Ferroelectric (Ba,Sr)1-xLaxTiO3 thin films electron field emission applications

Lu, Hua

2007

Lu, H. (2007). Ferroelectric (Ba,Sr)1-xLaxTiO3 thin films electron field emission applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/4822>

<https://doi.org/10.32657/10356/4822>

Nanyang Technological University

Downloaded on 26 Apr 2023 21:27:04 SGT

Ferroelectric $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ Thin Films For Electron Field Emission Applications

Lu Hua

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

2007

ACKNOWLEDGMENTS

I would like to express my deep gratitude to my supervisor Professor Zhu Weiguang for his invaluable guidance, help, and encouragement in the whole course of the work. His broad knowledge and enthusiasm has a very rewarding and lasting effect on me. His kindness and patience are also deeply appreciated.

My special thanks go to my co-supervisor Dr. Pan Jisheng for his invaluable direct instruction and discussions throughout my research. I am also indebted to Dr. Chen Xiaofeng for his advice and help during the study.

My sincere thanks go to many people who assisted me in the completion of this research work. The assistance provided by all the students, staffs and technicians of Sensors and Actuators Lab is highly appreciated.

I would like to express my boundless gratitude to my beloved wife, Yang Zixuan, for her love, patience and moral support over these years. Finally, I am also deeply thankful to my parents for their support and encouragement throughout my education.

TABLE OF CONTENTS

Acknowledgments	i
Table of Contents	ii
Summary	v
List of Figures	viii
List of Tables	xiii
List of Abbreviations	xiv
 1. Introduction	 1
1.1 Motivation	1
1.2 Objectives	4
1.3 Major contributions of the thesis	5
1.4 Organization of the thesis	9
 2. Literature Review	 12
2.1 Electron field emission	12
2.1.1 Theory of electron field emission	12
2.1.2 The present status of cold cathode materials	18
2.1.3 Electron field emission of Si tip arrays and Si tip arrays with coatings	22
2.1.4 The potential applications of cold cathode materials	34
2.2 Ferroelectric (Ba,Sr) _{1-x} La _x TiO _{3+y} materials	36
2.2.1 Physical structure	36
2.2.2 Electronic structure	39
2.2.3 <i>n</i> -type doped (Ba,Sr)TiO ₃	43

3. Experimental Procedures	47
3.1 Preparation of films	48
3.1.1 Fabrication of silicon tip arrays	48
3.1.2 Solution preparation	49
3.1.3 Deposition of thin films	51
3.2 Characterization	52
3.2.1 Characterization of ferroelectric thin films	52
3.2.2 Characterization of field emission properties	54
4. Field Emission of (Ba,Sr)TiO₃ Coated Si Tips Arrays	57
4.1 Preparation and characterization of BST films	59
4.1.1 Thermal decomposition properties	59
4.1.2 Microstructure and component analysis of BST thin films	60
4.1.2.1 X-ray diffraction	60
4.1.2.2 TEM observation	63
4.1.2.3 SIMS depth profile	66
4.1.2.4 FTIR analysis	69
4.1.3 X-ray photoelectron spectroscopy characterization	71
4.3.1.1 Effect of annealing temperature	72
4.3.1.2 Effect of thickness	80
4.2 Field emission properties of Si tip arrays coated with BST thin films	85
4.2.1 Emission current density-electric field (J - E) characteristics	85
4.2.2 Field emission stability	87
4.2.3 Analysis of emission data	91
4.2.3.1 Field enhancement factor	91
4.2.3.2 Effective work function	92
4.2.4 Field emission mechanism	96
5. Field Emission of (Ba,Sr)_{1-x}La_xTiO_{3+y} Coated Si Tip Arrays	102

Table of contents

5.1	Preparation and characterization of BSLT films	104
5.1.1	Thermal decomposition properties	104
5.1.2	Microstructure of BSLT thin films	105
5.1.2.1	X-ray diffraction	106
5.1.2.2	TEM observation	111
5.1.3	X-ray photoelectron spectroscopy characterization of BSLT films	113
5.2	Field emission properties of Si tip arrays coated with BSLT thin films	124
5.2.1	Emission current density-electric field (J - E) characteristics	125
5.2.2	Field emission stability	128
5.2.3	Analysis of emission data	131
5.2.4	La substitution effect on field emission mechanism	133
6.	Conclusion and Recommendations	137
6.1	Conclusions	137
6.2	Recommendations for further research	142
	Author's Publications	145
	Bibliography	147

SUMMARY

The study of cold cathode materials is currently a hot research topic for their important applications such as field emission displays and vacuum microelectronics devices. Among them, silicon (Si) tip arrays have attracted much attention owing to the compatible fabrication process with advanced integrated-circuit technology. However, the high threshold electric field and poor emission stability limit their use in some applications. In this thesis, ferroelectric $(\text{Ba}_{0.65}\text{Sr}_{0.35})\text{TiO}_3$ (BST) and $(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_{3+y}$ (BSLT with $0.1 \leq x \leq 1$) thin films as surface modification on Si tip arrays to improve the field emission behavior have been systematically investigated.

The BST thin films have been fabricated using sol-gel technology. Field emission properties of Si tip arrays coated with BST thin films have been investigated by varying annealing temperature and thickness of BST coatings. The microstructural evolution results indicate that the BST coatings exhibit the perovskite structure while annealed between 650 and 700 °C; a severe interfacial reaction between Si and BST coating while annealed above 750 °C. The crystallinity of perovskite structure is improved with the increasing thickness of BST film annealed at 700 °C. The 15-nm-thick BST film is amorphous in nature, and the polycrystalline perovskite grains develop in the thicker film with an amorphous layer existed in the bottom region of the film. The compositional analysis shows that the BST/Si interface is a solid-state reaction product of $(\text{Ba},\text{Sr})\text{Ti}_x\text{Si}_y\text{O}_z$. The study of electronic structure using X-ray photoelectron spectroscopy (XPS) shows that the Fermi level shifts up for BST film

Summary

with increasing annealing temperature from 600 to 750 °C, and it moves back slightly at 800 °C. The upward shift of the Fermi level from 600 to 750 °C is attributed to the increasing oxygen vacancy concentration in the films and the downward shift of the Fermi level at 800 °C is associated with severe interfacial reaction.

The BST coated Si tip arrays show considerable improvement in field emission behavior. The emission behavior is highly dependent on annealing temperature and thickness of BST coating. The threshold field could be lowered substantially from 36 V/ μm for bare Si tip arrays to about 19 V/ μm for 30-nm-thick BST coated Si tip arrays annealed at 700 °C. In addition, the BST coating improves the electron emission stability of Si tip arrays considerably. Analysis of the emission data using the Fowler-Nordheim (F-N) plot suggests that the improvement in electron emission originates from the lowering of effective work function with BST coatings. The field emission mechanism of BST-modified Si tip arrays has been discussed. It is found that the promising candidate for field emission applications is the BST film with high crystallinity of perovskite structure in surface region, decreased interfacial reaction, increased oxygen vacancy concentration, and upwards-moved Fermi level. Meanwhile, the thickness dependence originates from the developed microstructural features in BST films.

Studies have been extended using the sol-gel derived BSLT ($0.1 \leq x \leq 1$) thin films. Effect of lanthanum (La) concentration has been studied to optimize field emission properties. The films exhibit the perovskite structure at low La substitution levels ($0.1 \leq x \leq 0.5$) and the pyrochlore phase appearing at high La concentrations

Summary

($0.75 \leq x \leq 1$), respectively. Furthermore, it is found that the La substitution in BST films would suppress the interfacial reaction with Si substrate. The 30-nm-thick BSLT ($x = 0.25$) thin films exhibit high crystallinity of perovskite structure in the surface region. XPS study indicates that the oxygen vacancy concentration decreases with La substitution. With respect to the BST ($x = 0$) thin film, the Fermi level shifts down for BSLT sample with $x = 0.1$ ascribed to the decreasing oxygen vacancy concentration, shifts up for BSLT sample with $x = 0.25$ attributed to the increasing La substitution level, and shifts down again for BSLT samples with $x \geq 0.5$ which may be associated with the appearance of the second pyrochlore phase.

The effect of La substitution level on field emission properties has been investigated. The arrays coated with BSLT ($x = 0.25$) film shows the significant improvement in the field emission behavior with a threshold field of $15 \text{ V}/\mu\text{m}$ compared with other samples. In addition, it also shows great improvement in field emission stability. The lowering of effective work function of BSLT coated arrays is found using the F-N plot analysis. Correlated to the microstructure and electronic structure, the enhanced emission behavior of BSLT ($x = 0.25$) thin film coated Si arrays results from improved perovskite structure in the surface region, suppressed interfacial reaction, and up-moved Fermi level of the coating.

The studies demonstrate the advantages of ferroelectric materials on field emission by utilization of the BST and BSLT ferroelectric thin film coating on Si tip arrays. The field emission properties are closely correlated to the microstructure and electronic structure of ferroelectric thin films.

LIST OF FIGURES

Figure 2-1	Diagram of the potential energy of electrons at the surface of a metal. $-e^2/4x$ is the image force potential; $-eEx$ is external applied potential; ϕ is work function; E is electric field [25].	14
Figure 2-2	Schematic diagram of 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 [26].	17
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 [25].	17
Figure 2-4	Basic structure of a Spindt cathode [2].	19
Figure 2-5	SEM micrographs of randomly orientated CNTs (a) and aligned CNTs (b) [37-38].	20
Figure 2-6	Illustration of field electron emission from a tip [47].	23
Figure 2-7	Band diagram representation of the quasi tunneling process associated with a positive surface electron affinity (a) and an effective negative electron affinity (b) [50].	26
Figure 2-8	Band schemes of a semiconductor surface with PEA (a), true NEA (b), and effective NEA (c) [27].	28
Figure 2-9	A model based on the α -C:H:N acting as a space charge interlayer on the n^{++} -Si. No applied field top (a); an applied voltage of 10 V between the anode and n^{++} Si (b) [62].	32
Figure 2-10	Architecture of a Spindt cathode-based flat panel display [44].	36
Figure 2-11	Perovskite structure of BaTiO ₃ [67].	37
Figure 2-12	Schematic energy-level diagram for SrTiO ₃ [81].	41

List of figures

Figure 3-1	Fabrication schema of BST-coated Si tip arrays.	49
Figure 3-2	Flow-chart for preparation of BST and BSLT ($0.1 \leq x \leq 1$) solution.	51
Figure 3-3	Schematic diagram of the electron field emission characterization set up.	55
Figure 4-1	TGA and DTA curves of BST gel precursor.	60
Figure 4-2	X-ray diffraction patterns of sol-gel BST thin films annealed at 700 °C with different thicknesses.	61
Figure 4-3	X-ray diffraction patterns of sol-gel BST thin films with thickness of 90 nm annealed at different temperatures for 1 hour.	62
Figure 4-4	Cross-section images of sol-gel derived BST thin films deposited on Si substrate annealed at 600 (a) and 800 °C (b).	64
Figure 4-5	Cross-section images of sol-gel derived BST thin films annealed at 700 °C with thickness of 30 (a) and 90 nm (b). The insets show two-layer structure in the film.	65
Figure 4-6	TEM bight-field image for the lattice structure of BST annealed at 700 °C with thickness of 30 nm.	66
Figure 4-7	SIMS depth profiles for sol-gel BST thin film annealed at 600 (a), 700 (b), and 800 °C (c) for 1 hour.	69
Figure 4-8	FT-IR transmittance spectra of 30-nm-thick BST thin films annealed at different temperatures in air for 1 hour.	70
Figure 4-9	XPS survey spectrum of BST film with thickness of 30 nm annealed at 700 °C	74
Figure 4-10	XPS O1s core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures.	76
Figure 4-11	XPS Ti 2p core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures. The shift in the peak is attributed to the Fermi level change of BST thin films.	77

List of figures

Figure 4-12	XPS valence band spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures.	78
Figure 4-13	XPS Ba $3d_{5/2}$ core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures. Increased Ba(1)/Ba(2) ratio indicates improvement in crystallinity of the BST thin films.	79
Figure 4-14	XPS Ti $2p$ core level spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.	81
Figure 4-15	XPS Ba $3d_{5/2}$ core level spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.	83
Figure 4-16	XPS valence-band spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.	83
Figure 4-17	Field emission of Si tip arrays coated with 30-nm-thick BST thin films annealed at different temperatures. Increased Ba(1)/Ba(2) ratio indicates improvement in crystallinity of the BST thin films.	86
Figure 4-18	Field emission of Si tip arrays coated with BST thin films annealed at 700 °C with different thicknesses. The arrays coated with 30-nm-thick BST film show the optimal emission performance.	86
Figure 4-19	The emission current stability of bare Si tip arrays (a), Si tip arrays coated with 30-nm-thick BST thin films annealed at 600 °C (b), 700 °C (c), and 800 °C (d).	89
Figure 4-20	The emission current stability of bare Si tip arrays (a), Si tip arrays coated with 30-nm-thick (b) and 90-nm-thick (c) BST thin films annealed at 700 °C.	90
Figure 4-21	F-N plot of field emission from Si tip arrays and BST-coated Si tip arrays (a), Si tip arrays coated with BST thin films annealed at different annealing temperatures (b), Si tip arrays coated with BST thin films with different thicknesses (c).	94
Figure 4-22	Scanning electron micrographes (SEM) of uncoated (a), 30-nm-thick (b), and 90-nm-thick (c) BST-coated Si tip arrays.	95

