N-STO, and O-STO coated Si tips respectively. Table 4-2 lists the values of the estimated effective work function from the slopes of F-N plot.

Electron emission from the surface is enhanced with a lower work function. In correlation with the J - E characteristic (Figure 4-11), the sample with the smallest effective work function exhibits the maximize field emission improvement. This suggests that the decrease in the threshold electric field originates from a reduction of the effective work function of the STO coatings with the same field-enhancement factor.

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(a)

(b)

Figure 4-16 Scanning-electron micrographs of (a) a single bare silicon tip and (b) a single silicon tip with an STO coating.

Sample	Threshold electric field (V/ μ m)	$FN_{SL_{STO}}/FN_{SL_{Si}}$	Effective work function Φ (eV)	Average current $\langle I \rangle$ (mA)	Standard deviation ΔI (mA)	Coefficient of variation (%)
Bare Si tip	36.2	-	4.1	5.02E-04	4.11E-04	81.96
SrTiO ₃	21.8	0.4591	2.44	9.80E-04	2.51E-04	25.62
N rich -SrTiO ₃	17.4	0.3642	2.09	1.24E-03	3.54E-04	28.63
O rich -SrTiO ₃	26.4	0.8023	3.54	7.80E-04	2.99E-04	38.31

Table 4-2 The threshold electric field, E_{thr} , the ratio of the F-N plot slope ($FN_{SL_{STO}}/FN_{SL_{Si}}$), the effective work function Φ_{eff} , the average emission current $\langle I \rangle$, the standard deviation ΔI and the coefficient of variation of the Si tip arrays with and without sputtered SrTiO₃ coatings as a function of sputtering gasses such as pure Ar, the mixture of Ar + 50% N₂ and Ar + 20% O₂.

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According to the model of bonding and band-forming for oxides introduced previously in section 2.2, it is essential for a nitrogen atom, N, which also has one lone electron pair, to hybridize its sp orbital upon interacting with host atom Ti, to form a quasi-tetrahedron, NTi_4 , through bonding (sharing electron pair), nonbonding (lone electron pair), and antibonding (lone-pair induced dipole) states. Energy states near the edge of valence band, E_v , or below the Fermi-level (E_F) are emptied by transporting electrons to the bonding orbital of N and by the antibonding orbital of Ti. These resulting antibonding states are located well above E_F of the Ti due to the polarization, whereas the nonbonding and bonding bands are at slightly higher and lower energy levels respectively, than the $2p$ level of the isolated N atom. The presence of bonding, nonbonding lone-pair, and the lone-pair-induced antibonding states is of key importance to a nitride. It is proposed that this model should allow for a deeper insight into the enhanced emission properties of the N-STO coated silicon tip arrays, in which the localized nonbonding and atomic-bonding are proposed to be factors that result in the lowering of the threshold of field emission.

Figure 4-17 shows the schematic of the nitride quasi-tetrahedron (NTi_4) model. During film deposition, the N atom hybridizes and interacts with the carbon atom in solid phase through four directional orbitals. When a reaction takes place, all atoms change their sizes and valence states. Therefore, the resulting smaller spheres are Ti 1 and the larger one is the lone-pair induced Ti dipole with an expansion in size and elevation of energy state, which were experimentally validated by the shift of core level of Ti $2p$, shown previously in Figure 4-10. The N–Ti bonds are mainly polar-covalent due to a slight difference in electronegativity between the constituents. If the N is overdosed, a hydrogen-like bond is formed, which transports electrons from the antibonding states to the bonding orbitals of the acceptors.¹⁴⁰

Figure 4-17 the primary NTi_4 nitride quasi-tetrahedron model in which smaller ions donate electrons to the central Ti, of which the sp orbital hybridizes with the resultant production of a nonbonding lone pair. The larger sphere is the lone-pair induced Ti dipole. The smaller spheres donate electrons to the central N acceptor, with which the sp orbital hybridizes resulting in the production of a nonbonding lone pair. N hybridizes and interacts with the arbitrary element Ti through bonding and nonbonding lone pairs to form the quasi-tetrahedron: $\text{NTi}_4 = \text{N}^{3-} + 3\text{Ti}^+$ (labeled '1') + $\text{Ti}^{\text{dipole}}$ (labeled '2').

The cluster bonding results in a change of the density of states (DOS) of a semiconductor, as illustrate in Figure 4-18. The antibonding (dipole) states, being well

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above the Fermi level, reduce the work function, which can explain the N doping-induced enhanced electron emission.

Figure 4-18. Nitrogen-induced DOS difference $[n(\text{NTi}_4) - n(\text{Ti})]$. The lone-pair polarized antibonding state lowers the work function (and hence the threshold of field emission) while the processes of bonding and antibonding generate electron holes close to E_F .

4.3.2 Thickness effect

The effect of the STO coating film thickness on the field emission properties of the Si tip arrays is presented in this section.

4.3.2.1 The field emission current density-electric field (J-E) characteristics

Figure 4-19 illustrates the influence of the thickness of the STO coating on the field emission of Si FEAs. The samples are deposited for a varying time period in a mixture gasses of Ar + 50% N₂ at a substrate temperature of 600 °C under the deposition pressure of 1.6 Pa. The thickness is measured at 6 nm, 12 nm, 24 nm and 36 nm respectively. From the results, it is unambiguous that the field emission

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characteristic of N-STO coated Si tip arrays is highly sensitive to the coating thickness. The values of the threshold electric field are estimated at approximately 29.1 V/ μm , 17.4 V/ μm , 21.4 V/ μm and 35 V/ μm , for the 6 nm, 12 nm, 24 nm and 36 nm thick films respectively. It can be seen that the 12 nm thick film displays the lowest threshold electric field for field emission. Further thickness increases can be seen to result in a deterioration of the electron emission characteristics of the Si tip arrays. The U-shape dependence of the threshold electric field on the coating thickness is shown in Figure 4-20. The results therefore indicate that there is an optimum coating thickness to obtain the lowest threshold electric field.

Figure 4-19 Field emission of Si tip arrays coated with N-STO films deposited at substrate temperature of 600°C with different thicknesses. The arrays coated with a 12 nm thick N-STO film shows superior emission performance.

Figure 4-20 The variation of the threshold electric field of SrTiO_3 versus the thickness of the coatings.

4.3.2.2 Field emission stability

The stability plots of the emission current of the Si tip arrays coated with sputtered N-STO films of differing thickness are as shown in Figure 4-21. As stated previously, the initial current was maintained at approximately $1\mu\text{A}$ for all samples and the applied electric field was kept constant during the course of the measurement. Anode current of the bare silicon tip arrays was gradually decreased just after 600s as shown in Figure 4-21. The decrease of anode current was caused by the gradually degradation of emitter tips including residual gas or contaminant adsorption on the tip surface and/or destruction of sharp emission site, and/or worse more tip failure.¹⁶⁷ Compared with the bare Si tip arrays, the current magnitude of N-STO coated Si tip

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arrays remains relatively stable and is maintained at the same order as the initial current, during the measurement.

Figure 4-21. The field emission current stability of the uncoated and coated Si FEAs, where the N-STO films are of varying thickness as indicated.

As before, the coefficient of variation is used to measure the degree of dispersion of the average current. The corresponding average electrical current $\langle I \rangle$, standard deviation, ΔI , and CV are listed in Table 4-3. The coated arrays display a smaller fluctuation of 19.28%-50.46% compared with the bare Si tip arrays with large fluctuation of 81.96%. The emission current stability is also influenced by the coating thickness. The coefficient of variation of coated Si tip arrays are 19.28%, 28.63%, 43.42% and 50.46% at a coating thickness of 6 nm, 12 nm, 24 nm, 36 nm respectively, as shown in Figure 4-22. It is clear that the N-STO coatings can enhance the emission

current stability of the Si tips when compared to the bare Si tip arrays. However, it can be noted that the emission current instability increases as the N-incorporated SrTiO₃ coating thickness increases.

Figure 4-22 The variation in the CVs of the silicon-tip arrays with and without N-STO coatings of different thicknesses.

At present the origin of fluctuation of field emission current is not clear. Referred to the work on the electron emission of carbon related materials, the detailed mechanisms could be related to emitter heating, ion bombardments and so on. The intrinsic properties of Si tips coated with N-incorporated SrTiO₃ would be also considered. In ion bombardment damage model,^{168,169} ions formed by electron would impact ionization close to the field emission cathode return to the cathode, and then can cause emission current fluctuations along with sputtering of the cathode

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material. The high-voltage operation for long periods under not so perfect vacuum conditions results in destruction of the tip. The influence of the N-STO coating on the emission process may be considered in terms of an active and a passive role. The active role can be regarded as decreasing the effective work function, and correspondingly increasing the emissivity, as described previously in section 4.3.2.1. The passive role can be explained by the fact that the N-STO thin film acts as a protective layer for the sharp silicon tip. Provided that a stable interface is developed, this prevents or minimizes emission instabilities since the emitting tip is protected from absorption, ion bombardment, etc. On the other hand, because of a relative large resistivity of semiconductor, a large current makes Si tips be heated ohmically,¹⁷⁰ and so, the Si tips are thermally unstable. Furthermore, since the N-STO coating has a low thermal conductivity ($\sim 8.0 \text{ W m}^{-1} \text{ K}^{-1}$) compared to that of Si ($\sim 148 \text{ W m}^{-1} \text{ K}^{-1}$), there would be a possibility that Si tips might be overheated with the thickness increasing. The overheating of the Si tip may cause the emission current unstable as shown in Figure 4-22.

4.3.2.3 Analysis of emission data

It was previously shown (Figure 4-19) that the Si tip arrays coated with N-STO films of differing thickness, display substantial enhancements in field emissions as shown in the J - E characteristics. Again, the F-N equation, $I = AV^2 \exp(-B/V)$, is applied to analyze the emission data in this section. The effective work function of N-STO coated Si arrays is deduced using the F-N plot.^{165, 166} the detailed principle of the F-N plot has been stated previously in section 4.3.1.3.

Figure 4-23 shows the F-N plots of the field emission from Si tip arrays as a function of coating thickness. The F-N plot yields a linear relationship of differing

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slopes at high voltages. As before, the linear relationship suggests that the electron emission is controlled by tunneling through a potential barrier. This is due to the observation that the influence of the STO layer on the sharpness of Si arrays be omitted as shown previously in the SEM picture of Figure 4-16, hence the field enhancement factor β of the N-STO coated Si tip array is assumed to be the same as that of the bare Si tip. According to the F-N slope and Si work function of 4.1 eV (corresponding to the n-type silicon of 2 Ω /cm resistivity), the effective work function of the Si tips can be deduced by equation (4-10) and their values are estimated as 3.31 eV, 2.09 eV, 3.3 eV and 3.46 eV for Si tips coated with N-STO films with a coating thickness of 6 nm, 12 nm, 24 nm and 36 nm respectively, as listed in Table 4-3. Again, a correlation between the J-E characteristics is evident in that a sample with a low effective work function results in a small threshold electric field. It suggests that the improvement in the field emission originates from the lowering of the effective work function due to the N-doped SrTiO₃ coatings. The Si tip arrays coated with a 12 nm thick N-STO film exhibits the lowest effective work function.

It is proposed that the dependence of the effective work function on the film thickness is related to the so-called space-charge-induced band-bending interlayer at the STO/Si interface, which is similar to that in the amorphous carbon thin films proposed by Silva.¹⁷¹ The band-bending occurs as a result of carrier depletion across the entire thickness of the STO film, which gives rise to a maximum internal electric field close to the heterojunction. Therefore, there is an optimum thickness for a lower threshold electron emission. If the film is excessively thick, the STO film would not be fully depleted, and therefore the energy loss of the hot electrons would be large and potentially preventing its emission from the surface. If the film is excessively thin,

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electrons that are emitted from the heterojunction will not gain sufficient energy relative to the conduction band to be able to overcome the emission barrier.

Figure 4-23 F-N plots of the field emission from bare Si tip and those coated with N-STO films of different thicknesses.

Thickness	Threshold electric field (V/ μ m)	$FNLS_{STO}/FNLS_{Si}$	Effective function Φ (eV)	work $\langle I \rangle$ (mA)	Average current deviation ΔI (mA)	Standard variation (%)	Coefficient of
Bare Si tip	36.2	-	4.1	5.02E-04	4.11E-04	81.96	
6 nm	29.1	0.7247	3.31	1.66 E-03	3.20E-04	19.28	
12 nm	17.4	0.3642	2.09	1.24 E-03	3.54E-04	28.63	
24 nm	21.4	0.7225	3.3	1.41 E-03	6.11E-04	43.42	
36 nm	35.0	0.7753	3.46	4.31E-04	2.17E-04	50.46	

Table 4-3 The threshold electric field E_{thr} , the ratio of the F-N plot slop ($FNLS_{STO}/FNLS_{Si}$), the effective work function Φ_{eff} , the average emission current $\langle I \rangle$, the standard deviation ΔI and coefficient of variation of Si tip arrays with and without sputtered N-incorporated $SrTiO_3$ coatings with different thicknesses.

4.4 Conclusion

This chapter exposed the sputtering gasses dependence of the field emission characteristics of SrTiO_3 films coated silicon tip arrays, and unequivocally demonstrated that a film deposited in a mixture of $\text{Ar} + \text{N}_2$ results in a larger emission enhancement when compared to that from films deposited in pure Ar or a mixture of $\text{Ar} + \text{O}_2$. It was demonstrated that the presence of O_2 in the sputtering gasses had a detrimental effect on enhanced field emission properties of the SrTiO_3 coating. For the N-STO coating, the threshold field was lowered dramatically from $36.2 \text{ V}/\mu\text{m}$ for the uncoated silicon tip arrays to $17.4 \text{ V}/\mu\text{m}$ for the 12 nm thick coating deposited in a 50% N_2 gasses. The work function of emitter surface was also shown to have reduced from 4.1 eV to 2.09 eV correspondingly.

The bond-band-barrier model was extended and proposed as a mechanism of the observed nitride based field emission enhancements, which were attributed to the presence of lone-pair-induced antibonding states above the Fermi level. Meanwhile, the electron emission characteristic was also shown to be dependent on the thickness of N-STO coatings. A 12 nm thick film was shown to result in a local maximum in the field emission enhancements induced.

CHAPTER 5

THE EFFECT OF NITROGEN ADDITION

As shown in the previous chapter, significant field emission enhancement of bare Si FEAs is possible by functioning through chemical reaction to deposit a layer of a suitably selected material of lower (Φ)^{147,148,166}. This observation is theoretically verified by the Fowler-Nordheim (FN) equation. It was experimentally demonstrated previously that coatings which have been doped with certain materials can further improve field emission.^{18,19} In 1996, Okano et al.²³ observed that the addition of nitrogen can significantly reduce the effective work function of a chemical-vapor-deposited diamond thin film, and its resulting threshold electric field is even lower than that observed from a coating doped with boron and phosphorous. From the extensive research presented previously in Chapter 4, STO-coated Si tip arrays have demonstrated substantially enhanced field emission of lower threshold field and improved emission current stability when compared with bare Si tip arrays. It was also observed that further enhancement can be realized through nitrogen addition in the STO lattice. The work shows that a STO thin film with N addition presents a promising candidate as a coating material to

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improve the field emission properties. Therefore in the chapter, field emission studies are extended to N-STO Si tip arrays, where the microstructure and field emission behavior of films with various nitrogen dopant concentrations are compared. Furthermore, the development of a thorough understanding of N-STO properties is an important step towards the realization of the N-enhanced field emission mechanisms.

This chapter is organized as follows: Firstly, the experimental procedures necessary for the analysis performed in this chapter are briefly introduced. The following section then introduces the characterization of the sputtered N-STO films deposited at different nitrogen partial pressures. The section also includes the study of the effects of the N content on the microstructure, chemical compound formation and electronic properties of the N-STO films. The last section of the chapter provides a study of the field emission properties of N-STO coated Si tip arrays, analysis of emission data, and a discussion on the effect of N content effect on the emission mechanism.

5.1 Experimental details

The process of preparing the N-STO thin films using a sputtering technique has been previously outlined in Chapter 4. Briefly, the films were deposited onto the HF-cleaned n-type Si tip arrays. The tips were grown on a Si (100) wafer in an Ar+N₂ mixture gasses with nitrogen contents ranging from 0% to 100% in a vacuum chamber, at a substrate temperature of 600 °C. Five nitrogen concentrations (10%, 25%, 50%, 75% and 100%) were selected, and the resulting effects on the field emission properties are studied. To isolate the influence of the nitrogen content, the RF power and total deposition pressure were maintained at 200 W and 1.6 Pa,

respectively for each deposition. N-STO films of 12 nm and 36 nm thickness were deposited.

5.2 Microstructure and component analysis

This section presents the characterization analysis to gain new insights and understandings of the microstructure of the recently proposed N-incorporated films for field emission enhancement.

5.2.1 X-ray diffraction

Figure 5-1 XRD patterns of 36 nm thick sputtered N-STO films on Si wafer, deposited at 600 °C in gassess of different nitrogen concentration.

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The influence of nitrogen content on the microstructure of the sputtered N-STO films was examined using XRD techniques. The microstructure information is of vital importance in developing an understanding of the field emission mechanism. As before, the X-ray diffractometer measurement was carried out using the Rigaku system with Cu $K\alpha$ (1.54 Å) radiation source. The scanning angle range was varied from 20° to 70° in 2 θ with a scanning rate of 2 degrees/min. A small glazing angle, fixed at 2°, was used to ensure that the diffraction intensity came primarily from the thin film.

In the previous microstructure study of the STO films, it was observed that the microstructure is highly dependent on film thickness. Films of thickness below 12 nm are still at the nucleus formation stage and thus the likelihood exists that the formatted nuclei are nano-structured of very fine size. By increasing the thickness to 36 nm, the STO film achieves a well-developed perovskite structure. Therefore, the influence of nitrogen content in the sputtering gas on the structural evolution is demonstrated based on the XRD patterns of the 36 nm thick films, as shown in Figure 5-1. The film deposited in 10% N₂ gasses possesses a typical XRD pattern with the strongest (110) peak at 31.5°, which is similar to that of the polycrystalline STO films. However, it can be seen that the crystallinity of the films is enhanced due to nitrogen incorporation into the STO perovskite structure. The film deposited in 50% N₂ gasses exhibits the highest crystallinity. With further increases in the nitrogen content to 75% and 100%, the diffraction peaks are broadened and gradually weakened, which is an indication that the perovskite structure cannot be maintained due to an overdose of nitrogen in the films, and consequently, the development of the STO perovskite structure is hindered.

5.2.2 Ellipsometer spectroscopy analysis

Figure 5-2 $(\alpha h\nu)^2$ versus photon energy $h\nu$ for N-STO films deposited in gasses of differing nitrogen content.

The optical bandgap as a function of the nitrogen partial pressure was calculated from the ellipsometer spectra of the N-STO thin films. Figure 5-2 shows the $(\alpha h\nu)^2$ versus photon energy ($h\nu$), where α is the absorption coefficient, h is Plank's constant, and ν is light frequency, derived from the ellipsometer spectra. The Tauc relation, $(\alpha h\nu)^2 = C(h\nu - E_g)$, is applied to analyze the ellipsometer data in this section. A detailed principle of this process has been stated in section 4.2.3. From this principle, the optical band gap of the N-STO films deposited at 0%, 10%, 25%, 50%, 75% and 100% nitrogen content in deposition gasses can be calculated to be approximately 4.29 eV, 4.41 eV, 4.11 eV, 3.86 eV, 3.89 eV and 3.85 eV, respectively.