List of figures

Figure 5-1	TGA and DTA curves of BSLT ($x = 0.25$) gel precursor.	105
Figure 5-2	X-ray diffraction patterns of sol-gel BSLT ($x = 0.25$) thin films with different thicknesses annealed at 750 °C for 1 hour.	109
Figure 5-3	X-ray diffraction patterns of sol-gel BSLT ($0 \leq x \leq 1$) thin films with thickness of 90 nm annealed at 700 °C for 1 hour.	110
Figure 5-4	X-ray diffraction patterns of the sol-gel BST thin film annealing at 700 °C, and BSLT ($0.1 \leq x \leq 1$) thin films annealed at 750 °C for 1 hour. The thickness is about 90 nm.	110
Figure 5-5	Cross-section view of the sol-gel BSLT ($x = 0.25$) thin films annealed at 750 °C. The insets show two-layer structure in the film.	112
Figure 5-6	TEM bright-field image for the lattice structure of BSLT ($x = 0.25$) annealed at 750 °C with thickness of 30 nm.	112
Figure 5-7	XPS survey spectrum of the sol-gel derived BSLT thin film ($x = 0.25$) annealed at 750 °C with thickness of 30 nm.	114
Figure 5-8	XPS O 1s core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations.	117
Figure 5-9	XPS Ti 2p core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations. The shift in the peak is attributed to the Fermi level change of BSLT thin films.	118
Figure 5-10	XPS valence-band spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations.	121
Figure 5-11	XPS Ba 3d5/2 core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 0.75$) thin films with different La concentrations. Increased Ba(1)/Ba(2) ratio indicates improvement in crystallinity of the BSLT thin films.	122
Figure 5-12	Field emission of Si tip arrays coated with 30-nm-thick sol-gel BSLT ($x = 0.25$) thin film annealed at 700 and 750 °C.	127

List of figures

Figure 5-13	Field emission of Si tip arrays coated with 30-nm-thick sol-gel BSLT ($0 \leq x \leq 1$) thin films annealed at 750 °C. The arrays coated with BSLT ($x = 0.25$) yield the optimal emission performance.	127
Figure 5-14	Field emission of Si tip arrays coated with sol-gel BSLT ($x = 0.25$) thin films annealed at 750 °C with different thicknesses. The arrays coated with 30-nm-thick BSLT film show the optimal emission performance.	128
Figure 5-15	The emission current density stabilities of bare Si arrays (a), and Si arrays coated with BSLT thin films with $x = 0$ (b), 0.1 (c), 0.25 (d), 0.5(e), 0.75 (f), and 1 (g).	130
Figure 5-16	The emission current density stability of Si arrays coated with 30-nm-thick BSLT thin film ($x = 0.25$) for 12-hour measurement.	131
Figure 5-17	The F-N plot of field emission from bare Si tip arrays and Si tip arrays coated with 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations.	132

LIST OF TABLES

Table 4-1	Atomic percents of Ba, Sr, To and O in BST thin films obtained from XPS high-resolution spectra.	74
Table 4-2	Summary of the measured shift value of the Fermi level ΔE_F , the $O_{(2)}/O_{(1)}$ ratio, the binding energy of valence band maximum (E_{VBM}) and the $Ba_{(1)}/Ba_{(2)}$ ratio of BST thin films annealed at different temperatures.	80
Table 4-3	The threshold field, the fluctuation of emission current density, the ratio of the F-N plot slope ($FNSL_{BST}/FNSL_{Si}$), the effective work function of BST coated Si tip arrays as a function of annealing temperature and film thickness.	96
Table 5-1	Surface compositions (At%) of all BSLT ($0 \leq x \leq 1$) thin films obtained from XPS measurements.	115
Table 5-2	Summary of the measured shift value of binding energy of Ti 2p core level, the $O_{(2)}/O_{(1)}$ ratio, the $Ba_{(1)}/Ba_{(2)}$ ratio, and the binding energy of valence band maximum (E_{VBM}) of BSLT thin films with different La concentrations.	123
Table 5-3	The threshold field, the fluctuation of emission current density, the ratio of F-N plot slope ($FNSL_{BST}/FNSL_{Si}$), the effective work function of BSLT coated Si tip arrays as a function of La concentrations.	133

LIST OF ABBREVIATIONS

Ba	Barium
BSLT	$(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_{3+y}$ ($0.1 \leq x \leq 1$)
BST	$\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$
BT	Barium Titanate
Cs	Cesium
CMOS	Complementary Metal Oxide Semiconductor
CNTs	Carbon Nanotubes
CSD	Chemical Solution Deposition
CVD	Chemical Vapor Deposition
DRAM	Dynamic Random Access Memories
DTA	Differential Thermal Analysis
FEAs	Field Emission Arrays
FEDs	Field Emission Displays
F-N	Fowler-Nordheim
FNSL	Fowler-Nordheim Slope
FT-IR	Fourier Transform Infrared
FWHMs	Full Widths at Half Maximum
La	Lanthanum

List of abbreviations

LO	Longitudinal Optical
Mo	Molybdenum
NEA	Negative Electron Affinity
PEA	Positive Electron Affinity
PZT	Lead Zirconium Titanate
SBT	Strontium Bismuth Tantalate
SEM	Scanning Electron Microscopy
Si	Silicon
SIMS	Second Ion Mass Spectroscopy
Sr	Strontium
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
Ti	Titanium
TO	Transverse Optical
UPS	Ultraviolet Photoelectron Spectroscopy
VBM	Valence-Band Maximum
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

CHAPTER ONE

INTRODUCTION

1.1 Motivation

The early history of electron field emission was traditionally studied within the discipline of the surface science. A relationship between the emission current density and the electric field was calculated by Fowler and Nordheim in 1928 [1]. Serious investigations of cold cathode materials took off in the late 1960s and early 1970s, when Spindt-type field emitter arrays (FEAs), microfabricated molybdenum tips in gated configuration, were developed [2]. The advent of microfabrication technology changed the situation dramatically and considerable progress has been made in novel cathode materials including Si FEAs [3], carbon-based films [4], carbon nanotubes (CNTs) [5], other films [6], and other one-dimensional nanomaterials [7].

The novel cold cathode materials have important applications in consumer goods, military industries and also space technology [8-10]. There has been a very significant

growth in interest and activities in field emission-based devices. Compared with old vacuum tubes by using thermionic cathodes, field emission devices offer some unique advantages including unheated “cold” cathodes under an electric field, instantaneous response to field variation, resistance to both temperature fluctuation and radiation, small size, modest power consumption and capability to integrate with solid-state electronics. Applications include flat panel displays (FPDs) [8], microwave-generation devices [9], vacuum sensors [10], space instruments, and so on.

In effect, the promising multiple applications provide the necessary accelerating force for the further investigation of cold cathode materials. Among them, Si tip arrays have attracted much attention owing to easy fabrication due to the available advanced semiconductor technology and the compatible fabrication process with advanced integrated-circuit technology. However, high threshold electric field and poor emission stability limit their use in many applications. In recent years, the search for tip arrays with low operating voltage, high and stable emission current has been a major focus of vacuum microelectronics. Surface modification on Si tip arrays is usually performed to lower operating electric field and improve emission intensity and stability. The carbon-based materials [11-13], nitrides [14-15], silicides [16], carbides [17], and refractory metals [18] coated on Si tip arrays have been a topic of research and appeared to be an attractive method to enhance emission properties of Si tip arrays.

Recently the approaches using silicon tip arrays modified by sol-gel $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST) ferroelectric thin film with enhanced electron field emission have been demonstrated by Kang [19-20] and Zhu [21]. The BST coated Si tip arrays exhibit low threshold field and stable emission current. Such enhanced emission behavior is highly correlated with their microstructure and stoichiometric composition of sol-gel coated BST thin films. The detailed field emission mechanism of such enhanced emission behavior has not been well understood at present. It is known that field emission in this configuration involves an externally applied extraction field and differs from ferroelectric electron emission where emission of electrons is achieved by the spontaneous polarization fields of the ferroelectric material itself [22-23]. The ferroelectric electron emission current occurs from the negatively charged faces of ferroelectrics and is a transient emission current which screens spontaneous polarization.

These exciting results on field emission drive us to further develop the novel application of BST thin films. Moreover, the *n*-type thin film is required for field emission applications since it can achieve enough conduction electrons to be supplied to the emitting surface, and also raising the Fermi level and thus reducing the tunneling barrier. It is reported that *n*-type doped thin film could be induced via employing La^{3+} to substitute A sites in ABO_3 -type perovskite film according to the following the equations [24]

Thus, we extend the studies on La substitution in BST thin films. The sol-gel technique has been demonstrated to be a very effective route for growing multi-element thin films. It has overwhelming advantage of ease of stoichiometric control and therefore La substitution in BST films can be well controlled. The project will focus on field emission studies and related characterizations of sol-gel derived $(Ba,Sr)_{1-x}La_xTiO_{3+y}$ films on Si tip arrays. The investigations would be important evolutions in the realization of the fundamental issues and practical applications for field emission devices.

1.2 Objectives

In this thesis, the goal is to approach the fundamental understanding on these ferroelectric thin films using sol-gel technique for potential field emission device applications. The main objectives include:

- 1) $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) and $(Ba_{0.65}Sr_{0.35})_{1-x}La_xTiO_{3+y}$ (BSLT with $0.1 \leq x \leq 1$) precursor solutions are prepared using the sol-gel method. The ferroelectric thin films are spin-coated on flat Si substrate and Si tip arrays.
- 2) The properties of the ferroelectric thin films are systematically investigated, which include microstructure, component analysis, chemical compound formation, and electronic structure. This information is of vital importance in

understanding the field emission mechanism of ferroelectric thin film coated Si tip arrays.

- 3) The field emission properties including threshold field and emission current stability for Si tip arrays coated with BST and BSLT films are characterized. The emission data are analyzed using the Fowler-Nordheim (F-N) plot. It is expected to give further understanding of the field emission principle and mechanism through above investigations.

1.3 Major contributions

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

- 1) The ferroelectric thin films of BST and BSLT have been synthesized on Si tip arrays by the sol-gel technique successfully. The thermal treatment processes have been optimized by thermogravimetric analysis (TGA) and differential thermal analysis (DTA).
- 2) The microstructural features and the component analysis have been investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), second ion mass spectroscopy (SIMS), and fourier transform infrared (FT-IR) spectroscopy. The microstructure of BST thin film is strongly dependent on annealing temperature. The BST film exhibits an amorphous phase while annealed at 600 °C, the perovskite structure when annealed at 650 and 700 °C, and a severe interfacial reaction between Si substrate and BST films annealed at 750 and 800

°C. The microstructure of BST thin films annealed at 700 °C shows thickness dependence. The crystallinity of perovskite structure is improved with the increase of BST film thickness. The 15-nm-thick BST film is amorphous in nature, and then the polycrystalline perovskite grains develop in the thicker film with an amorphous layer existing in the bottom region of film. SIMS depth profile shows that the BST/Si interface is a solid-state reaction layer of $(\text{Ba,Sr})\text{Ti}_x\text{Si}_y\text{O}_z$. FT-IR spectroscopy indicates interfacial products appearing when the films were annealed above 750 °C.