Figure 5-3 The optical band gap of the N-STO films as a function of different nitrogen partial pressures.

The relationship between the optical band gap and the nitrogen partial pressure is shown in Figure 5-3. It is apparent that the optical band gap decreases with increasing nitrogen partial pressure up to a 50% concentration, and remains constant thereafter. The nitrogen doping can induce a significant decrease in the bandgap of the STO film by modifying its electronic structure.¹⁵³ The film deposited in 10% N₂ gasses induces a larger bandgap than that deposited in pure Ar because of its poor crystallinity¹⁵⁶, which is evident from the XRD pattern in section 5.2.1. Once the nitrogen atom is doped into the STO lattice at 50% nitrogen content in the gasses mixture gas which can be seen from XPS spectra of N 1s core level energy discussed in the next session, the optical band gap has been decreased from 4.29 eV to 3.86 eV. From the valence-band spectrum of N-doped SrTiO₃ with nitrogen substitution,¹⁷²

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it was found that N 2p states are localized above O 2p states which produce a significant band gap narrowing in SrTiO₃. And the Tauc gap subsequently remains constant as the nitrogen is overdosed and doped into the films at higher nitrogen partial pressure although the atomic nitrogen content increases in the SrTiO₃ film.

5.2.3 Water contact angle analysis

The nitrogen content effect on the surface energy of N-STO thin films was characterized by water contact angle measurements of the wetting behavior of pure water droplets on the surface. Figure 5-4 shows photographs of a 3 μ L water droplet shape on the surface of an N-STO thin film with a water contact angle of 48.9°, 50.8°, 58.9°, 53.5° and 49.1° for the nitrogen partial pressures of 10%, 25%, 50%, 75% and 100% respectively. A plot of the water contact angle as a function of nitrogen content is shown in Figure 5-5. Since a higher water contact angle corresponds to a lower surface energy of the test surface, the inverted U-shape demonstrates a local minimum surface energy for the 50% N-STO thin film.

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Figure 5-4 Water contact angle measurement images for the N-STO thin films deposited in gasses of different nitrogen content.

Figure 5-5 The variation of the water contact angle as a function of the nitrogen content in the sputtering gasses.

5.2.4 X-ray photoelectron spectroscopy characterization

From the XRD, ellipsometry and VCA experiments outlined in the previous subsections, a strong dependency has been exposed between the N concentration in the sputtering gasses, and the microstructure as well as the surface energy of the N-STO thin film. The film has been shown to exhibit a good perovskite structure at an optimum N content. At high nitrogen partial pressure (100%), the development of perovskite grains in the film is suppressed. However, it is also hypothesized that the electronic structure of the N-STO thin films is influenced by the doped nitrogen. This is due to the N^{3-} , substituting the O^{2-} in the STO lattice, which would form a quasi-tetrahedron with the surrounding host atoms through bonding and nonbonding interactions, associated with the production of electronic holes and antibonding dipoles. These events add corresponding features of density of states (bonding electrons, nonbonding lone pairs, antibonding dipoles, and holes) to the valence band of the host material.

An X-ray photoelectron spectroscopy (XPS) is a unique surface-sensitive method of chemical analysis. The effects of nitrogen content on the core level shift and the valence electronic structure of electron emission from the STO thin films are therefore investigated using an XPS technique in this section. 12 nm thick N-STO films with different N content are studied because they exhibit field emission enhancements, which will be discussed in the next section. The nitrogen chemical bonding states and variation of nitrogen concentration are firstly estimated from the N 1s core level spectra. The shift of the Fermi level due to variations of nitrogen concentration is then studied from examination the of core level and valence band spectra.

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As is presented in chapter 4, equation (4-4) is used to for a quantitative analysis of the XPS data. Table 5-1 lists the surface compositions obtained from high resolution spectra of Sr 3d, Ti 2p, O 1s, and N 1s. It reveals that the atomic ratio of N is 14.3%, 3.3%, 3.4%, 3.6%, and 5.0% for N-STO films deposited in a mixture gas of 10%, 25%, 50%, 75%, and 100% N₂ +Ar respectively. The high ratio (14.3%) of N in the SrTiO₃ films can be attributed to the nitrogen chemical bond state, which will be discussed in the next session.

Nitrogen content	Sr (at%)	Ti (at%)	O (at%)	N (at%)
10%	17.8	18.2	49.8	14.3
25%	11.2	18.2	67.3	3.3
50%	11.7	19.9	65.0	3.4
75%	12.1	19.2	65.1	3.6
100%	11.1	20.4	63.6	5.0

Table 5-1 Atomic percentages of Sr, Ti, O and N in the N-STO thin films deposited at different nitrogen concentrations as obtained from XPS high-resolution spectra.

In order to determine the chemical states of the nitrogen atoms, the nitrogen chemisorptions' states in the lattice were identified by N 1s core-level spectroscopy, as shown in Figure 5-6. It can be observed that the nitrogen bonding states in the films are sensitive to the deposition gasses. These spectra contain two peaks of N 1s, centered at approximately 396 eV and 404 eV. With 10% and 25% nitrogen concentrations, the N 1s peak at the higher-binding energy of 404 eV becomes

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evident, which can be attributed to the poorly screened final state of molecularly chemisorbed N_2 .¹⁷³ When the nitrogen content is increased to 50% or higher, the lower-binding energy at 396 eV appears which is in accordance with the atomic β -N state.¹⁵⁹ This energy shift clearly indicates that high nitrogen pressure leads to nitrogen substitution of oxygen¹⁵³ and the formation of Ti-N bonding, since the peak at 396 eV corresponds to an N 1s peak of TiN. It is proposed that the rich lone pairs and the lone-pair-induced dipoles will reduce the crystal field through screening and hence a negative energy shift of the N 1s level is evident.

Figure 5-6 XPS spectra of the N 1s core level energy obtained from the STO films deposited in different nitrogen gasses.

5.3 Field emission properties

It has been previously observed that the sputtered N-doped coated Si tip arrays demonstrate a substantially enhanced field emission. The previous section examined the nitrogen incorporation into the STO film, as well as the resulting surface energy at different nitrogen concentrations. In order to further study the effect of the nitrogen addition, the emission properties of the Si FEAs coated with N-STO films of different concentrations are investigated in this section. The effect of nitrogen addition on the J - E characteristic is firstly provided. This is followed by a study of the stability of the resulting field. The effective work function of the N-STO coated Si tips is then deduced using the F-N plot. Finally the effect of nitrogen addition on the field emission mechanism is discussed.

5.3.1 The J-E characteristics

Figure 5-7 shows the typical plots of emission-current density versus electric field strength (J - E) for silicon-tip arrays with SrTiO_3 coatings, which were deposited in gasses of different nitrogen contents varying from 0% to 100%. The results indicate that the threshold electric field of electron emission is highly correlated with the nitrogen content in the sputtering gasses, as depicted in Figure 5-7. As the nitrogen was introduced into the sputtering chamber, the film initially shows a slight increase in the threshold electric field when compared to the undoped STO film. When the nitrogen content is increased from 10% to 50%, the threshold electric field reduces and reaches a local minimum of 17.4 V/ μm . Further increases of the nitrogen concentration towards 100%, induces an increase in the threshold electric field to a maximum value of 28.0 V/ μm . The variation of the threshold

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electric field for field emission of the STO films deposited in different nitrogen a concentration is shown in Figure 5-8.

Figure 5-7 Field emission properties of Si tip arrays with 12 nm thick N-STO coatings deposited with differing nitrogen concentrations.

Figure 5-8 Variation of the threshold electric field for electron emission of the N-STO thin films deposited at different nitrogen concentrations.

5.3.2 Field emission stability

The effect of the nitrogen content on the stability of the emission current density is under study in this section. The results of Figure 5-9 show the current measurements over time from each surface. As with the previously presented study of the field emission stability, the initial current was maintained approximately 1 μA using a computer-controlled system. For each trial, the applied electric field was kept constant over the course of the measurement process. The coefficient of variation is used to measure the degree of dispersion of the average current. The corresponding average electrical current $\langle I \rangle$, standard deviation ΔI and the

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coefficient of variation, ($CV=\Delta I/\langle I \rangle$) are listed in Table 5-2. An observation from these results is that the emission stability is also influenced by the nitrogen content.

Figure 5-9 The field emission current stability of silicon-tip arrays coated with N-STO thin films deposited with different concentrations of nitrogen.

Figure 5-9 illustrates the variations of the emitted current from the films deposited in different sputtering gasses as a function of time. It is shown that the coefficient of variation remains at a low level (18.48% to ~25.62%) when the nitrogen content is below 50%. Further increases of the nitrogen content results in the deterioration of the current stability when compared to that from the films deposited at lower nitrogen partial pressures. The CV values from the N-STO coated Si tip arrays with nitrogen content of 75% and 100% are 56.63% and 37.71% respectively, as listed in Table 5-2. The dependence of the coefficient of variation on the nitrogen content is depicted in Figure 5-10. The results highlight a reduced

level fluctuation for lower (<50%) nitrogen contents. These results, when considered in conjunction with previous discoveries from the J-E, lead to the conclusion that 50% nitrogen content is optimum and results in the maximization of the enhanced electron properties of the N-STO coated Si tip arrays.

Figure 5-10 The variation of the CV of the silicon-tip arrays coated with N-STO coatings deposited in gasses of different nitrogen concentration.

5.3.3 Analysis of emission data

The previous studies have indicated that the N-STO coated Si tip arrays display substantial enhancements in field emission, shown by the *J-E* characteristics (Figure 5-7 and Figure 5-8). The F-N equation,^{31,33} $I = AV^2 \exp(-B/V)$, is applied to analyze this emission data in this section. The effective work function of the coated Si arrays is also derived from the F-N plot.^{10,20,165,166} A detailed principle of using the F-N plot has been introduced previously in section 4.3.1.3.

Figure 5-11 F-N plots of the field emission from N-STO Si tip arrays, deposited in gasses of different nitrogen content.

The variation of the threshold electric field originates from variations of the effective work function ($\phi_e = \phi / \beta$) of the STO coatings with the same field-enhancement factor. The FN equation was applied to characterize the emission data and the corresponding FN plots are shown in Figure 5-11. The measured emission current conforms to the FN behavior as seen from the linear $\ln(I/V^2)$ versus $1/E$ plot. Previous SEM images, given in section 4.3.1.3, showed that the sharpness of the silicon tip remained unchanged following coating with the STO films. Therefore, as before, it is reasonable to assume the same field enhancement factor for both the STO-coated tip and the bare silicon tip. The effective work function of silicon-tip arrays with STO coatings can be derived from the ratio of the

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FN slope (FNSL) of the silicon tips with coatings to bare silicon tips as $\phi_{\text{SrTiO}_3} = \phi_{\text{Si}} (FNSL_{\text{SrTiO}_3} / FNSL_{\text{Si}})^{2/3}$. By using the FNSL data of the uncoated silicon tip and silicon work function (4.1 eV), the effective work function of the silicon-tip arrays with STO coatings can be deduced, as given in Table 5-2. The effective work functions of the silicon-tip arrays coated with N-STO deposited in gasses of different nitrogen contents varies from 2.09 eV to 3.68 eV. The film deposited at the optimum nitrogen concentration of 50% exhibits the lowest effective work function. This reconfirms the surface energy measurements presented previously in section 5.2.3.

Nitrogen content	Threshold field (V/ μ m)	FNSL _{STO} /FNSL _{Si}	Work function (eV)	I _{average} (μ A)	Δ I (μ A)	CV
0%	21.8	0.4591	2.44	0.98	+/-0.25	25.62%
10%	24.2	0.5918	2.89	0.88	+/-0.23	26.66%
25%	19.8	0.3914	2.19	1.35	+/-0.25	18.49%
50%	17.4	0.3642	2.09	1.24	+/-3.54	28.63%
75%	25.8	0.694	3.21	0.74	+/-0.42	56.63%
100%	28.0	0.8514	3.68	0.88	+/-0.33	37.71%

Table 5-2 The threshold electric field E_{thr} , the ratio of the F-N plot slop (FNSL_{STO}/FNSL_{Si}), the effective work function Φ_{eff} , the average emission current $\langle I \rangle$, the standard deviation ΔI and the coefficient of variation of Si tip arrays coated with sputtered SrTiO₃ films as a function of the nitrogen content in sputtering gasses.

5.3.4 A discussion of the nitrogen addition effects on the field emission properties

According to the effective work functions listed in Table 5-2, the influence of nitrogen incorporation on the Fermi level shift is investigated in this section. It is found that the Fermi level shifts up for N-STO thin films with increasing nitrogen content in the sputtering gas, and then retreats for concentrations above 75%. The shift (ΔE_F) of the E_F with respect to that of the pure STO film is around -0.45 eV, 0.25 eV, 0.35 eV, -0.77 eV and -1.24 eV, corresponding to the films deposited with P_N (nitrogen partial pressure) of 10%, 25%, 50%, 75% and 100%, respectively. The valence band spectra of the N-STO films deposited at different P_N are shown in Figure 5-12. The binding energy of the valence band maximum (E_{VBM}) can be determined by extrapolating the leading edge of the valence band spectrum to its base line.¹⁷⁴ The E_{VBM} of the STO films deposited in Ar and Ar-N₂ mixture gasses with a nitrogen content of 10%, 25%, 50%, 75% and 100% is approximately 2.11 eV, 2.07 eV, 2.02 eV, 2 eV, 2.19 eV and 2.16 eV respectively. Considering the shift in the E_F , the influence of nitrogen addition on the VBM shift (ΔE_{VBM}) of the N-STO films relative to pure STO can be derived by,

$$\Delta E_{VBM}(P_N) = E_{VBM}(P_N) - E_{VBM}(\text{SrTiO}_3) - \Delta E_F(P_N) \quad (5-1)$$

The ΔE_{VBM} obtained for each of the films is 0.41 eV, -0.34 eV, -0.46 eV, 0.85 eV and 1.29 eV respectively. The negative value indicates an upward-shift of the VBM. According to the E_g and ΔE_{VBM} , the corresponding shift of the conduction band minimum (CBM) (ΔE_{CBM}) of the N-STO films with respect to STO can be derived from the following relation,

$$\Delta E_{CBM}(P_N) = E_g(P_N) - E_g(\text{SrTiO}_3) - \Delta E_{VBM}(P_N) \quad (5-2)$$

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The obtained ΔE_{CBM} for each film is -0.29 eV, 0.16 eV, 0.03 eV, -1.25 eV and -1.73 eV respectively. The CBM can be seen to shift upwards for films deposited in gasses from 10% to 50% nitrogen concentration and then shifts downwards with further increases in the nitrogen content. The calculated values of E_g , ΔE_F , ΔE_{VBM} , and ΔE_{CBM} versus P_N are summarized in Table 5-3. The polycrystalline N-STO deposited at 50%-nitrogen gasses exhibits a narrow band gap, upwards-shifted Fermi level and downwards-shifted CBM, which results in the enhancement of the field emission of N-STO coated Si tip arrays.

Figure 5-12 The valence band obtained from the N-STO thin films deposited in different nitrogen content gasses.

These observations can be understood in terms of the bond-band-barrier correlation mechanism.^{140, 141} According to the bond-band-barrier correlation, a nitrogen atom would hybridize its *sp* orbital upon interacting with another element B and form a quasi-tetrahedron through four directional orbitals in a solid phase during

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the film deposition. During this process, the nitrogen atom would capture three electrons from other atoms and then its $2s$ and $2p$ shells would be fully occupied with eight electrons that will then repopulate in the four directional orbitals. Therefore, three of the four hybridized orbitals are occupied by shared electron pairs (bonding orbitals). The remaining one orbital is occupied by the lone electron pair of nitrogen (nonbonding orbital).

The neighboring atom is likely to be polarized by the lone pair which then becomes a dipole associated with an increase in size and elevation of the energy of the polarized electrons that occupy the anti-bonding energy levels. The cluster bonding (bonding electrons, nonbonding lone pairs, antibonding dipoles, and holes) results in a change of the density of states (DOS). From a band structure point of view, the nonbonding lone pair states of N^{-3} locates itself below E_F and the anti-bond derived DOS is located at energies above E_F , due to the energy rise of the polarized electrons. This effect is responsible for the reduction of the local work function and N-enhanced electron emission.

The presence of antibonding states is of vital importance to an enhanced field emission. However, upon receiving a nitrogen overdose, the nitrogen will consume the polarized electrons from the dipoles and the dipole becomes a $+/-$ dipole resulting in the formation of a hydrogen-like (H-like) bond ($N^{-3}-B^{+/-dipole}:N^{-3}$). The ‘-’ and ‘:’ represent the bond and lone pairs, respectively. The anti-bonding states above E_F will be reduced, as will be the work function. The production of H-like bonds at the surface due to nitrogen over-dosing has a detrimental influence on the effective work function. Therefore appropriate nitrogen doping is necessary to avoid H-like bond formation that could raise the work function and the surface energy, causing subsequent deterioration of the field emission.

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Nitrogen content	Band gap (eV)	VBM (eV)	ΔE_F (eV)	ΔE_{VBM} (eV)	ΔE_{CBM} (eV)
0%	4.29	2.11	-	-	-
10%	4.41	2.07	-0.45	0.41	-0.29
25%	4.11	2.02	0.25	-0.34	0.16
50%	3.86	2	0.35	-0.46	0.03
75%	3.89	2.19	-0.77	0.85	-1.25
100%	3.85	2.16	-1.24	1.29	-1.73

Table 5-3 Summary of the measured band gap energy, the shift of Fermi level, ΔE_F , VBM (ΔE_{VBM}), and CBM (ΔE_{CBM}) of the N-STO coatings deposited in different nitrogen content gasses.

So, it needs to be noted that the nitrogen chemical bonding state in the film that is the most important factor which can influence the field emission properties of Si tip coated with N-incorporated STO. The nitrogen chemical bonding state differs with different nitrogen content in sputtering gasses. This means that the enhancement of field emission properties is determined by nitrogen chemical bonding state in the film which is influenced by the nitrogen content in sputtering gasses. So the variation of the threshold field with N content in deposition ambient not N content in the film was discussed in our results. Only after ensuring the nitrogen is chemically doped into the STO lattice, we discussed the effect of nitrogen content in thin film on field emission.

The narrowed optical band gap and N-enhanced field emission behaviors under different nitrogen contents, conforms with the bond-band-barrier correlation prediction. It is noted that molecularly adsorbed N_2 has little effect on the optical band

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gap, the electron emission behavior and the N 1s level energy under low nitrogen content. However, the optical band gap and the threshold electric field at 50%-nitrogen gasses is reduced significantly due to N being bound to Ti, which is believed to induce the formation of nonbonding and antibonding states near the Fermi level. It is proposed in this work that the non-bonding states of N^{-3} located between the valence band edge of O and the Fermi level result in a reduction of the band gap of the N-STO, which coincides with the optical band gap results as discussed above.

As for the N-STO thin films deposited at 10% and 25% nitrogen partial pressures, the nitrogen dopant is only molecularly adsorbed and little interaction exists with the band state of the STO in the lattice, and is thus unlikely to be effective in narrowing the band gap. The antibonding state located above the Fermi level reduces the work function, but the formation of antibonding states is very sensitive to the nitrogen content. From the experiments carried out in this section, as the nitrogen content in the thin film increases beyond 3.69%, the threshold electric field and work function were seen to rapidly increase. The reduction of enhanced field emission behaviors with overdoses of nitrogen verified the prediction of the bond-band-barrier correlation, which is ascribed to the formation of H-like bonds at the film surface from anti-bonding dipoles.