- 3) The chemical compound formation and the electronic structure of BST films have been studied by X-ray photoelectron spectroscopy (XPS). Fermi level shifts up for BST films with increasing annealing temperature from 600 to 750 °C, and then moves back slightly at 800 °C. The upward shift of Fermi level from 600 to 750 °C is attributed to the increasing oxygen vacancy concentration in the films, and the downward shift of Fermi level at 800 °C is associated with severe interfacial reaction. The crystallinity information of BST thin films with different thicknesses are offered from the studies of Ba $3d_{5/2}$ core level spectra and valence band spectra. They give an evidence of the structure evolution, and the results are consistent to previous XRD and TEM studies.
- 4) The field emission properties of BST coated Si tip arrays have been investigated. The BST coated Si tip arrays show considerably improvement in field emission. The threshold field could be lowered substantially from 36 V/ μm for bare Si tip

arrays to about 19 V/ μm for 30-nm-thick BST coated Si tip arrays annealed at 700 °C. Neither lower (≤ 650 °C) nor higher (≥ 750 °C) annealing temperature can further improve field emission behavior. Also, it is found that there is U-shape dependence of the threshold field on film thickness. The 30-nm-thick BST coated Si tip arrays demonstrate the lowest threshold field for field emission. In addition, the BST coatings considerably improve field emission stability of Si tip arrays. Analysis of the emission data using the F-N plot suggests that the field emission is controlled by tunneling mechanism and the improvement in field emission originates from the lowering of effective work function with BST coatings.

- 5) The field emission mechanism of BST-modified Si tip arrays has been discussed based on the proposed model. From the effect of annealing temperature, it is found that the promising candidate for field emission applications is the BST film with high crystallinity of perovskite structure in surface region, decreased interfacial reaction, increased oxygen vacancy concentration, and upwards-moved Fermi level. Meanwhile, the thickness-dependent field emission behavior could originate from the developed microstructure features in BST films. The increasing thickness of BST films could limit the supply of the emitted electrons.
- 6) The studies have been extended using the sol-gel derived BSLT ($0.1 \leq x \leq 1$) thin films. La concentration has been optimized for field emission. It is revealed that the film microstructure is strongly dependent on La concentration. The films exhibit perovskite phase (ABO_3) at low La substitution level ($0.1 \leq x \leq 0.5$) and

pyrochlore phase ($A_2B_2O_7$) appearing at high La concentration ($0.75 \leq x \leq 1$). The cross-sectional structure of TEM study suggests that the substitution with La in BST film suppresses the interfacial reaction and the 30-nm-thick BSLT ($x = 0.25$) thin film exhibits high crystallinity of perovskite structure in surface region.

- 7) The 30-nm-thick BSLT thin films have been studied using XPS. The oxygen vacancy concentration decreases with La substitution. With respect to the BST ($x = 0$) thin film, the Fermi level shifts down for BSLT sample with $x = 0.1$ ascribed to the decreasing oxygen vacancy concentration, shifts up for BSLT sample with $x = 0.25$ attributed to the increasing La substitution level, and shifts down again for BSLT samples with $x \geq 0.5$, which may be associated with the second pyrochlore phase appearing. The Ba $3d_{5/2}$ core level spectrum gives the information of crystallinity of perovskite phase in the surface region of the film.
- 8) The effect of La concentration on field emission properties has been investigated. The BSLT sample with $x = 0.25$ shows the best improvement in field emission with threshold field of 15 V/ μm . In addition, it also shows highly improved electron emission stability compare with that of bare Si tip arrays. By analysis of emission data using the F-N plot, it is found that the improvement in field emission originates from the lowering of effective work function with BSLT coatings. Correlated to the microstructure and electronic structure of the BSLT

thin films, the enhancement in field emission of BSLT ($x = 0.25$) coated Si arrays results from improved perovskite structure in surface region, suppressed interfacial reaction and up-moved Fermi level of the coating.

1.4 Organization

This thesis emphasizes on the novel application of ferroelectric thin films for potential field emission devices. It comprises six chapters.

In Chapter 1, the motivations for developing ferroelectric thin films for the field emission study are explained. Then, the objectives, major contributions, and organization of the thesis are presented.

Chapter 2 devotes to the fundamental background and related literature review with respect to theory of field emission, present status of cold cathode materials, field emission of Si tip arrays without and with coatings, potential field emission applications, the physical structure and electronic structure of perovskite $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ materials, and electron-doped BST. The aim of this chapter is to provide foundation and basis for the work on ferroelectric thin films for field emission applications.

In Chapter 3, the experimental procedures used in this research work are presented. The preparation of the ferroelectric BST and BSLT thin films, the characterization of the microstructure and component of the thin films, the characterization of the photoelectron spectroscopy of the thin films, and the characterization of the field emission properties of the ferroelectric $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ thin film coated Si tip arrays are described in detail.

Chapter 4 presents and analyzes various experimental results based on the microstructural features, component analysis, chemical compound formations and electronic properties of BST thin films, and field emission properties of BST coated Si tip arrays. Firstly, the preparation and characterization of BST thin films are given, including the study of thermal decomposition behavior of dried BST gel powders, microstructural features, component analysis, chemical compound formations and electronic properties of the BST films. Then, the second section provides the field emission properties of BST coated Si tip arrays, analysis of emission data, and a mechanism discussion.

Chapter 5 gives the experimental results and discussion of the BSLT ($0.1 \leq x \leq 1$) thin films for field emission applications. Firstly, the preparation and characterization of BSLT thin films with different La concentrations are presented, including the thermal decomposition behavior of dried BSLT gel powders, the microstructural features,

chemical compound formation, and electronic properties of the BSLT films. Then, the field emission behaviors of BSLT coated Si tip arrays, analysis of emission data, and La concentration effect on field emission mechanism are given and discussed.

Finally, the conclusion and recommendations are presented in Chapter 6.

CHAPTER TWO

LITERATURE REVIEW

In this chapter, the fundamental knowledge and related literature review with respect to ferroelectric thin films for electron field emission applications are presented. It is composed of two sections. The first section gives the background and knowledge related to electron field emission theory, present status of cold cathode materials, field emission of Si tip arrays without and with coatings, and potential applications. The second part provides the background of physical and electronic structure of perovskite ferroelectric $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_3$ thin films, and n -type doped BST.

2.1 Electron field emission

2.1.1 Theory of electron field emission

(a) Electron field emission from metals

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. Field emission is distinct from thermionic emission and photoemission in which electrons acquire sufficient energy via heating or energy exchange with photons, respectively, to overcome the potential barrier. In field emission external electric fields in the order of $10^7 - 10^8$ V/cm are required for appreciable electron currents. The presence of the electric field makes the width of the potential barrier finite, and therefore permeable to the electrons. This can be seen in Figure 2-1 which presents a diagram of the electron potential energy at the surface of a metal [25].

The dash line in Figure 2-1 shows the shape of the 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 electron from the Fermi level of the metal to the vacuum level. However, an abrupt potential step at the metal surface is not to be expected because the charge cloud does not terminate sharply. The potential near the surface is decreased by an image term V_{im} [26]

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

for the 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 the 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

Figure 2-1 Diagram of the potential energy of electrons at the surface of a metal. $-e^2/4x$ is image force potential; $-eEx$ is external applied potential; ϕ is work function; E is electric field [25].

solid in the vacuum. In the presence of an applied field E , the potential at a metal surface has the term [26-27]

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

where e is the elementary charge.

In addition to the barrier becoming triangular in shape, the height of the barrier in the presence of the electric field is smaller, 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, one can calculate the probability of an electron with a given energy tunneling through the

barrier. 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 [28].

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

where J is in units of A/cm², E is in units of V/cm and ϕ in units of eV. Plotting $\log(J/E^2)$ vs. $1/E$ results in a straight line with the slope proportional to the work function value, ϕ , to the 3/2 power. Equation (2-4) applies strictly to a temperature equal to 0 K. However, it can be shown that the error involved in the use of the equation for moderate temperatures (~300 K) is negligible [26].

(b) Electron field emission from semiconductors

The theory for electron field emission from semiconductors can be derived parallel to the theory for metals to a large degree. However, special effects are associated with semiconductors due to the state of their surface and the fact that an external field applied to a semiconductor may penetrate to a significant distance into the interior [26].

Firstly, the electrons or holes concentrated on 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 sign, decaying slowly toward the interior as shown in Figure 2-2. The charge carriers must do work in approaching the surface from the interior due to the potential of this layer. This can be considered the analog of the work-function increment in adsorption on metals. The relationship between the contact potential ϕ' and the layer thickness l (Figure 2-2) is shown as [26]

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

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

Secondly, for the case when the external electric field penetrates into the interior of an n -type semiconductor and the surface states are neglected, $\log(J/E^2)$ is shown to be a linear function of $1/E$, as for metals, in early description. However, in the place of work function ϕ in the Fowler-Nordheim (F-N) equation one needs to substitute a quantity $\chi - \delta$, where χ is the electron affinity defined as the energy required for removing an electron from the bottom of the conduction band of the semiconductor to 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 a subject of more recent theoretical considerations, which takes into account complications due to electron scattering, surface state density, temperature, and tip curvature [29-31].

Figure 2-2 Schematic diagram of 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 [26].

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 [25].

2.1.2 The present status of cold cathode materials

Owing to the important applications in consumer goods, military industries and space technologies, some kinds of novel cold cathode materials have been developed in the past decades. These include Mo/Si tip arrays, diamond and related films, carbon nanotubes, other quasi one dimensional nanomaterials, which will be described below.

2.1.2.1 Tip arrays

More than 40 years ago, Shoulders of Stanford Research Institute proposed device concept of microminiaturized vacuum tubes incorporating a field emission electron source [32]. Then, Spindt, who was hired by shoulders to carry on the work, displayed unyielding persistence in pursuing the device concept that shoulders had dreamed of. In the late of 1960s and early of 1970s, Spindt-type cathodes also known as Spint-type FEAs were successfully developed as shown in Figure 2-4, which consisted of a multilayer structure of Mo gate/SiO₂ insulator/Mo cathode cone on Si substrate fabricated by thin film vacuum deposition techniques [2]. Si tip arrays were successfully fabricated subsequently. This tip arrays technology led to a development of a new research area called “vacuum microelectronics”. A number of prototype devices, such as field emission displays, microwave power tubes and X-ray sources, have been demonstrated. These devices utilize the local field enhancement at the apex of each tip to lower the threshold electric field. However, bare Si tip arrays have high threshold electric field and unstable emission current. A number of coatings have been

Figure 2-4 Basic structure of a Spindt cathode [2].

applied to modify these tip arrays including carbon-based materials [11-13], nitrides [14-15], silicides [16], carbides [17], and refractory metals [18], etc. The detailed review of the tip arrays will be provided in section 2.1.3.

2.1.2.2 Carbon based materials

Since the invention of FEAs, there have been considerable efforts in exploring novel cold cathode materials with enhanced field emission behavior. A new class of carbon-based cathode materials that has emerged as promising field emitters, including diamond, diamond like carbon, amorphous carbon in thin film forms, and carbon nanotubes (CNTs). In 1970s, the graphite fibers showed better stability than refractory metals, suggesting that carbon-based materials are suited as stable field emitters. In the early 1980s, the ability of depositing diamond in thin film forms by low pressure chemical vapor deposition (CVD) [33], integrated with the discovery of

Figure 2-5 SEM micrographs of randomly orientated CNTs (a) and aligned CNTs (b) [37-38].

negative electron affinity deposition (CVD) [33], integrated with the discovery of negative electron affinity (NEA) on hydrogen-terminated diamond surface [34-35], has promoted the development of carbon-based materials as cold cathode materials. Diamond and related films have the properties of low and negative electron affinity, chemically inert, and high thermal conductivity and toughness. Therefore, they become a hot topic for research and show good candidates for cold cathode. Another carbon-based material, CNTs, is also a good candidate and meets a host of requirements for field emission applications [36]. Figure 2-5 shows the scanning electron microscopy (SEM) of randomly oriented CNTs and aligned CNTs [37-38].

The tips of the CNTs have diameter in range of 1 - 30 nm and the lengths can be $> 1 \mu\text{m}$, 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 be induced locally at the tips of the nanotubes, and allow electron to be emitted at low voltages. Moreover, such CNT arrays may be grown using simple deposition techniques and make them very attractive for application in cold cathodes.

2.1.2.3 Other cold cathode materials

Field emission from thin films other than carbon based materials, and quasi one dimensional nanomaterials other than CNTs have become two other active areas of research on cold cathode materials. Wide band gap materials, nitrides such as carbon nitrides [39], boron nitrides [5], and aluminum nitrides [40] are wide band gap materials with low or negative electron affinity shows enhanced emission current and low threshold field. Carbide films with excellent hardness are resistant to ion sputtering [41]. They can be operated under poor vacuum conditions and in environments where oxygen is present. The forms of the quasi one dimensional nanomaterials include wide and narrow band gap semiconductor nanowires [42-44], and refractory metals [45] and their oxide nanowires [46]. It is found that the field emission properties of such nanowires have the best values close to CNTs. In addition, it is possible to prepare the above nanowires with a unique electron property, i.e.

either semiconductor or metallic, unlike CNTs with semiconducting and metallic forms co-existing. Moreover, some aligned nanowires may be prepared at room temperature.