Surface energy measurements also provide indirect evidence for the presence of antibonding dipoles induced by the nitrogen doping. According to the bond-band-barrier correlation theory, the formation of non-bonding lone pairs and the lone-pair-induced anti-bonding dipoles will cause the energy of polarized electrons to increase because the polarization provides additional energy to the polarized electrons, resulting in a lowering of the surface energy from the increased chemical potential. From the work of this chapter it can be concluded that that at 50%-nitrogen gasses,

the surface energy and work function are minimized. The contact angle measurements also provide direct evidence for the presence of the antibonding states.

5.4 Conclusion

This chapter addressed the influence of nitrogen partial pressure on field emission performance of the proposed N-STO coated Si FEAs. The primary experimental observation of this chapter was that low dose incorporation of nitrogen enhances crystallinity in STO films. However, the perovskite structure deteriorated in nitrogen-overdosed films, which are deposited under higher (>50%) nitrogen partial pressures. The resulting observations of the electron emission behavior from the N-STO coated silicon tips showed that nitrogen doping could considerably alter the Fermi level, the VBM, as well as the CBM, depending on nitrogen partial pressure. The polycrystalline STO thin film deposited at 50%-nitrogen gasses exhibited a narrow band gap, upwards-moved Fermi level and downwards-moved CBM, which are believed to contribute to the observed enhancements of field emission. Further increasing nitrogen partial pressure resulted in the Fermi level moving downwards rapidly, which subsequently deteriorates the electron emission. The proposed mechanism of bonding and band-forming provides a feasible mechanism for N-enhanced threshold electric field in cold cathode emission because of the (experimentally verified) presence of the lone-pair-induced antibonding states above the Fermi level.

CHAPTER 6

THE EFFECTS OF SUBSTRATE TEMPERATURE AND TOTAL SPUTTERING PRESSURE

The field emission properties of sputtered SrTiO₃ coated Si tip arrays have been extensively analyzed and discussed in chapters 4 & 5. Substantial enhancements of field emission with lower threshold fields and improved emission current stability when compared to that of bare Si tip arrays, have been demonstrated. It is found that the enhanced field emission is highly correlated with the microstructure and electronic properties of the N-STO coating. A film with perovskite grains in the surface region can induce a reduction in the threshold electric field, whose presence in the N-STO films was demonstrated previously through XRD measurements. The field emission enhancements were proposed to be attributed to antibonding dipoles induced by nitrogen addition in the SrTiO₃ perovskite lattice. The lone-pair dipoles and anti-bonding dipoles induced by nitrogen doping can result in strong localization of dipole electrons at the thin film surface. These events add corresponding features of density of states (bonding electrons, nonbonding lone pairs, antibonding dipoles, and holes) to the valence band of the host material. The Fermi level of the N-STO film shifts upward with the formation of the antibonding states which are located at

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energies above the Fermi level¹⁴³ and leads to enhanced field emission. The research presented in chapters 4 & 5 has revealed that ferroelectric thin films with nitrogen doping can improve the electron emission behaviors of silicon tip arrays.

The primary methods of ferroelectric film deposition are sol-gel and sputtering processes.¹⁶⁶ When compared to the sol-gel process, sputtering is believed to further suppress the formation of the interface layer between the silicon substrate and the ferroelectric thin film.¹⁷⁵ In the sputtering process, the microstructure, surface energy, optical band gap, and chemical composition of the ferroelectric thin films are highly sensitive to the deposition parameters, such as substrate temperature (T_s), the total sputtering pressure (P_{total}) and, as was exhibited extensively in the previous chapters, the content of the sputtering gases. The fact that the microstructure of STO thin films and nitrogen incorporation states are strongly affected by the deposition conditions necessitates and intensifies the effort to further study the influence of varying deposition conditions on the microstructure and nitrogen incorporation states of the deposited films. Therefore, in this chapter, the effects of varying substrate temperatures and sputtering pressures, which can be readily controlled, on the field emission behaviors of silicon tip arrays coated with N-STO thin films will be studied.

This chapter is organized as follows: The first section briefly outlines the experimental procedures necessary for the analysis of this chapter. The next section then introduces the characterization of sputtered N-STO thin films deposited at different substrate temperatures and sputtering pressures. The section includes the study of the resulting effects of the N content on microstructure, chemical compound formation and electronic properties of the N-STO thin films. The following section then provides a study of the field emission properties of the resulting coated Si tip

arrays, extensive analysis of the emission data, and a discussion on the influence of substrate temperature and sputtering pressure on the field emission mechanism.

6.1 Experimental details

The process of preparing the N-STO thin films using a sputtering technique has been previously outlined in Chapter 4. The films were deposited onto HF-cleaned n-type Si tip arrays grown on a Si (100) wafer in a mixture of Ar and N₂ with Ar-to-N₂ ratio of 1:1 in the vacuum chamber. The sputtering power was maintained at 200 W. The samples were then separated into two groups. One is used to study the effects of substrate temperature, for which all samples are deposited at same deposition pressure of 1.6 Pa and substrate temperatures of 400 °C, 500 °C, 550 °C and 600 °C. The thickness of each film is kept constant at 12 nm. The other group is prepared to examine the effects of the sputtering pressure. The samples are deposited at a substrate temperature of 600 °C but at differing sputtering pressures. Control of total deposition pressure (P_{total}) was conducted by adjusting the sputtering gas flow rate which is set at 160 sccm, 80 sccm, 40 sccm and 20 sccm. It should be noted that the deposition rates were also varied for the different sputtering pressures, to maintain equal coating thickness. In this work, the deposition rates were 0.1333 nm/min, 0.2222 nm/min, 0.2727 nm/min and 0.3871 nm/min which correspond to total deposition pressures of 1.6 Pa, 0.9 Pa, 0.5 Pa and 0.3 Pa respectively. It was also necessary that the deposition time be adjusted to maintain an approximately equal 12 nm thickness for each film.

6.2 Microstructure and component analysis of the N-incorporated SrTiO₃ thin films

This section discusses the results obtained from the microstructure and component analysis of the N-STO thin films deposited at different substrate temperatures and total sputtering pressures. The research presented in this section furthers the understanding of the effects on field emission due to the varying deposition conditions of N-incorporated films.

6.2.1 X-ray diffraction

Figure 6-1 XRD profiles of 36 nm thick N-STO films on Si substrate deposited at different substrate temperatures in Ar-50%N₂ gasses.

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In the previous microstructure study of SrTiO₃ thin films in Chapter 4, it was found that the microstructure is dependent on film thickness. Therefore, the microstructural evolution of the sputtered N-STO thin film is demonstrated here based on the XRD patterns of a 36 nm thick film. The XRD patterns of the sputtered N-STO were studied at various substrate temperatures and total sputtering pressures as shown in Figure 6-1 and Figure 6-2, respectively. The diffraction patterns indicate that the microstructural evolution is strongly dependent on the substrate temperature and the total sputtering pressure.

Figure 6-1 shows the XRD patterns of stoichiometric N-STO thin films deposited at substrate temperatures of 600 °C, 550 °C, 500 °C and 400 °C. It is observed that the films possess perovskite structures with the strongest peak (110) appearing at 31.5°, which is similar to that of the polycrystalline STO films. The intensity of the diffraction peaks increases as the substrate temperature increases. However, when it increases to 600 °C, the intensity of the diffraction peak at 31.5° becomes weaker and other peaks become apparent, corresponding to the (111) and (220) planes. This may be due to competition between thermally-activated crystal-grain growth and N incorporation in perovskite structure at high temperature.

Figure 6-2 shows the typical XRD patterns from 36 nm thick N-STO thin films as a function of the total deposition pressure. The diffraction experiments reveal that polycrystalline N-STO films deposited at different total sputtering pressure possess the same perovskite structure. No other phases were detected by the XRD. All the films display a dominant peak at 31.5°, which can be attributed to the (110) plane of perovskite STO. While the film deposited at a lower total deposition pressure (0.3 Pa) is poorly crystallized, the intensity of the diffraction peaks increases with an increasing total pressure. When the pressure is increased to 1.6 Pa, the magnitude of

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the intensity of the diffraction peak at 31.5° becomes the strongest and other diffraction peaks also become evident at the (111) and (220) planes.

Figure 6-2 XRD profiles of 36 nm thick N-STO films on Si substrate, deposited at different sputtering pressures in an Ar-50%N₂ gasses.

6.2.2 X-ray photoelectron spectroscopy characterization

Changes in the microstructure of the N-STO thin films should be accompanied by variations in the electronic structure.¹⁷⁶ In this section, the substrate temperature effects on the surface composition and natural bonding states of the N-STO thin films is firstly discussed. The nitrogen chemical bonding states are estimated from the N 1s core level spectra. The antibonding states above the Fermi level induced by the lone

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pairs of doped nitrogen could cause a reduction in the work function of STO. The crystallinity information of the N-STO thin films is obtained from the studies of O 1s and Sr 3d core level. Similar studies are also carried out on the total sputtering pressure effects.

6.2.2.1 Effect of substrate temperature

Figure 6-3 XPS N 1s core level spectra obtained from the N-incorporated SrTiO₃ thin films deposited at different substrate temperatures.

Figure 6-3 shows the high resolution N 1s spectra obtained from 12 nm thick N-STO films deposited at the substrate temperatures of 600 °C, 550 °C, 500 °C and 400 °C. Two nitrogen incorporation states can be seen in the resulting sputtered films. When the substrate temperature is increased from 400 °C to 550 °C, only a broad

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higher-binding energy peak at approximately 404.6 eV appears. It is attributed to the poorly screened final state for molecularly chemisorbed N_2 ,¹⁷³ which is confined under the oxide layer or literally adsorbed by the film surface. When the substrate temperature is increased to 600 °C, the lower-binding energy at ~396 eV also appears, corresponding to an atomic β -N state bonding with Ti.¹⁵⁹ The presence of a high-binding energy N 1s indicates that Ti-N bonds are formed by the substitutional replacement of O atoms by N at the high substrate temperature of 600 °C.¹⁵³

The stronger intensity of the atomic β -N state at 600 °C indicates that most of the nitrogen incorporated in the perovskite lattice is atomic nitrogen. Experimental evidence of the presence of different nitrogen bonding states in the STO thin films can also be provided from the XRD result at 600 °C. The nitrogen atomic substitution in the STO lattice may distort the perovskite structure of the film, resulting in the suppression of the polycrystalline perovskite grain growth at 600 °C. This induces competition on perovskite structure grain growth between the promotion induced by the high deposition temperature and the suppression induced by nitrogen substitution in the lattice. From the peak ratio of N 1s to O 1s, estimates of the N concentration can be derived at approximately 8.0%, 4.2%, 3.9% and 3.5% corresponding to the different substrate temperatures of 400 °C, 500 °C, 550 °C and 600 °C respectively. The decrease in nitrogen content at increasing substrate temperatures corresponds to the thermal instability of the molecularly chemisorbed N_2 . From the N 1s core level spectrum, it is evident that the nitrogen bonding states in the N-STO films are sensitive to deposition temperature, which may affect the Fermi level, microstructure and surface energy.

Figure 6-4 XPS O 1s core level spectra obtained from the N-STO thin films deposited at different substrate temperatures.

Figure 6-4 shows the high resolution O 1s XPS spectra of N-STO thin films. The result indicates that O is also present in two chemically distinct environments. There are two well-resolved peaks, located at binding energies of 530.2 eV and 532.2 eV respectively in the O 1s spectra. The peak at the lower binding energy (marked as O₍₁₎) corresponds to the lattice oxygen in the STO thin film.^{177,178,179} The higher binding energy (marked as O₍₂₎) peak is assigned to the chemically adsorbed oxygen on the STO thin film surface.^{162,163,180} It has been reported that the levels of adsorbed oxygen increases with increases in oxygen vacancies,^{160,161,162} thus the magnitude of the O peaks gives an indication of the number of oxygen vacancies in the film. It is observed that the peak of adsorptional oxygen is much weaker than that of lattice oxygen at a substrate temperature of 600 °C. This implies that few oxygen vacancies exist or little chemically adsorptional oxygen exists on the surface of the N-STO thin

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film deposited at high deposition temperature. Furthermore, it can be seen that the intensity of the O₍₂₎ peak significantly decreases relative to that of O₍₁₎ as the substrate temperature increases.

The ratio of the lattice oxygen and adsorbed oxygen was estimated to be 1.9, 1.6, 1.1 and 1.0 corresponding to substrate temperatures of 600 °C, 550 °C, 500 °C and 400 °C, respectively. And it is also shown that the intensity of the lattice oxygen peak increases with an increase in substrate temperature up to 600 °C. This ratio reduction of adsorbed oxygen and the increase in the intensity of the lattice oxygen with increasing substrate temperature implies that a high substrate temperature will enhance the growth of the polycrystalline STO perovskite grain and suppress the formation of oxygen vacancies during the thin film deposition process. This observation is further reinforced by the previously presented XRD results.

Figure 6-5 XPS Sr 3d core level spectra obtained from the N-STO thin films deposited at different substrate temperatures.

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Figure 6-5 and Figure 6-6 shows the Sr 3d and Ti 2p spectra of sputtered N-STO thin films at different substrate temperatures. At lower substrate temperatures, the spectra of the Sr 3d shown in Figure 6-5 have a poorly resolved doublet which may be resolved into two peaks of Sr 3d_{5/2} and Sr 3d_{3/2} corresponding to 133.3 eV and 135.02 eV, respectively, which are identified as signals from an Sr-O bond. The resolution of the Sr 3d doublet is improved with an increasing substrate temperature. Note that the intensity of the Sr 3d peak has a reverse trend to that of the adsorbed oxygen peak. It is reasonable to deduce that some Sr-O bonds are produced under a lattice oxygen-rich ambience at high temperature. Therefore the resolution improvement of the Sr 3d doublet may be due to a reduced contribution from the relaxed Sr phase, likely as a result of oxygen vacancies and adsorbed oxygen.

Figure 6-6 XPS Ti 2p core level spectra obtained from the N-STO thin films deposited at different substrate temperatures.

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In Figure 6-6, the fitted Ti 2p spectra display two wide peaks of Ti 2p_{3/2} and Ti 2p_{1/2} with binding energies of 458.8 eV and 464.5 eV respectively. These are caused by Ti-O bonds. There is no significant change in the peak shape and shift of Ti 2p for different nitrogen incorporation states and partially oxidized Ti³⁺ was not detected, which indicates that Ti is present in the Ti⁴⁺ state in all the films. This illustrates that the atomic nitrogen incorporation into the STO lattice does not alter its perovskite structure, which is consistent with the XRD pattern. The Sr/Ti molar ratio was determined by dividing the elemental peak area by the relative sensitivity. The Sr/Ti molar ratio is calculated at 0.99, 1.31, 1.43 and 1.32 at substrate temperatures of 600 °C, 550 °C, 500 °C and 400 °C. This indicates that there is Sr enrichment (~30%) on the film surface at lower deposition temperatures and that the composition gradually converges to stoichiometric SrTiO₃ with a Sr to Ti ratio of 1:1 when deposited at 600 °C.

6.2.2.2 Effect of total sputtering pressure

The nitrogen chemisorptions states in the STO thin films prepared at different deposition pressures were identified by N 1s core-level spectroscopy, as shown in Figure 6-7. As expected, it is observed that the nitrogen bonding states are sensitive to the deposition pressure. When the deposition pressure is at 0.3 Pa or 0.5 Pa, only a singular high-binding energy peak at around 404.6 eV is evident. This is ascribed to the poorly screened v-N₂ state for molecularly chemisorbed N₂,¹⁷³ which is confined under the oxide layer or literally adsorbed on the film surface. When the deposition pressure increases to 0.9 Pa, two additional peaks can be observed. The peak centered at 397.4 eV is caused by the α-N₂ state, whereas the peak at 396 eV is attributed to the atomic β-N state.¹⁵⁹ The presence of a β-N state indicates that Ti-N bonds are formed

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by the substitutional replacement of an O atom by the N dopant. As the deposition pressure is increased to 1.6 Pa, the β -N state is the dominant state in the film. From the peak ratio of N 1s to O 1s, the amount of incorporated β -N in the films can be estimated to be approximately 3.8% and 1.4% for total sputtering pressures of 1.6 Pa and 0.9 Pa respectively. This suggests that incorporating nitrogen into the STO perovskite lattice could modify the effective work function, optical band gap, surface energy and further increase the electron field emission.

Figure 6-7 XPS N 1s core level spectra obtained from the N-STO thin films deposited at different sputtering pressures.

High resolution O 1s XPS spectra are shown in Figure 6-8. It is notable that the all of the O 1s asymmetric peaks can be deconvoluted into two components with binding energies of 530.2 eV and 532.2 eV. The peak at the lower binding energy corresponds

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to the lattice oxygen in the STO thin film,¹⁷⁷ while the peak of higher binding energy can be assigned to the chemically adsorbed oxygen on film surface.¹⁸⁰ The intensity of the lower binding energy peak decreases relative to that of the higher binding energy peak, as the deposition pressure is increased to 0.9 Pa and 1.6 Pa. It is proposed that a higher deposition pressure will suppress the formation of oxygen vacancies in the films.

Figure 6-8 XPS O 1s core level spectra obtained from the N-STO thin films deposited at different sputtering pressures.

The XPS spectra of Sr 3d are shown in Figure 6-9. It is observed that the Sr 3d spectra have a poorly resolved doublet at the lower deposition pressure of 0.3 Pa and 0.5 Pa. These peaks are identified as a signal from a Sr-O bond. The resolution of the Sr 3d doublet is improved with increases in the deposition pressure. It is noted that the

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intensity of Sr 3d peak has an opposite intensity trend to that of the adsorbed oxygen peak. The resolution improvement of the Sr 3d doublet may be due to a reduction in the contribution from the relaxed Sr phase, caused by oxygen vacancies and adsorbed oxygen. It is reasonable to propose that some Sr-O bonds are produced under a lattice oxygen-rich ambience at high deposition pressure. The results of the O 1s and Sr 3d XPS spectra show a strong correlation with the XRD measurements presented previously. Therefore, it can be concluded that the N-STO thin films possess a well-developed polycrystalline grain at high deposition pressure.

Figure 6-9 XPS Sr 3d core level spectra obtained from the N-STO thin films deposited at different sputtering pressures.

6.2.3 Ellipsometer spectroscopy analysis

The variation of the band gap of N-STO films deposited at different substrate temperatures was also investigated by ellipsometer spectra. Figure 6-10 shows the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) derived from the ellipsometer spectra of the films deposited at different substrate temperature, where as before, α is the absorption coefficient, h is Plank's constant, and ν is frequency of frequency. Again, the Tauc relation, $(\alpha h\nu)^2 = C(h\nu - E_g)$, is applied to analyze the ellipsometer data in this section. A detailed principle of this process has been previously outlined in section 4.2.3. The value of the optical band gap of the N-STO films deposited at 600 °C, 550 °C, 500 °C and 400 °C can be calculated as approximately 3.86 eV, 4.21 eV, 4.23 eV, and 4.29 eV respectively.

Figure 6-10 $(\alpha h\nu)^2$ versus photon energy $h\nu$ for N-STO thin films deposited at different substrate temperatures. The inset shows the optical band gap as a function of different substrate temperatures.