2.1.3 Electron field emission of Si tip arrays and Si tip arrays with coatings

We have previously reported that active investigations on tip arrays began in the 1970s with a view to develop vacuum microelectronic devices including field emission displays (FEDs) and microwave power tubes. Historically, microstructured tips have been at the heart of the field emission technology. Si tip arrays have attracted much attention owing to easy fabrication by the advanced semiconductor technology and compatible fabrication process with advanced integrated-circuit technology. It is pursued aggressively worldwide as a new generation technology in many applications. In this section, field emission of bare Si tip arrays is introduced. In order to achieve an improvement of the field emission, coatings are employed as surface modification on Si tip arrays and related field emission mechanisms are provided.

2.1.3.1 Field emission of bare Si tip arrays

The principle of field emission is based on the application of a very high electric field to extract electrons from a metal or a highly doped semiconductor surface. Generally the field is in the order of 10^7 - 10^8 V/cm. In practical terms, this means approximately

Figure 2-6 Illustration of electron field emission from a tip [47].

1000 kV 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 cathode surface has a high point or a protrusion as shown in Figure 2-6.

This is because the physical geometry of the tips provides a field enhancement and the lines of force converge at the sharp point. If E_t is assumed as an 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 [47]

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

Therefore, large value of the geometrical enhancement factor β can result in high electric field E_t at the tip apex.

The current generated by field emission could be described by the F-N equation, as expressed in equation (2-4) early. It can be seen that 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 ϕ is affected by the electronic properties of the emitter surface. It is clear that materials with low work function can produce high emission current at a specific field. However, not all materials with low work function are ideal as field emission cathodes. This is because their other material properties may not be suitable. For example, the work function ϕ of cesium is only 1.8 eV, however, it is difficult to obtain stable emission current and long lifetime from cesium cathodes. The value of the field enhancement factor β depends on geometrical parameters of a tip and can be expressed as [48-49]

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

where h is the height of the tip, 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 realized by the advanced semiconductor technology, using the conventional photolithographic patterning, silicon anisotropic etching, oxidation for tip sharpening and buffered oxide etching [19].

2.1.3.2 Field emission of Si tip arrays with coatings

However, the practical applications of Si tip arrays are highly suppressed owing to their high threshold electric field and unstable emission current. The search for tip

arrays with low operating voltage and a high and stable emission current has been a major focus of vacuum microelectronics. In order to obtain enhancement and stability of electron field emission from Si tip arrays, a large number of coatings have been used and appeared to be an excellent method to enhance emission properties of silicon tip arrays. These coatings include diamond and related materials, nitrides, silicides, and carbides refractory metals. The role that coatings play in the emission process may be considered in terms of two roles. One role is to decrease the effective work function and correspondingly enhance the emission behavior. The other role is that the coating acts as a protective layer for the sharp conductive core to avoid absorption and ion bombardment. In addition, 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 acts as a radiator.

It is widely accepted that field emission, from Si tip arrays coated with a wide band gap thin film, is a three-step process, including supplying electrons to the thin film at the Si/film interface, transporting them through the bulk to the film surface, and emitting them into vacuum as shown in Figure 2-7 [27,50]. There are a number of mechanistic models proposed to account for the emission characteristics. All of the models are not necessarily mutually exclusive, because each addresses a particular part of an overall field emission process. Overall the physics remains ambiguous. The models are illustrated as follows.

Figure 2-7 Band diagram representation of the quasi tunneling process associated with a surface positive electron affinity (PEA) (a) and an effective NEA (b), where E_v is the valence band, E_c is the conduction band, E_F is the Fermi energy, and U is the energy from E_F and top electron energy level [50].

(a) Low or negative electron affinity

Si tip arrays coated with diamond films show an enhancement in field emission compared with bare Si tip arrays. The original work on field emission from diamond surface was motivated by the discovery of its low or negative electron affinity [34]. It is proposed that electrons are injected into the conduction band of the low/negative electron affinity material, from which there is a small barrier that needs to overcome for electron emission to take place. Recently, some wide band-gap materials, such as carbon nitride, boron nitride, and aluminum nitride, showed the property of NEA and were applied as effective coatings on tip arrays to improve emission behavior [13-15].

The electron affinity χ of a wide band-gap material is defined as the energy required

remove an electron from the conduction band minimum to a distance macroscopically away from the material. At the surface, this energy is simply the different 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. The electron affinity of a material is closely related to both the fundamental atomic structure of the material and surface dipoles created by surface terminations, including steps, reconstructions, and adsorbate [51]. While the atomic arrangements are an intrinsic property of the material, the surface dipoles can readily be altered and manipulated to affect the electron affinity.

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 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 in Figure 2-8 (b), and the electron affinity is thus negative. In such conditions, the electrons in conduction band are not bound to the sample but can escape from the surface, although 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 positive electron affinity (PEA) and depleted band bending at the surface of the material. This band bending can result in the vacuum energy level occurring at an energy below the

Figure 2-8 Band schemes of a semiconductor surface with PEA (a), true NEA (b), and effective NEA (c) [27].

minimum of the conduction band. The magnitude of the effective NEA is determined as $\chi_{eff} = \phi_{BB} - \chi$, where ϕ_{BB} is band bending and χ is positive electron affinity. The low or even negative electron affinity property of surface may be important to explain the thin film enhancing field emission but it is not adequate. 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 electrons to reach the surface. Moreover, 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 practically 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 above, the electrons at the surface can emit easily when the thin film has a low or even negative electron affinity. But before that, there must be enough electrons reaching the surface of the thin film. The thin film coating is usually a semiconductor or insulator with a 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 can illustrate the electron transport in thin films, which suggests that structural defects and impurities can form energy states within the band gap of thin films [52-53]. 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, the electron hopping mechanism within the bands, similar to the Poole–Frenkel conduction mechanism or the Hill type conduction [54], could easily provide a steady flow of electrons to the surface and sustain a stable electron emission. The electrons can either be excited into the conduction band or unoccupied surface states from these defect/impurity bands and emit, or tunnel directly from the defect/impurity bands and emit. 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 responsible defects has not been identified, and the very existence of many defect/impurity energy bands and their locations within diamond band gap have not been firmly confirmed or linked to the field emission. Recently, the origin of the emitting electrons can be determined using field emission energy distribution [55-56].

(c) Other conduction channels

Except that defect/impurity in wide band-gap material acts as conduction channel, graphite phase and/or grain boundaries have been suggested as other conduction channels in diamond film by Athwal [57] and Kim [58]. It is suggested that a field-induced hot electron emission process from isolated conductive particle (i.e. graphite) inclusions in an insulator matrix (i.e. diamond), where an antenna effect results in field concentrations on a “floating” conductive particle. Cui [59] has concluded from their 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 path for electrons to reach the surface and emit. Grain boundaries have also been suggested to function as conduction channels.

(d) Back-contact interface mechanism

One of the important parameters governing the internal emission is the potential barrier height at the back-contact interface. For the undoped wide band-gap insulator, the Fermi level is commonly assumed to be at the middle of the band gap. The electrons at the Fermi level of Si tips will see a potential barrier height equal to $E_g/2$ (Figure 2-7). The emission current here is limited by tunneling of electrons through a potential barrier height equal to $E_g/2$ to conduction band of thin film, 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 emit into vacuum. This can be illustrated as follows. After the electrons inject, they may become hot at the surface due to being accelerated by a penetrating field that is high in the coating due to the local enhancement. Little energy is lost since their mean-free path may be compatible with the thickness of the coating. They will see a low surface potential barrier, and may tunnel out into vacuum. This electron injection role is supported by the observation that a roughened interface between the nickel contact and nitrogen-doped diamond improved electron emission due to local field enhancement effects at the interface that facilitate tunneling through the Schottky barrier [60]. This model emphasizes the importance of the back contact, and indicates that the rate limiting process for field emission may also be associated with it.

(a)

(b)

Figure 2-9 A model based on the a -C:H:N acting as a space charge interlayer on the n^{++} -Si. No applied field top (a); an applied voltage of 10 V between the anode and n^{++} -Si (b) [62].

Silva and his coworkers [61] proposed another model that electron injection is facilitated by band bending at the interface. In this model shown in Figure 2-9 [62], a fully depleted, 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 conduction band gain energy and become “hot” due to higher internal field and see a lower 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, and because of this, it is difficult to differentiate between this interface barrier mechanism and the surface barrier mechanism from current-voltage data alone. Additionally, it is difficult to identify the barrier structure at the interface of Si and the thin film that is highly defective.

(e) Sharp morphological features model

Among the various models, the simplest and most obvious argument cites the classic field emission theory by noting that there are local field enhancements on sharp morphological features protruding on the thin film surface. For example, surfaces of 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 vacuum at the protruding small features, facilitated by the enhanced local electric fields. This could certainly be a working and contributing mechanism, but it also addresses neither the source of electrons in the wide band gap thin film nor the issue of effective electron transport to the surface of the thin film.

(f) Other models

Other proposed models include dielectric breakdown that provides conductive channels in diamond [63], surface arcing that results in the formation of tips and protrusions and thus provide additional geometric field enhancement [64], space

charge limited conduction current through the bulk of thin film [65], and surface conduction enhanced electron emission [66].

2.1.4 The potential applications of cold cathode materials

Field emission is based on physical phenomenon of quantum tunneling, in which electrons are injected from the surface of the materials into vacuum under the influence of the electric field. Compared to the presently used thermionic emission from hot filaments, field emission occurs at room temperature from cold cathodes. In addition, 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 advantages, there have 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 can be applied 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 the electrons and/or the high electric field of vacuum. Some devices (e.g., x-ray source) require the high kinetic energy that only free electrons can achieve. Other devices (e.g., instrument using in nuclear reactors and space) take the

advantages of vacuum microelectronics, where electrons transport through vacuum and therefore immune to radiation and high temperatures.

We state FEDs as an example owing to its most prominent and commercially attractive application in flat panel displays. The FEDs have several advantages over other technologies including low power consumption, higher brightness, wider view angle and fast response time. It is predicted that FEDs will replace the existing cathode ray tube displays, competing with technologies as liquid crystal display, plasma discharge panel display and organic light emitting display. The principle of operation of FEDs is similar to a cathode ray tube displays in the sense that the display image comes from cathodoluminescence of phosphor materials. Figure 2-10 shows the architecture of a Spindt cathode-based flat panel display. The difference between them is how electrons are generated and delivered to excite phosphor coated anode. Instead of one or three electron guns in CRTs, miniaturization allows every pixel to have its own electron source, which is independently addressed, and hundreds of emitters are made to define a pixel. No scanning of electron beams line by line is required as CRTs. In FEDs, the selection of cold cathode materials is very important to achieve the low threshold electric field and stable emission current.

Figure 2-10 Architecture of a Spindt cathode-based flat panel display [47].

2.2 Ferroelectric $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ materials

2.2.1 Physical structure

Ferroelectricity is defined as the spontaneous alignment of electric dipoles by their mutual interaction [67]. Many perovskite ferroelectric materials, such as barium strontium titanate (BST), lead zirconium titanate (PZT), barium titanate (BT) and strontium bismuth tantalate (SBT), have been extensively investigated because of their interesting ferroelectric properties [68]. BT ceramics as shown in Figure 2-11 can be used as an example to illustrate the basics of ferroelectrics. Each large barium ion is surrounded by twelve nearest-neighbor oxygen ions; each titanium ion has six oxygen ions in octahedral coordination. The barium ion and oxygen ions together form a face-centered cubic lattice, with titanium ions fitting into octahedral interstices. The characteristic structural feature shared by barium titanate seems to be that the large size of the barium ions increases the size of the cell of the face-centered cubic BaO_3 structure so that the titanium atom is at the lower edge of stability in the octahedral

Figure 2-11 Perovskite structure of BaTiO_3 [67].

interstices. The rattling titanium hypothesis suggests that there are minimum-energy positions for the titanium ion which are off center and consequently give rise to an electric dipole. At high temperatures the thermal energy is such that the titanium ion has no fixed unsymmetrical position, but the open octahedral site allows the titanium ion to develop a large dipole moment in an applied field. On cooling below the Curie temperature, the position of the titanium ion and the octahedral structure change from cubic to tetragonal symmetry with the titanium ion in an off-center position corresponding to a permanent electrical dipole. These dipoles are ordered, giving a domain structure. The change from the paraelectric to the ferroelectric state can be illustrated in terms of crystallographic changes and corresponding dielectric constant changes.

Ferroelectric perovskite materials are widely used in bulk capacitors and transducers, and are now candidate dielectrics for integration in the microelectronics industry. In the paraelectric state they offer some of the largest dielectric constants attainable. This makes them attractive for applications in which transient charge storage is required, such as capacitors in dynamic random access memories (DRAM) [69] and decoupling capacitors in circuit power distribution systems. In the ferroelectric state, below the ferroelectric transition temperature, the ability to reorient the spontaneous polarization makes them used as nonvolatile memory elements possible [70]. Because all ferroelectrics are a subset of the polar crystal classes, they are also pyroelectric and piezoelectric. Consequently, they can be used as pyroelectric elements in infrared detectors [71], as well as electromechanical transducers for actuators in microelectromechanical structures [72].

The other end ($x = 1$) of the $(\text{Ba,Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ is possible to have a general formula of $\text{La}_2\text{Ti}_2\text{O}_7$. Lanthanum titanate oxide $\text{La}_2\text{Ti}_2\text{O}_7$ has been known to form perovskite layer structures built up of corner-shared TiO_6 octahedra bonded together by the interlayer La cations [73-74]. It possesses monoclinic symmetry with space group P2_1 and has high melting points. Lanthanum titanate oxide ($\text{La}_2\text{Ti}_2\text{O}_7$) single crystal was found to show ferroelectricity with very high coercive field and Curie temperature, to have excellent electrooptic and piezoelectric properties at room temperature [75]. The unique properties make them ideal candidates for applications ranging from

high-temperature transducer [76], photocatalysts [77] to immobilization hosts of actinides in nuclear waste [78].

2.2.2 Electronic structure

As mentioned early, the field emission process of Si tip arrays with coating includes three steps: electron injection from the back contact Si substrate into the film, electron transport from the substrate/film interface to the emission site at the film surface, and electron emission into the vacuum. Thus, the field emission properties are closely related to electronic structure of the coating. In this part, the electronic structures of heterostructure of BST/Si interface, bulk BST film, and BST film surface are introduced.

The heterojunctions of BST and SrTiO₃ thin films with Si have already been studied as alternative gate dielectric oxides to replace silicon dioxide in complementary metal oxide semiconductor (CMOS) services. However, the studies were focused on epitaxial thin films with carefully controlled interface. XPS is an effective experimental tools to investigate heterojunction band discontinuities between BST/SrTiO₃ and Si. Generally, this method require the thickness of BST thin film to be very thin, i.e., about lower than ~20 Å for XPS due to limited penetrating depth of X-ray. Amy [79-80] and Chambers [81] have investigated the electronic structure of BST and SrTiO₃ thin films and their heterojunctions with Si recently using XPS or/and

and ultraviolet photoelectron spectroscopy (UPS). It was shown that the position of the valence-band maximum (VBM) of BST and SrTiO₃ varies substantially with film preparation [79-80]. The maximum conduction band offset for the SrTiO₃/Si interface is around 0.1 eV, almost independent of the presence of silicates at interface [81]. The small band offset between BST and Si is expected to benefit supply of electrons at the back contact (BST/Si interface) for field emission.

The study of the electronic structure of bulk BST materials could be helpful in understanding the electron transport in the film. These electronic properties have been extensively investigated in the past. The electronic structures of BST, in which the Ba/Sr cation has a valence of 2+, are close to TiO₂ [82]. This is because the highest filled and the lowest empty Ba/Sr orbitals are significantly farther away from E_F than are the O 2*p* and Ti 3*d* levels as shown in Figure 2-12 [82]. Thus the electronic structure in the vicinity of E_F and the vacuum level is dominated by the Ti and O ions. Accordingly the corner-shared TiO₆ octahedra dominate the main electronic properties of BST. In a simplified ionic picture this would lead to a completely full O 2*p* valence band and an empty Ti 3*d* conduction band for BST. The *n*-type thin film is required for field emission applications since it can achieve enough conduction electrons to be supplied to the emitting surface, and also raising the Fermi level and thus reducing the tunneling barrier. The *n*-doped perovskite BST films could be induced via either controlling non-stoichiometric composition (oxygen vacancy), or introducing

Figure 2-12 Schematic energy-level diagram for SrTiO_3 [82].

transition metal dopant. The typical transition metal dopant like lanthanum cation (La^{3+}) or niobium cation (Nb^{5+}) is usually employed to substitute barium/strontium cation ($\text{Ba}^{2+}/\text{Sr}^{2+}$) or titanium cation (Ti^{4+}) sites in BST films, respectively. The *n*-type doped BST thin film will be discussed in detail in Section 2.2.3

The surface electronic structure of BST is reviewed here since it would affect electron tunneling from the surface into vacuum. As illustrated in previous Figure 2-3, a small surface work function (ϕ) or low surface electron affinity (χ) could enhance the probability of an electron with an given energy tunneling through the barrier.

Therefore, materials with low work function can produce high emission current at a specific field. The surface work function, ϕ , is defined as the energy necessary to remove an electron from the Fermi level in a material and put in at rest in vacuum an infinite distance away from the material (This is usually several or tens of nanometer), as given in equation below

$$\phi = E_{vac} - E_f \quad (2-8)$$

where E_{vac} and E_f is the vacuum level and Fermi level in a material, respectively. It is known that the variation of the work function could be studied by comparing the shift of the Fermi level in thin films. XPS technology has been widely employed to study the shift of the Fermi level by comparing the core-level binding energies [83-86]. Besides, the work function of a material can be measured in several ways, including thermionic emission, the low-energy cut-off in photoelectron emission [87], contact potential difference measured by a Kelvin probe, and retarding potential methods [82]. It is noted that the work function is a sensitive measure of the state of a surface. In fact, it is so sensitive for metal oxides that its absolute value has little significance. Differences in step or point defect densities, trace of adsorbed molecules too small to be observed by any surface spectroscopy, slight changes in surface reconstruction, etc., can cause significant changes in ϕ .

2.2.3 *n*-doped (Ba,Sr)TiO₃

For electron field emission at the surface of BST films, emitting electrons can originate from either the conduction band, the surface state, and/or the valence band. However, BST has a moderate wide band gap and stoichiometric BST is thus generally thought to be unable to produce sustained electron field emission because of its insulating nature. Although electrons emitting from surface states in stoichiometric BST can occur, there are no obvious mechanisms by which electrons can be transported through the bulk to the surface states. Therefore, either the bulk or the surface of BST must be made conductive in order to sustain the electron field emission process. This would require the BST to be *n*-type doped.

The *n*-type perovskite ABO₃ structure can be achieved by altering any of the three sublattices, namely, those of A (Ba/Sr), B (Ti), and O. Specifically, La substitution at the A site (A_{1-x}La_xBO₃), Nb substitution at the B site (AB_{1-x}Nb_xO₃), and vacancies at the oxygen sites (ABO_{3-δ}) dope electrons into the system. Oxygen vacancies, La at Ba/Sr (A) sites, and Nb at Ti (B) sites can donate electrons according to the following equations [24].

In the case of oxygen vacancies, $\text{ABO}_{3-\delta}$ is expected to have 2δ number of electrons doped for every formula unit. In contrast, it is found that there are only $\delta/2$ number of conduction electrons in $\text{ABO}_{3-\delta}$ for larger value of δ (≈ 0.28) by Hall measurements [88]. Oxygen vacancies directly influence the fundamental interactions of the electronic structure by disrupting the Ti-O network. It is reported that the low vacancy concentration results in the Fermi energy progressively shift to the conduction band and every electron doped into the system contributes to the conduction process. With increasing δ , however, it is found that vacancy clustering seriously distorts the bottom of the conduction band, and leads to the formation of localized midgap states in $\text{ABO}_{3-\delta}$. Thus only a part of the electrons doped contributes to the conduction process, with a sizable portion being trapped by the vacancy clusters [88]. The doping effect of La is different from that of oxygen vacancy. In case of $\text{A}_{1-x}\text{La}_x\text{BO}_3$, the Fermi level goes into the conduction band due to electrons doping. But there is no noticeable contribution from La partial densities of states (PDOS) near the Fermi energy level, the band structure near the band gap has no change with different La doping concentrations, which can be described within rigid band model [89]. Nb doping in SrTiO_3 does not only make the Fermi level move into conduction band, but also make the band structure near the energy gap changed, with a slight shift of conduction bands to lower energy region [89]. Nb doping effect on the electronic structures near the energy gap of SrTiO_3 can not be describe well within the rigid-band model, even at low Nb concentration.

It is well known that the perovskite structure ABO_3 can tolerate significant amounts of oxygen vacancies, still retaining the perovskite or deformed-perovskite structure. Copel *et al.* [90] have reported that the nominally undoped BST thin films, prepared by metal organic chemical vapor deposition or a chemical solution, are *n*-type doped. La substitution in BST is proposed to supply conduction electron as shown in equation (2-9). However, some researchers have found that the films showed enhanced resistivity [91] or a large decrease in the leakage current [92] when the La substitution concentration was lower than 10% mol, in comparison to undoped films. The large decrease in leakage current was attributed to the formation of highly resistive layer and could be originated from compensation defect chemistry involved in a donor doped sample. Lanthanum acting as a donor in the system could suppress the inherent oxygen vacancy concentration when processed under an oxidizing environment [93], which may lead to a reduction in the concentration of the charge carrier. The equation is expressed as [86]

Tokura and co-workers [94-95] have extensively studied a mixed-crystal system $Sr_{1-x}La_xTiO_3$ ($0.1 \leq x \leq 1$) with a view of understanding the concentration dependence of the electronic properties of correlated electron system. The samples were grown by the floating-zone method in a reducing or inert atmosphere. The end compounds $SrTiO_3$ ($x = 0$) is a closed shell (i.e., no *d* electron) oxide with cubic perovskite

structure. The topmost valence and lowest unoccupied conduction bands in SrTiO_3 are of O $2p$ and Ti $3d$ character, respectively. The other end compound LaTiO_3 with a half-filling titanium $3d$ band is a Mott insulator [96] with an orthorhombically distorted perovskite (GdFeO_3 -type) structure, in which the Ti-O-Ti angle ($\sim 157^\circ$) deviates from 180° [97]. The formal valence of Ti in this compound is $3+$, the number of $3d$ electron per Ti site being exactly 1 ($3d^1$ configuration). In $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ system, a number of $3d$ electrons can be varied from 0 to 1 with a change of x from 0 (SrTiO_3) to 1 (LaTiO_3). La substitution in SrTiO_3 makes samples metallic with $0.1 \leq x \leq 1$. However, the samples with $x \leq 0.1$ show some carrier localization effect, perhaps due to poor shielding of the impurity (La^{3+}) potential by low carrier density [98].

CHAPTER THREE

EXPERIMENTAL PROCEDURES

The ferroelectric $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST) and $(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_{3+y}$ (BSLT $0.1 \leq x \leq 1$) thin films have been fabricated on Si tip arrays using sol-gel technique for electron field emission applications. The microstructure and electronic structure of ferroelectric thin films, and the electron field emission properties of ferroelectric thin film coated Si tip arrays have been systematically investigated in this study. In this chapter, the detailed experimental procedures are described:

- a) Preparation of ferroelectric thin films by the sol-gel technique.
- b) Characterization of the ferroelectric thin films using X-ray diffraction (XRD), transmission electron microscope (TEM), fourier transform infrared (FT-IR) spectroscopy, second ion mass spectroscopy (SIMS), and X-ray photoelectron spectroscopy (XPS).
- c) Characterization of the electron field emission properties.

3.1 Preparation of films

Si tip arrays were fabricated by Micro Fabrication Lab in NTU. The process is introduced in this part. The ferroelectric thin films were then deposited on Si tip arrays using the sol-gel technique. The sol-gel technique is applied for the deposition of thin films due to its good homogeneity, ease of chemical composition control, ease of process integration with the standard semiconductor manufacturing technology, and comparatively lower cost than other techniques. Four steps are involved in the process: (1) solution preparation, (2) film deposition, (3) low temperature heat treatment for organic pyrolysis, and (4) high temperature annealing for film crystallization.

3.1.1 Fabrication of Si tip arrays

Figure 3-1 shows device fabrication scheme of Si tip arrays. The tip arrays were fabricated starting from the (100) n-type Si wafer with resistivity of 2-5 $\Omega\cdot\text{cm}$. First, one 0.3 μm thick silicon dioxide layer was thermally grown on the silicon wafer. Then, conventional photolithographic patterning of circular dots with 4 μm diameter was performed and silicon dioxide circular “dots” were obtained after buffered oxide etching. Silicon wafer was wet etched by anisotropic KOH solution (KOH:H₂O:IPA=24:63:13) at 80 °C followed by isotropic acid mixture (HNO₃:CH₃COOH:HF=25:10:3) at 20 °C. Tip sharpening treatment was performed

Figure 3-1 Fabrication schema of BST-coated Si tip arrays.

by dry oxidation at 950 °C to reduce the tip radius to ~ 30 nm. Si tip arrays, with a tip height of 1.5 μm and the tip density of $1.6 \times 10^6 \text{ cm}^{-2}$, were obtained after the SiO₂ layer was etched away. Finally, ferroelectric thin films were coated on Si tip arrays by the sol-gel process for further study.