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The relationship between the optical band gap and the substrate temperature is inserted in Figure 6-10. It is seen that the optical band gap decreases gradually as the nitrogen is molecularly adsorbed in the films at substrate temperatures from 400 °C to 550 °C. Upon nitrogen substitution into the SrTiO₃ lattice at 600 °C, the band-gap decreases rapidly from 4.21 eV to 3.86 eV. This decrease in the optical band gap can be mainly attributed to nitrogen incorporation into the STO lattice at higher substrate temperatures. When nitrogen atoms substitute oxygen sites and are subsequently bound to Ti, the corresponding N 2*p* states are located above the valence band edge. Mixing of N 2*p* states with O 2*p* states results in a reduction of the band gap of the N-STO, which coincides with the result from the optical band gap measurement as was discussed above. However, as for the N-STO films deposited below 550 °C, nitrogen dopant is only molecularly chemisorbed with a poor screened and little interaction exists with the band state of the STO in the lattice, and thus is unlikely to be effective in narrowing the band gap. The slight decrease of the band gap can be attributed to the growth of perovskite structure grains, however, the rapid decrease may be induced by the nitrogen substitution in the STO lattice.

Figure 6-11 shows the $(ah\nu)^2$ versus photon energy ($h\nu$) derived from the ellipsometer spectra of the STO thin films deposited at different total sputtering pressures to determine the optical band gap, in which the linear portion of the plot is used to deduce the indirect band gap. The value of the optical band gap of the films deposited at deposition pressures of 1.6 Pa, 0.9 Pa, 0.5 Pa and 0.3 Pa can be determined as approximately 3.86 eV, 4.11 eV, 4.27 eV, and 4.39 eV respectively. The relationship between the optical band gap and the deposition pressure is shown in the inset of Figure 6-11. The narrowed optical band gap of the N-STO can be explained by the formation of nonbonding states. According to bond-band-barrier

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correlation theory, the nonbonding states are at a slightly higher level than the initial 2p level of an isolated N atom, which is located above the valence band edge of O. Consequently, the formation of nonbonding states in DOS can result in a reduction of the band gap of the N-STO, which coincides with the optical band gap results discussed above. However, as for the films deposited at lower deposition pressures, nitrogen dopant is only molecularly chemisorbed with poorly screened and exhibits little interaction with the band state of the STO_3 in the lattice, thus is not expected to be effective in narrowing the band gap.

Figure 6-11 $(\alpha h\nu)^2$ versus photon energy $h\nu$ for N-STO thin films deposited at different sputtering pressures. The inset shows the optical band gap of films as a function of different sputtering pressures.

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Therefore, the slight decrease of the band gap can be attributed to the growth of perovskite structure grains; again however, the rapid decrease may be induced by the nitrogen substitution in STO lattice.

6.3 Field emission properties

In this section, the effects of varying substrate temperature and total sputtering pressure on the field emission properties of silicon tip arrays coated with N-STO thin films is investigated. Due to the fact that the microstructure of the STO thin films and nitrogen incorporation states are strongly affected by the deposition conditions, further study is necessary to understand the influence of varying deposition conditions on the resulting field emission properties. The effect of sputtering conditions on the *J-E* characteristic is initially provided. The effective work function of the N-STO coated Si tips is then deduced using the F-N plot. Finally, the effect of the varying deposition conditions on the field emission mechanism is discussed.

6.3.1 The J-E characteristics

The field emission characteristics of the silicon tip arrays coated with N-STO films deposited at different substrate temperatures are shown in Figure 6-12. From the *J-E* curves, it is found that with an increasing substrate temperature from 400 °C to 600 °C, the threshold electric field for electron emission is gradually reduced from 30.6 V/μm to 17.4 V/μm. The threshold electric field experimentation results, listed in Table 6-1, highlights the benefits of a high substrate temperature and subsequent improvement of the field emission properties.

Figure 6-12 Field emission properties of Si tip arrays with 12 nm thick N-STO coatings deposited at different substrate temperatures.

The emission current density-electric field (J-E) plots as a function of the total deposition pressure are shown in Figure 6-13. From the J-E curves, it is shown that the threshold electric fields of all the thin films are in the range of 17.4 V/μm - 27.4 V/μm, as are listed in Table 6-2. The field emission behavior was not improved as the deposition pressure increased from 0.3 Pa to 0.5 Pa. However, the threshold field will decrease with further increases of deposition pressure. The J-E results show that the field emission behaviors of Si tip coated with N-incorporated SrTiO₃ are influenced by the deposition pressure and a high deposition pressure favors more improvements the field emission properties.

Figure 6-13 Field emission properties of Si tip arrays with 12 nm thick N-STO coatings deposited at different sputtering pressures.

6.3.2 Analysis of emission data

From Fowler-Nordheim theory, a decrease in the threshold electric field may originate from a reduction of the effective work function ($\phi_e = \phi / \beta$) of the N-STO films coated on silicon tip arrays with the same field-enhancement factor. Here, the emission data is analyzed using the Fowler-Nordheim (F-N) equation, $I = AV^2 \exp(-B\phi^{3/2} / V)$, where A and B are constant, I is the emission current, and ϕ is the effective work function of the field emission emitter. The FN plots, i.e., $\log(I/V^2)$ vs. $1000/V$, of the coated silicon tip arrays as a function of substrate temperature are given in Figure 6-14. It is found that their field emission behaviors are strongly aligned with the Fowler-Nordheim characteristic. From the linear approximations, the effective work function can be deduced by

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$\phi_{STO} = \phi_{Si} (FNSL_{STO} / FNSL_{Si})^{2/3}$ where FNSL is the slope of F-N plot. By using the FN slope data listed in Table 6-1 and silicon work function (4.1 eV), the effective work function of the coated silicon tip arrays coated deposited at different substrate temperatures can be calculated to be 2.09 eV, 2.82 eV, 3.38 eV and 3.69 eV for substrate temperatures of 600 °C, 550 °C, 500 °C and 400 °C respectively. This work exposes that the substrate temperature enhanced field emission behaviors originate from a reduction of the effective function and that the lowest effective work function is achieved when deposition occurs at 600 °C. It is believed that the electron field emission behaviors of are affected by the substrate temperature through its effects on the microstructure of the STO thin films and the state of incorporated nitrogen in the STO perovskite lattice. Recent advances^{20,21} indicate that well-developed perovskite grains are a critical factor in a film being adopted to achieve low threshold electric fields.

Figure 6-14 F-N plots of field emission from Si tip arrays coated with N-STO coatings deposited at different substrate temperatures.

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Substrate temperature (°C)	Threshold	FNSL _{STO} /FNSL _{Si}	Effective work function (eV)
	electric field (V/μm)		
600	17.4	0.3642	2.09
550	22.2	0.5704	2.82
500	24.6	0.7485	3.38
400	30.6	0.8538	3.69

Table 6-1 The threshold electric field, FNSL parameters and effective work function of silicon tip arrays coated N-STO thin films deposited at different substrate temperatures.

The FN plots, i.e., $\log(I/V^2)$ vs. $1000/V$, of the silicon tip arrays are given in Figure 6-15. Again, the field emission behaviors of silicon tip arrays coated by N-STO films can be seen to follow the Fowler-Nordheim theory. From the linear approximations of the F-N plots, the effective work functions were calculated to be 2.09 eV, 3.16 eV, 3.24 eV and 3.4 eV for each of the N-STO films deposited at 1.6 Pa, 0.9 Pa, 0.5 Pa and 0.3 Pa respectively. Further details are listed in Table 6-2. From Fowler-Nordheim theory, the decrease in the threshold electric field may originate from the reduction of the effective work function ($\phi_e = \phi / \beta$) of the N-STO films coated on silicon tip arrays with the same field-enhancement factor. It is interesting to note that the effective work function decreases with an increasing the deposition pressure and reaches to the lowest value at 1.6 Pa.

Figure 6-15 F-N plots of field emission from Si tip arrays coated with N-STO coatings deposited in different sputtering pressures.

Total sputtering pressure (Pa)	Threshold electric field (V/ μ m)	$FNSL_{STO}/FNSL_{Si}$	Effective work function (eV)
1.6	17.4	0.3642	2.09
0.9	24.1	0.6766	3.16
0.5	26.8	0.7025	3.24
0.3	27.4	0.7552	3.4

Table 6-2 The threshold electric field, FNSL parameters and effective work function of silicon tip arrays coated N-STO thin films deposited at different sputtering pressures.

6.3.3 The discussion of sputtering conditions effects on the field emission properties

According to the bond-band-barrier correlation mechanism,^{140,141,143} nitrogen incorporation in the STO lattice would significantly modify the effective work function. This is a chemical bonding formation process with valence electron transfer. According to the bond-band-barrier correlation, when nitrogen substitutes oxygen and bonds to neighboring atoms, the nitrogen atom would hybridize its *sp* orbital upon interacting with another element B of less-electronegative to form a quasi-tetrahedron through three bonding orbitals (sharing electron pairs) and one nonbonding electron lone pair. During this process, the *sp*-hybridization and non-bonding lone pair will induce dipoles of neighboring atoms associated with an increase in size and elevation of the energy of the polarized electrons that occupy the anti-bonding energy levels. From a band structure point of view, the bonding band is divided into a *sp*-bonding sub-band and a nonbonding (lone pair) sub-band. The lone pair sub-band is located between the *sp*-bonding sub-band and Fermi level. The lone-pair induced dipoles sustain the antibonding features above the Fermi level in the energy band which are responsible for the reduction of the local work function. The effective work function of silicon tip arrays with N-STO coatings is reduced upon N being bound to Ti, which is believed to induce the antibonding state that reduces the work function under certain sputtering conditions. Therefore, the presence of antibonding states is of vital importance to the N enhanced field emission. The N-enhanced field emission behaviors at a high substrate temperature of 600 °C and a high sputtering pressure of 1.6 Pa conform closely with the bond-band-barrier correlation prediction.