3.1.2 Solution preparation

The starting raw organic materials used in the study were titanium (IV) butoxide Ti(OC₄H₉)₄, barium acetate Ba(CH₃COO)₂, strontium acetate Sr(CH₃COO)₂, and lanthanum acetate La(CH₃COO)₃. The whole solution process is described by flow-chart in Figure 3-2. The titanium butoxide precursor solution was first

thoroughly mixed with acetylacetone C_5H_7OOH with a mole ratio of 1:2. This acted to stabilize and prevent the titanium butoxide from forming gel when exposed to the moisture in the ambient environment. The solution was continuously mixed using a magnetic stirrer. Then the barium acetate, strontium acetate, and/or lanthanum acetate with desired molar ratios were dissolved in glacial acetic acid CH_3COOH . De-ionized water was added in a molar ratio of 1:4 to promote the dissolution process. The solution was kept stirring at 60 °C to help dissolve the acetate powders. During the mixing, the beaker was sealed with a transparent micro-film to prevent further evaporation of water or acetic acid during the mixing. Next, the dissolved (Ba, Sr, La) precursor solution was dripped into the titanium butoxide precursor solution, and 2-methoxyethanol was added to achieve a final concentration of 0.10 mol/l. The mixed solution was continuously stirred using a magnetic stirrer for 30 minutes. A clear yellowish solution was obtained and finally filtered into storing amber bottles using 0.1 μm Teflon micropore filters. The solution was then aged in a desiccator for a period varying from 24 to 48 hours.

The thermal decomposition properties of synthesized BST and BSLT precursors were analyzed to determine the thermal treatment processes. The Perkin-Elmer thermogravimetric analyzer (TGA-7) and differential thermal analyzer (DTA-7) were used for the analysis. The temperature range from room temperature to 800 °C was chosen and the heating rate was set at 2 °C/min.

Figure 3-2 Flow-chart for preparation of BST and BSLT ($0.1 \leq x \leq 1$) solution.

3.1.3 Deposition of BST and BSLT thin films

The ferroelectric thin films were deposited on *n*-type (100) Si wafer and Si tip arrays substrate, respectively. The former substrate was used for physical and electronic structure studies of the thin films, and the later was employed for field emission characterization. The wafers were first cleaned with sequential rinses of de-ionized water, iso-propanol, acetone, and then dried by nitrogen gas. The native oxide layer on Si substrate was removed by 1:10 di-ionized water diluted HF. The substrate was finally baked in the oven at 110 °C for 30 minutes. Such cleaned wafers would allow

good quality thin films to be deposited. The spin-coating process was performed at 4000 rpm for 30 seconds. The samples were pyrolyzed at 200 and 400 °C for 2 minutes to decompose residual organics and then cooled to room temperature. The coating and pyrolyzing processes were repeated several times to obtain the desired film thickness.

The as-coated thin films were annealed at different temperatures for 1 hour in a quartz furnace, where a mixed gas of oxygen and nitrogen ($O_2:N_2=1:4$) was introduced. The thickness of sol-gel film was controlled according to various layers, which was calibrated using SLOAN Dektak 8000 surface profilometer, and the films with thickness of 15, 30, 60 and 90 nm are obtained by 1, 2, 4 and 6 layer-coating, respectively.

3.2 Characterization

3.2.1 Characterization of thin films

The microstructural evolution of sol-gel derived BST and BSLT films was investigated using a Rigaku X-ray diffractometer with a thin film attachment cum Ultima⁺ wide-angle goniometer (40 kV, 40 mA). Cu K α radiation source (1.54 Å) was used for phase identification. The scanning range was from 20° to 60° in 2 θ with a scan rate 2°/min. A small glazing angle fixed at 0.5° was used to ensure that the diffraction intensity mostly came from the measured thin films.

The transmission electron microscopy (TEM) was employed to evaluate the cross-section of the BST and BSLT thin films. In this study, we use the Philips CM 200 FEG transmission electron microscope operating at 200 keV. Thin film cross-section samples for TEM were prepared by the standard method and ion beam thinned by Gatan 691 PIPS system.

Material depth profile was carried out using secondary ion mass spectroscopy (SIMS) with a secondary ion mass spectrometer (TOF SIMS IV from Ion TOF, Germany). It was operated in the dual beam interlaced mode. Depth profiling was achieved by employing low energy 1 keV Ar^+ ion beam to raster and sputter a surface area of $200\ \mu\text{m} \times 200\ \mu\text{m}$. The secondary ions were analyzed using 25 keV Ga^+ primary ion beam with an ion current of 1.5 pA. The ion beam was raster-scanned over an area of $150\ \mu\text{m} \times 150\ \mu\text{m}$ in the center of the sputtered crater.

In order to investigate interfacial component at high annealing temperature for the thin films, the chemical bonding configuration of the thin films was evaluated by using Fourier transform infrared (FT-IR) spectroscopy at room temperature using a Perkin-Elmer spectrum 2000 in the wavelength range of $1000 - 390\ \text{cm}^{-1}$. The incident angle of the IR beam to sample surfaces was 90 degree and FTIR spectra were obtained by the transmittance radiation from the surfaces.

XPS characterization was performed to investigate 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 done at a take-off angle of 90° with respect to 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 quantification was carried out using the relative sensitivity factors (RSFs) 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 binding energy of 285.0 eV. After a Shirley-type background subtraction, an XPS spectral deconvolution was achieved by a curve fitting procedure based on Lorentzians broadened by a Gaussian, due to the instrumental resolution, using the manufacturer's standard software. Component peak shape and full widths at half maximum (FWHMs) for a particular peak envelope were kept the same during the curve fitting.

3.2.2 Characterization of field emission properties

Before 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). Then, a plane Si wafer was used as cathode to ensure that no field emission current could be measured within the sensitivity of the instrumentation with the applied electric field lower than $100 \text{ V}/\mu\text{m}$, which is much higher than the real electrical field in measurement. This is to ensure that no parasitic field emission currents occur during the real measurement.

Field emission characterization was carried out in a diode configuration in a vacuum chamber of 10^{-7} mbar as shown in Figure 3-3. A stainless steel base was used to make electrical contact to the Si tip arrays, and an ITO glass with a sheet resistance of $10 \text{ } \Omega/\square$ was placed $50 \text{ } \mu\text{m}$ above the cathode as an anode via a Teflon spacer. The diameter of the opened Teflon hole is 6.0 mm . The measurement system is computer-controlled, integrated with a Keithley 248 high voltage supply and a Keithley 487 picoammeter/voltage source.

Figure 3-3 Schematic diagram of the electron field emission characterization set up.

Surface cleaning of BST-coated Si FEAs was performed first under low emission current of 1 μA by applying a voltage on FEAs before measurement. The emission data were taken at room temperature after stabilized emission current was achieved. The threshold electric field is defined as the electric field required to induce an emission current density of 10^{-8} A/cm^2 , corresponding to the signal-to-noise ratio of 1000:1. The field emission stability characterization was carried out in an electric field which could induce an initial emission current density around several $\mu\text{A/cm}^2$ for each sample. The applied electrical field was then kept in constant during the measurement. Field emission current data were read every 2 seconds. The field emission of BST coated Si tip arrays was confirmed by the F-N plot and light generation on a phosphorous anode of ITO glass.

CHAPTER FOUR

FIELD EMISSION OF $(\text{Ba}_{0.65}\text{Sr}_{0.35})\text{TiO}_3$ COATED SI TIP ARRAYS

In recent years Si tip arrays have been very attractive for field emission applications due to easy fabrication by the available advanced semiconductor technology and the compatible fabrication process with advanced integrated-circuit technology. However, the high threshold electric field and poor emission current stability limit their use in many applications. Therefore, the search for electron field emitters with low operating voltage, high and stable emission current has been a major research focus. Surface modification on Si tip arrays is currently studied to lower operating electric field and improve emission stability [11-18]. Recently, sol-gel $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) ferroelectric thin films on Si tip arrays have been demonstrated an enhancement in field emission by Kang [19] and Zhu [21]. The field emission behavior was found to be highly correlated with the structure [20] and stoichiometric composition [21] of BST thin films. However, this is a new research area and many fundamental questions still keep

open. A systematic study is necessary to explore and verify the properties and mechanism of field emission of BST coated Si tip arrays.

In this chapter, we describe in detail the microstructural properties, component analysis, chemical compound formation and electronic properties of BST thin films, field emission properties of BST coated Si tip arrays and related discussions for field emission mechanism. The field emission properties of BST coated Si tip arrays were investigated by varying annealing temperature and thickness of BST coatings. The field emission characteristics were studied by using the home-designed automatic field emission characterization system.

This chapter is composed of two sections. The first section will present the preparation and characterization of BST thin films. It includes the study of thermal decomposition behavior of dried BST gel powders, and the investigation of microstructural evolution, component analysis, chemical compound formation and electronic properties of the BST thin films. Then, the study of field emission properties of BST coated Si tip arrays, the analysis of emission data, and the discussion of field emission mechanism will be provided in the second section.

4.1 Preparation and characterization of BST films

4.1.1 Thermal decomposition properties

Figure 4-1 illustrates the thermal decomposition behavior of the BST gel. With increasing temperature, a significant weight loss is observed below 300 °C due to the evaporation of residual solvent in the xerogel. Then, two exothermic peaks at 301 and 402 °C appear successively in the DTA curve, corresponding to the decomposition of metal-organic precursors. It is known that the precursors of barium acetate and strontium acetate are decomposed around 300 °C, and the titanium butoxide is decomposed around 400 °C. The resultant (Ba,Sr)TiCO_x complex is stable up to 550°C, and shows a flat region in the TGA curve. With further increasing temperature, a step is found in the TGA curve between 550 and 620 °C, accompanied by an exothermic peak in the DTA curve. The weight loss between 520 °C and 620 °C has been identified as a solid reaction, presented as [99]

Based on the results of thermal decomposition analysis, the heat treatment processes were determined. During the BST thin film deposition, the pyrolyzed processes at 200 and 400 °C were chosen for heat-treatment after each layer of BST film coated on substrate to dry the solvent and burn off the bound organic components. After all the layers were coated, the films were annealed at temperatures above 600 °C to achieve desired structure.

Figure 4-1 TGA and DTA curves of BST gel precursor.

4.1.2 Microstructure and component analysis of BST thin films

4.1.2.1 X-ray diffraction

The X-ray diffractometer measurement was carried out using the Rigaku system with $\text{Cu } K\alpha$ ($1.54 \text{ \AA}$) radiation source. The scanning angle range was from 20° to 60° in 2θ with a scan rate of $2^\circ/\text{min}$. A small glazing angle fixed at 0.5° was used to ensure that the diffraction intensity mostly came from the thin films. The JCPDS files were employed for the analysis of all XRD results.

The microstructural evolution of the sol-gel BST films was studied by varying thickness and annealing temperature as shown in Figures 4-2 and 4-3, respectively. Apparently, the diffraction patterns indicate that the microstructural evolution is strongly dependent on the film thickness and the annealing temperature. Figure 4-2

shows the XRD patterns of stoichiometric BST thin films with thickness of 15, 30, 60 and 90 nm deposited on Si substrates annealed at 700 °C. It is found that there are not obvious diffraction peaks of perovskite structure in BST thin films with thickness of 15 and 30 nm. The sol-gel thin films were crystallized during annealing process and perovskite grains could not be well-developed in such thin films. The crystallinity of the sol-gel BST thin films was improved with the increasing film thickness. The 60-nm-thick film shows the desired perovskite diffraction peaks in XRD patterns. The peaks are getting higher and narrower while further increasing thickness to 90 nm, indicating improved crystallinity of the films.

Figure 4-2 X-ray diffraction patterns of sol-gel BST thin films annealed at 700 °C with different thickness.

Figure 4-3 X-ray diffraction patterns of sol-gel BST thin films with thickness of 90 nm annealed at different temperatures for 1 hour.