From the N 1s spectra, it is observed that the N chemical bonding state is affected by the sputtering conditions. At lower substrate temperatures of 400 °C and 500 °C or

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lower pressures of 0.3 Pa and 0.5 Pa, the nitrogen is molecularly adsorbed by the STO thin film. Since molecularly adsorbed nitrogen is not bound to Ti, the field emission properties of the STO coated silicon tip arrays are not improved when compared to that without nitrogen incorporation. When the substrate temperature is increased to 600 °C or the deposition pressure is increased to 1.6 Pa, nitrogen atoms are chemically adsorbed into the STO perovskite lattice meaning that the N reacts with the Ti. The nonbonding lone pairs of nitrogen polarize the Ti to induce an antibonding state above the Fermi level which is responsible for the reduction of the local work function. From the FN plot, the effective work function is decreased from 3.6 eV to 2.09 eV as the substrate temperature is increased from 400 °C to 600 °C. On the other hand, the effective work function is reduced from 3.4 eV to 2.09 eV with increases in the deposition pressure from 0.3 Pa to 1.6 Pa.

The lone-pair dipoles and anti-bonding dipoles induced by nitrogen doping can result in strong localization of dipole electrons at the thin film surface. Such charge redistribution and polarization could be responsible for the adsorbate-induced surface stress and the corresponding reconstruction.¹⁸¹ Further characterization of the surface energy can be achieved by using contact angle measuring to study the nitrogen doping effect. Figure 6-16 shows the contact angle of the films deposited at different substrate temperatures and the threshold electric field. It is illustrated that the contact angle has a maximum value upon nitrogen doping into the STO lattice and displays an opposite trend to that of the threshold electric field as a function of substrate temperature.

Figure 6-16 Variation of the threshold electric field for electron emission (■) and the water contact angle (★) of STO thin films deposited at different substrate temperatures.

Figure 6-17 plots the water contact angle of the films as a function of deposition pressure and the threshold electric field. It is shown that the contact angle displays its minimum value at a lower deposition pressure and increases with the deposition pressure up to 1.6 Pa. An opposite trend is again evident to that of the threshold electric field as a function of sputtering pressure. This clearly indicates that the surface energy of STO can be reduced upon nitrogen doping into its lattice. The correlation of the surface energy and the work function of N-STO can be explained by a strong localization of dipole electrons with energies above E_F when N is atomically

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adsorbed in the surface. The contact-angle results clearly indicate the presence of the same correlation. Therefore, the model of bonding and band-forming proposed in this work and verified through rigorous experimentation, provides a mechanism for improving the field emission properties of STO thin films through a narrowed band gap, a lowered surface energy and a lowered work function.

Figure 6-17 Variation of the threshold electric field for electron emission (■) and the water contact angle (★) of STO thin films deposited at different sputtering pressures.

6.4 Conclusion

In this chapter, the strong dependence of the field emission behavior from the N-STO coated Si FEA on the substrate temperature and total sputtering pressure during the deposition process were highlighted. The deposition temperature and

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pressure parameters were then optimized to achieve the maximum field enhancement. The threshold electric field was seen to decrease with an increase in substrate temperature and total sputtering pressure, and reached a local minimum value of 17.4 V/ μm at substrate temperature of 600 °C and deposition pressure of 1.6 Pa. It was proposed that the enhanced field emission behaviors originate from the different states of incorporated nitrogen. Nitrogen substitution in the films reduces the effective work function of the silicon field emitter and thus enhances the field emission properties according to the proposed nitride-based bonding and band-forming model.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

This chapter summarizes the work and major findings of this dissertation as well as outlining future compelling research directions to further the newly developed proposals and contributions.

7.1 Conclusions

In this dissertation, ferroelectric N-incorporated SrTiO_3 thin films have been proposed to improve field emission from Si cold cathode emitters, and were deposited using an RF sputtering technique. Characterizations of the films and their field emission properties have been systematically studied, under varying sputtering gasses and parameters. A significant reduction in the work function and dramatic improvement of the emission current was observed from the N-incorporated SrTiO_3 coated arrays. A band-band-barrier based field emission mechanism has been proposed to account for the experimentally observed improvements, which was continuously discussed throughout the dissertation by examination of the microstructural features and electronic properties of the coatings. The main conclusions can be summarized as follows:

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1. The reactive RF magnetron sputtering technique has been successfully employed to deposit the N-doped SrTiO_3 thin films on silicon tip arrays. Successful nitrogen doping into the perovskite SrTiO_3 lattice during the sputtering process was confirmed by XPS measurements. A high substrate temperature of 600 °C and high deposition pressure of 1.6 Pa have been verified as the optimal sputtering settings for maximizing field emission enhancements.
2. Due to the proposed coating, the threshold field has been significantly lowered from 36.2 V/ μm for uncoated silicon tip arrays to 17.4 V/ μm for 12 nm thick SrTiO_3 coated silicon tip arrays deposited in a 50% N_2 gasses. The work function of the emitter surface was also reduced from 4.1 eV to 2.09 eV correspondingly. The enhanced field emission properties of silicon tip arrays were attributed to the lower effective work function of the SrTiO_3 coatings due to the presence of lone-pair-induced antibonding states above the Fermi level.
3. Field emission characteristics of SrTiO_3 deposited in different sputtering gasses proved that film deposited in a mixture of Ar + N_2 achieves increased enhancements of field emission properties when compared to those deposited in pure Ar or a mixture of Ar + O_2 . Experimental verification proved that the existence of O_2 in the sputtering gasses has a detrimental effect on the enhancement of the field emission properties of the coating. Furthermore, the electron emission characteristics were also shown to be highly dependent on the coating thickness. The work of this dissertation proved that a 12 nm thick

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N-doped SrTiO_3 film is the optimal thickness for maximization of the field electron emission enhancements.

4. Crystallinity in the SrTiO_3 film was enhanced by the low dose incorporation of the nitrogen dopant. However, the perovskite structure was seen to deteriorate in nitrogen-overdosed films, which are deposited by higher nitrogen content gasses. Electron emission characteristics of SrTiO_3 coated silicon tip arrays are found to be highly correlated with the sputtering gas nitrogen content. By changing the nitrogen content value, the Fermi level, the VBM, and the CBM of the N-doped SrTiO_3 thin films could be altered considerably. The polycrystalline SrTiO_3 thin film deposited at 50%-nitrogen gasses exhibits a narrow band gap, upwards-moved Fermi level and downwards-moved CBM, which contribute to the enhanced field emission characteristics. Further increasing the nitrogen partial pressure results in the Fermi level moving rapidly downwards, which deteriorates the electron emission accordingly. The proposed mechanism of bonding and band-forming provides a feasible mechanism for N-enhanced threshold electric field in cold cathode emission because of the presence of the lone-pair-induced antibonding states above the Fermi level. Water contact angle measurements provided further evidence for the presence of anti-bonding state induced by nitrogen doping.
5. Optimization of the substrate temperature and total sputtering pressure parameters was also achieved in a mixture gasses of Ar + 50% N_2 to maximize the enhancements of the field electron emission properties. The threshold electric field of each sample decreased with an increase in substrate temperature and total

sputtering pressure, and it reached a minimum value of 17.4 V/ μm at 600 °C. This enhanced field emission characteristic of N-doped SrTiO₃-coated silicon tip arrays was attributed to a reduction of the effective work function, which decreased to 2.09 eV. The enhanced field emission behaviors were proposed to originate from the different states of incorporated nitrogen. From the XRD and XPS results, the polycrystalline grain growth intensifies with increasing substrate temperature and total sputtering pressure. When the substrate temperature and sputtering pressure is increased up to 600 °C and 1.6 Pa respectively, the N-doped SrTiO₃ thin film exhibited a well-developed perovskite microstructure and atomic nitrogen was doped into the SrTiO₃ lattice.

6. The emission current stabilities tests indicated that at a substrate temperature of 600 °C, a sputtering pressure of 1.6 Pa and an gasses mixture of Ar + 50% N₂, a high and stable emission current can be achieved.

This dissertation showed that a conformal, stable N-doped SrTiO₃ thin film coating on Si tip arrays can be realized with a simple reactive RF magnetron sputtering technique. The sputtered N-doped SrTiO₃ coatings have been shown to be a practical method of improving field emission of Si tip arrays. The field emission properties are closely correlated to the microstructure and electronic properties of the films which are influenced by the nitrogen chemical bonding states.

7.2 Recommendations for future work

In this dissertation, it is evident that the sputtered N-doped SrTiO₃ thin films exhibit a promising prospect for potential field emission device applications. The

Chapter VII Conclusion and recommendations

enhanced field emission properties of coated arrays are clear and unambiguous when compared with that of uncoated arrays. The N-enhanced field emission properties of silicon tip arrays were attributed to the low effective work function of SrTiO₃ coatings because of the presence of non-bonding lone pairs of nitrogen, which can induce an antibonding state above the Fermi level. The work of this dissertation, therefore verifies the merits and potential improvements obtained through further research and analysis of N-enhanced coatings.

Further field emission enhancements may be possible by co-doping with both low- Φ metals, such as Li or Cs and N as this could form metal dipoles at the surface, which reduces the work function of the low- Φ metals even further ($\sim 1.25 \text{ eV} < 3.5 \text{ eV}$). Therefore, co-doping low- Φ metals with N could be beneficial in further reducing the work function of cold cathode materials. However, the production of H-like bonds at the surface due to N overdosing may have detrimental effects on the work function reduction. A well controlled doping process would be vital to avoid such pitfalls.

In such a doping process, the role of a plasma environment could prove very important as it would affect the incorporated nitrogen content and chemical bonding states in the host lattice. A well controlled plasma assisted technique may be adopted to achieve this. Investigating the dynamic self consistent processes of the formation of cold cathode materials doped with low- Φ and N, as tailored building units with the desired size, composition, and architecture is a very interesting and worthwhile research direction. The new insights and understandings obtained may prove invaluable to the design and control of work functions for electron source applications.

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