Since the diffraction peaks are not obvious for the very thin films, the 90-nm-thick BST films were employed to study the effect of annealing temperature. The XRD patterns of the BST thin films annealed at different temperatures for 1 hour are shown in Figure 4-3. It is found that the film annealed at 600 °C is still in an amorphous state, whereas the desired peaks of the perovskite structure can be easily indexed for the samples annealed at 650 and 700 °C. However, with further increasing annealing temperatures to 750 and 800 °C, an additional phase appears, which could be attributed to $(\text{Ba,Sr})_2\text{TiSi}_2\text{O}_8$ phase [100], accompanied with broadening of the perovskite peaks. It is believed that $(\text{Ba,Sr})_2\text{TiSi}_2\text{O}_8$ phase is the product of the interfacial reaction between BST and Si at high annealing temperatures. The

interfacial reaction impedes the development of BST perovskite structure, and results in poor crystallinity in the films as shown in their XRD patterns.

4.1.2.2 TEM image

The cross-section images of the 15-nm-thick sol-gel derived BST films annealed at 600 and 800 °C are shown in Figure 4-4. The uniform contrast of the BST films indicates that the deposited films are composed of a dense and crack-free amorphous phase. It is found that such thin films are hard to be crystallized even though they are annealed at a high temperature. On the other side, the contrast change at BST/Si interface is also noticed in TEM observation. The thickness of the interfacial layer is 2.4 and 4.0 nm for the BST thin film annealed at 600 and 800 °C, respectively. It is indicated that the solid-state reaction between BST and Si substrate is enhanced with the increasing annealing temperature.

The cross-sectional structures of BST films annealed at 700 °C with different thicknesses are also examined as shown in Figure 4-5. It is found that the BST films are non-uniform and composed of two-layer structure in the films (shown in insets), an amorphous layer on the bottom and then a polycrystalline layer on it. The 30-nm-thick BST film is generally amorphous in nature. But we still can find some small grains near the surface region of the film. The 90-nm-thick BST film demonstrates higher crystallinity which contains randomly oriented polycrystalline grains.

(a)

(b)

Figure 4-4 Cross-section images of sol-gel derived BST thin films deposited on Si substrate annealed at 600 (a) and 800 °C (b).

(a)

(b)

Figure 4-5 Cross-section images of sol-gel derived BST thin films annealed at 700 °C with thickness of 30 (a) and 90 nm (b). The insets show two-layer structure in the film.

A high-resolution photograph shown in Figure 4-6 exhibits the lattice structure of BST annealed at 700 °C with thickness of 30 nm. The interplanar distance of (110) is about 0.2760 nm, which is consistent with the value of 0.2805 nm calculated from XRD results.

Figure 4-6 TEM bright-field image for the lattice structure of BST annealed at 700 °C with thickness of 30 nm.

4.1.2.3 SIMS depth profile

It was found that there is an additional phase, which is attributed to the product of interfacial reaction between BST and Si, for the 90-nm-thick BST thin films annealed above 750 °C from the XRD results. Moreover, we also noticed the contrast change at BST/Si interface in TEM observation. To clarify the interface structure, SIMS depth profile of BST film on Si was investigated using ToF-SIMS (ION-ToF GmbH).

Figure 4-7 presents the SIMS depth profiles around the interface between the BST films and Si substrate for the samples annealed at different temperatures. These profiles are qualitative, i.e., the relative ion counts for different elements do not indicate their relative concentrations. It is indicated that distribution of Ba, Sr, Ti and O through the BST film is homogeneous. Moreover, diffusion of Si atoms from Si substrate into the BST films is noted in the depth profiles. It is found that Si signals increase before Ba, Sr, Ti and O signals decrease. It means that there is a mixture region with Ba, Sr, Ti, Si and O presented at BST/Si interface. The mixture layer originates from the solid-state reaction between BST and Si during the annealing process of the films. Therefore, the interface layer is believed to be composed of $(\text{Ba,Sr})\text{Ti}_x\text{Si}_y\text{O}_z$. With the increase of the annealing temperature, the overlapping of Si, Ba, Sr, Ti and O profiles becomes broader, indicating the increase of the interdiffusion between BST and Si. It is related to severe interfacial reaction between BST and Si substrate at such high annealing temperature. The results are consistent with previous XRD finding that an $(\text{Ba,Sr})_2\text{TiSi}_2\text{O}_8$ phase exists when BST thin films were annealed at 750 and 800 °C. In addition, there is a small hump for all the elements in the interface region. This is the outcome of the matrix effects when profiling heterolayer structure, which result in the increase of the ion yield [101].

(a)

(b)

(c)

Figure 4-7 SIMS depth profiles for sol-gel BST thin film annealed at 600 (a), 700 (b), and 800 °C (c) for 1 hour.

4.1.2.4 FT-IR analysis

It is revealed that the solid-state reaction occurs between BST and Si substrate and the thickness of the interface layer of $(\text{Ba,Sr})\text{Ti}_x\text{Si}_y\text{O}_z$ increases with increasing annealing temperature. The change of interface layer may influence the chemical bonding configuration which would be demonstrated by Fourier transform infrared (FT-IR) spectroscopy analysis below.

Figure 4-8 illustrates the FT-IR transmittance spectra of BST thin films, 30 nm thick, annealed at different temperatures ranging from 600 to 800 °C. For the films annealed in a temperature range between 600 and 750°C, there are three major absorption peaks appearing in their FT-IR spectra, located at 443, 547, and 703 cm^{-1} . The peak at 547 cm^{-1} is due to transverse optical (TO) mode of Ti-O bonds in TiO_6 octahedra, and the peaks at 703 and 443 cm^{-1} are attributed to the longitudinal optical (LO) phonon mode [102-105]. It is shown that with increase of the annealing temperature from 600 to 700 °C, these absorption peaks are sharpened and narrowed, corresponding to the development of crystallinity. However, the interfacial reaction between BST film and Si would be enhanced while further increasing annealing temperature to 750 and 800 °C. As a result, the peaks of Ti-O bond in TiO_6 octahedra are lowered and broadened

Figure 4-8 FT-IR transmittance spectra of 30-nm-thick BST thin films annealed at different temperatures in air for 1 hour.

correspondingly, accompanied by two additional peaks at 907 and 860 cm^{-1} . The additional absorption peaks at 907 and 860 cm^{-1} are attributed to the vibrations of Si-O bonds and Ti-O bonds respectively [100,106]. It means that the severe solid-state interfacial reaction occurs at high annealing temperature.

From the studies in this section, it is found that the microstructure of BST thin film is strongly dependent on annealing temperature and film thickness. The BST films exhibit the perovskite structure while annealed between 650 and 700 °C, and a severe interfacial reaction between Si and BST while annealed above 750 °C. The crystallinity of perovskite structure is improved with the increasing thickness of BST film annealed at 700 °C. The 15-nm-thick BST film is amorphous in nature, and the polycrystalline perovskite grains develop in the thicker film with an amorphous layer existed in the bottom region of the film. The component analysis shows that the BST/Si interface is a solid-state reaction product of $(\text{Ba,Sr})\text{Ti}_x\text{Si}_y\text{O}_z$. The change of microstructure of BST films could in turn influence the field emission properties of BST coated Si tip arrays which will be discussed in detail later.

4.1.3 X-ray photoelectron spectroscopy characterization

The change of the microstructure of BST films should accompany a variation of the electronic structure [107]. In this section, the effect of the annealing temperature is discussed firstly. The variation of oxygen vacancy concentration is estimated from the

O 1s core level spectra. The electrons donated by the oxygen vacancy could induce the Fermi energy shift, studied using core level spectra. The effect of thickness is then studied and the crystallinity information of BST thin films with different thicknesses is obtained from the studies of Ba 3d_{5/2} core level and valence band spectra.

4.1.3.1 Effect of annealing temperature

Figure 4-9 shows the XPS survey spectrum of the 30-nm-thick sol-gel BST thin film annealed at 700 °C. It can be seen that the thin film is composed of Ba, Sr, Ti and O.

A quantitative analysis of XPS data is obtained using high resolution spectra of Ba 3d, Sr 3d, Ti 2p, and O 1s. This can be explained as follows. For a homogeneous sample, the number of photoelectrons per second in a specific spectra peak is given by [108]:

$$I = \eta f \sigma \theta y \lambda A T \quad (4-2)$$

Where n is the number of atoms of the element per cm³ of the sample, f is the X-ray flux in photons/cm²-s, σ is the photoelectric cross-section for the atomic orbital of interest in cm², θ is an angular efficiency factor for the instrumental arrangement based in the angle between the photon path and detected electron, y is the efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy, λ is the mean free path of the photoelectrons in the sample, A is the area of the sample from which photoelectrons are detected, and T is the detection efficiency for

electrons emitted from the sample. From Equation (4-2), the number of atoms of the element per cm³ of the sample can be expressed as:

$$n = I / f\sigma\theta y\lambda AT \quad (4-3)$$

The denominator in Equation (4-3) can be defined as the atomic sensitivity factor, S.

The number of atoms of the element per cm³ of the sample can be expressed simply as

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

where I and S are peak area and atomic sensitivity factor of the element. A general expression for determining the atom fraction of any constituent in a sample, C_x, can be written

$$C_x = (I_x / S_x) / (\sum I_i / S_i) \quad (4-5)$$

Based on equation 4-5, atomic percents of Ba, Sr, To and O in BST thin films are obtained from the XPS high-resolution spectra as shown in Table 4-1. This leads to atomic ration Ba:Sr:Ti:O equal to 0.65:0.35:1:3-δ. The ratio of O/Ti is less than 3 which is possibly due to oxygen vacancy in the thin films.

Figure 4-9 XPS survey spectrum of BST film with thickness of 30 nm annealed at 700 °C.

Table 4-1 Atomic percents of Ba, Sr, Ti and O in BST thin films obtained from XPS high-resolution spectra.

	Ba (%)	Sr (%)	Ti (%)	O (%)
600°C (30 nm)	13.7	8.2	23.6	54.5
650°C (30 nm)	12.3	7.5	25.5	54.7
700°C (15 nm)	13.4	6.0	20.7	59.8
700°C (30 nm)	16.3	9.1	21.4	53.2
700°C (60 nm)	14.2	8.7	21.1	56.0
700°C (90 nm)	15.0	10.0	21.2	53.8
750°C (30 nm)	11.5	7.4	21.4	58.5
800°C (30 nm)	11.8	6.7	19.6	61.9

Figure 4-10 shows the high resolution O 1s spectra obtained from 30-nm-thick BST films annealed at various temperatures. A good fitting is obtained to the spectrum as indicated in the figure. It is remarkable that all O 1s spectra can be fitted with two peaks at binding energies of about 530.2 and 532.2 eV. The low binding energy at 530.2 eV, denoted by O₍₁₎, is assigned to oxygen in the lattice, and the high binding energy at 532.2 eV, denoted by O₍₂₎, is reported to be adsorbed oxygen species and hydroxyl ion [109-112]. Furthermore, the O₍₂₎ peak is broader than that of O₍₁₎, suggesting that the former contains at least two components (adsorbed oxygen and hydroxyl group). It has been reported that the adsorbed oxygen increases with the increase of a number of oxygen vacancies [109-112]. The change of oxygen vacancy concentration can be estimated from the variation of the intensity ratio of the two fitted O1s peaks. From

Table 4-2, it is found that the intensity ratio of the O₍₂₎ to O₍₁₎ peaks increases for BST thin films annealed from 600 to 750 °C and decreases above 750 °C. Since the samples were prepared and measured in the same oxygen atmosphere, it is reasonable to attribute the increased O₍₂₎/O₍₁₎ intensity ratio to the increase of oxygen vacancy concentration in BST thin films annealed from 600 and 750 °C. The decrease of the intensity ratio of the O₍₂₎ to O₍₁₎ peaks above 750 °C may be associated to interfacial reaction as shown in previous structural measurements. It is well known that oxygen vacancies donate electrons, resulting in an *n*-type conductivity in the BST thin films according to the following defect equation.

The electrons donated by the oxygen vacancy could induce the Fermi energy shift [113].

Figure 4-10 XPS O 1s core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures.

Figure 4-11 shows XPS Ti 2p core-level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures. There is a binding energy shift of Ti $2p_{3/2}$ peak. The shift in the peak is attributed to the Fermi level change rather than chemical effects since all Ba $3d_{5/2}$, O 1s, Ti 2p and Sr 3d peak undergo the same shift. Therefore, the binding energy shift of Ti $2p_{3/2}$ peak gives the relative shift of the Fermi level [83-86]. It is found the Fermi level shifts up for BST films annealed from 600 to 750 °C with increasing temperature due to increasing oxygen vacancy concentration, and then moves back slightly after annealed at 800 °C, attributed to the severe interface reaction between BST and Si substrate. The shift value (ΔE_F) of the Fermi level with respect to that of the film annealed at 600 °C are around 0.1, 0.3, 0.5,

and 0.3 eV, corresponding to the films annealed at 650, 700, 750 and 800 °C, respectively.

Figure 4-11 XPS Ti $2p$ core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures. The shift in the peak is attributed to the Fermi level change of BST thin films.

The valence band spectra of BST thin films annealed at different temperatures are demonstrated in Figure 4-12. The valence electronic structure of BST considered here is determined by Ti $3d$ and O $2p$ states in the corner sharing Ti-O_6 octahedral units that make up the perovskite structure. In a simplified ionic picture this would lead to a completely full O $2p$ valence band and an empty Ti $3d$ conduction band for BST. The valence band extends from about 2 to 9 eV below Fermi level and is derived primarily O $2p$ states of the Ti-O_6 octahedra. The binding energy of valence band maximum (E_{VBM}) could be determined by extrapolating the leading edge of the valence band

spectrum to its base line [114]. The E_{VBM} of BST films annealed at 600, 650, 700, 750 and 800 °C are around 2.5, 2.5, 2.6, 2.7, and 2.5 eV, respectively. That means the Fermi level shifts away from the valence band maximum (VBM) for BST film annealed from 600 to 750 °C, and shift close to the VBM for BST film annealed at 800 °C. The main reason of this phenomenon is mainly attributed to the shift of the Fermi level.

Figure 4-12 XPS valence band spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures.

Figure 4-13 XPS $\text{Ba } 3d_{5/2}$ core level spectra obtained from the 30-nm-thick BST thin films annealed at different temperatures. Increased $\text{Ba}_{(1)}/\text{Ba}_{(2)}$ ratio indicates improvement in crystallinity of the BST thin films.

Figure 4-13 shows XPS $\text{Ba } 3d_{5/2}$ core level spectra of 30-nm-thick BST films annealed at different temperatures. The spectra obtained from films annealed at 700 and 750 °C can be fitted with two peaks with the lower binding energy at 779.1 eV and the high binding energy at 780.5 eV, denoted by $\text{Ba}_{(1)}$ and $\text{Ba}_{(2)}$ respectively. The $\text{Ba}_{(1)}$ is assigned to Ba with 12-fold oxygen coordination representative of bulk stoichiometry, and $\text{Ba}_{(2)}$ originates from uncoordinated Ba in the surface region [115-116]. It is clear that the coordinated $\text{Ba}_{(1)}$ peak could only be observed in the films annealed at 700 and 750 °C, indicating the formation of bulk perovskite phase. Their $\text{Ba}_{(1)}/\text{Ba}_{(2)}$ ratios were estimated to be around 0.30 and 0.11, respectively. In the other films, only the uncoordinated $\text{Ba}_{(2)}$ could be found, suggesting amorphous structure. In particular, the

films annealed above 750 °C exhibit degraded crystallinity owing to the severe solid-state reaction at the BST/Si interface. It is concluded that the BST with thickness of 30 nm annealed at 700 °C has the best crystallinity compared with others.

Table 4-2 Summary of the measured shift value of the Fermi level ΔE_F , the O₍₂₎/O₍₁₎ ratio, the binding energy of valence band maximum (E_{VBM}) and the Ba₍₁₎/Ba₍₂₎ ratio of BST thin films annealed at different temperatures.

Annealing temperature	O ₍₂₎ /O ₍₁₎	ΔE_F (eV)	E_{VBM} (eV)	Ba ₍₁₎ /Ba ₍₂₎
600°C	0.55	-	2.5	0
650°C	0.64	0.1	2.5	0
700°C	0.76	0.3	2.6	0.30
750°C	0.88	0.5	2.7	0.11
800°C	0.53	0.3	2.5	0

4.1.3.2 Effect of thickness

High-resolution Ti 2p_{3/2} core level spectra of BST films annealed at 700 °C with different thickness are shown in Figure 4-14. It is clear that Ti 2p_{3/2} peak shifts to lower binding energy with the increase of the film thickness. The shift values of the Ti 2p_{3/2} binding energy with respect to that of the film with thickness of 15 nm are around -0.08, -0.26, and -0.32 eV, corresponding to the films with thickness of 30, 60, 90 nm respectively. Consistent changes are observed in other core levels. Due to the various thickness of the BST thin films, the binding energy shift of the Ti 2p peak is

possibly affected by the band bending (bulk charge redistribution) in BST layer [90]. Near the interface the local charge-density distribution may differ from that deeper in the bulk semiconductor [117]. Consequently, Poisson's equation predicts a spatially varying electrostatic potential which bends all of the bands or energy levels by an amount that depends only on the distance from the interface. This assumes that the energy band gap in the space-charge region is the same as it is deeper in the bulk semiconductor. Copel and his coworkers [90] reported that the initial position of the Ti 2*p* core level depends on the film thickness. This is due to the influence of the underlying Pt layer which bends the band. The depletion width of chemical solution deposition BST films are reported as 130 nm.

Figure 4-14 XPS Ti 2*p* core level spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.

The studies below of Ba $3d_{5/2}$ core level and valence band spectra could offer the crystallinity information of BST thin films with different thicknesses. Figure 4-15 shows high resolution Ba $3d_{5/2}$ core level spectra of BST films annealed at 700 °C with different thickness. The spectra obtained from films above 30 nm can be fitted with two peaks at the low binding energy around 779.1 eV and the high binding energy around 780.5 eV, denoted by Ba₍₁₎ and Ba₍₂₎ respectively. The Ba₍₁₎ is assigned to Ba with 12-fold oxygen coordination representative of bulk stoichiometry, and Ba₍₂₎ could originate from uncoordinated Ba atoms in a different chemical state [115-116]. In the 15-nm-thickness BST film, only the uncoordinated Ba₍₂₎ peak could be found, suggesting the amorphous structure. While it is clear that the coordinated Ba₍₁₎ peak could be observed in the films with thickness of 30, 60 and 90 nm, indicating the formation of the bulk perovskite phase. Their Ba₍₁₎/Ba₍₂₎ intensity ratios are estimated to be around 0.30, 2.27 and 4.17, respectively. The ratios increase largely with the increasing film thickness, attributed to the substantially increase of crystallinity with the increasing thickness. This is consistent with the above XRD and TEM results.

Figure 4-16 shows XPS valence band spectra of the BST thin films annealed at 700 °C with different thicknesses. The valence band extends from about 2 to 9 eV below the Fermi level and is derived primarily O $2p$ states of the Ti-O₆ octahedra. With increasing thickness of BST film, this structure appears to be better defined, a double peak of this band arising from the hybridization of Ti and O valence state is exhibited,

Figure 4-15 XPS Ba 3d_{5/2} core level spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.

Figure 4-16 XPS valence-band spectra obtained from the BST thin films annealed at 700 °C with different thicknesses.

and the width of the band increases. The values of binding energy of valence band maximum (E_{VBM}) [114] of BST films with thickness of 15, 30, 60, and 90 nm are around 2.67, 2.58, 2.18, and 2.03 eV, respectively. It is demonstrated that the valence electronic structure is substantially influenced by the crystallinity in our BST films.

The XPS results demonstrate that the electronic structures of BST thin films are influenced by the annealing temperature. The Fermi level shifts up for BST film with the increasing annealing temperature from 600 to 750 °C, and it moves back slightly at 800 °C. The upward shift of the Fermi level from 600 to 750 °C is attributed to the increasing oxygen vacancy concentration in the films and the downward shift of the Fermi level at 800 °C is associated with the severe interfacial reaction. Moreover, the crystallinity information of BST thin films with different thicknesses are obtained from the studies of Ba $3d_{5/2}$ core level and valence band spectra, which is consistent with previous studies. The investigations of the electronic structure and microstructure of BST coatings using various techniques could be vitally important to understanding the field emission mechanism of BST coated Si tip arrays which will be discussed in detail in next section.

4.2 Field emission properties of Si tip arrays coated with BST thin films

In this section, the field emission properties of Si tip arrays coated with BST thin films were investigated. Firstly, the emission current density-electric field (J - E) characteristics are studied by varying annealing temperature and thickness of BST coatings. The field emission stability is then included in the following part. Next, the J - E data are analyzed using the F-N plot and the effective work function of the BST-coated Si tips is estimated. Finally, the field emission mechanism is discussed in the last part.

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

Figure 4-17 illustrates the influence of annealing temperature on field emission behavior of Si tip arrays coated with 30-nm-thick sol-gel BST thin films. It is obvious that the threshold electric field of Si tip arrays could be largely lowered from 36 V/ μ m for the bare Si tip arrays to 19 V/ μ m for that with a 30-nm-thick BST coating annealed at 700 °C. Moreover, the coated Si tip arrays exhibit an increase in maximum emission current compared with bare Si arrays. It is also shown that the electron emission characteristics of the BST-coated Si tip arrays strongly depend on the annealing temperature. For the arrays coated with 30-nm-thick BST layer annealing at 600 °C, the threshold electric field is about 28.5 V/ μ m. The threshold electric field is lowered to about 27 and 19 V/ μ m for the samples annealed at 650 and 700 °C,

Figure 4-17 Field emission of Si tip arrays coated with 30-nm-thick BST thin films annealed at different temperatures. The BST coated arrays annealed at 700 °C yield the optimal emission performance.

Figure 4-18 Field emission of Si tip arrays coated with BST thin films annealed at 700 °C with different thicknesses. The arrays coated with 30-nm-thick BST film show the optimal emission performance.

respectively. However, further increasing annealing temperature does not lead to further improvement in field emission. The threshold electric fields measured are about 22.5 and 25.2 V/ μm for the samples annealed at 750 and 800 °C respectively.

Moreover, the thickness of BST layer annealed at 700 °C also impacts the field emission behavior of coated silicon emitter arrays as shown in Figure 4-18. The threshold fields are of 27, 19, 23 and 28 V/ μm corresponding to the BST thin film of 15, 30, 60, and 90 nm, respectively. It is found that the 30-nm-thick BST films demonstrate the lowest threshold field for electron emission. The threshold fields of Si tip arrays coated with different BST films are listed in Table 4-3.

It demonstrates that the BST coated Si tip arrays show considerable improvement in field emission. The enhancement of field emission shows the annealing temperature dependence and thickness dependence, which could originate from the microstructural evolution features and electronic properties in BST films. The details will be discussed later.

4.2.2 Field emission stability

Furthermore, the BST-modified Si tip arrays also demonstrate an improved stability for field emission. The influence of annealing temperature and the impact of film thickness on emission stability of BST coated Si tip arrays are investigated.

As shown in Figure 4-19, the emission current density of four kinds of Si tip arrays, namely, bare Si arrays and the arrays coated with the 30-nm-thick BST film annealed at 600, 700, and 800 °C, respectively, was examined as the function of time. The initial current density was maintained around several $\mu\text{A}/\text{cm}^2$ for all samples. During the measurement, the value of current density from BST-coated arrays still maintained in the same order, whereas that from the bare Si arrays exhibited remarkable decrease after 180 s and fluctuation during the measurement. The average emission current density J_{average} , standard deviation ΔJ , and fluctuation f , ($f = \frac{\Delta J}{J_{\text{average}}}$), are determined for these arrays [118]. Large difference is found between the fluctuation of the bare Si arrays and that of BST-coated arrays. Si arrays coated with 30-nm-thick BST film annealed at 700 °C displays smaller fluctuation of 0.30 compared with that of the bare Si arrays with fluctuation of 1.4. The emission stability is influenced by the annealing temperature. The fluctuation of BST-coated arrays annealed at 600, 700, and 800 °C are 0.55, 0.30 and 0.62, respectively. Moreover, the effect of thickness on emission stability of BST coated Si arrays annealed at 700 °C is also investigated as shown in Figure 4-20. Small difference of fluctuations between 30-nm-thick ($f = 0.30$) and 90-nm-thick ($f = 0.35$) BST coatings is found. Table 4-3 lists the fluctuation values of Si tip arrays coated with different BST films. It means that BST coated Si tip arrays could behave as stable electron sources compared with bare Si tip arrays.

Figure 4-19 The emission current stability of bare Si tip arrays (a), Si tip arrays coated with 30-nm-thick BST thin films annealed at 600 °C (b), 700 °C (c), and 800 °C (d).

Figure 4-20 The emission current stability of bare Si tip arrays (a), Si tip arrays coated with 30-nm-thick (b) and 90-nm-thick (c) BST thin films annealed at 700 °C.

4.2.3 Analysis of emission data

As essential data, the emission current density-electric field (J - E) characteristics were investigated by varying annealing temperature and thickness of BST coatings in section 4.2.1. These emission data were analyzed by plotting them according to the F-N formula [26-27]. The important parameters, the field enhancement factor (β) [119-120] and the effective work function (ϕ) [11,19,121-122], are obtained from the slope of the F-N plot.

4.2.3.1 Field enhancement factor

The F-N equation is expressed as

$$I = A \times V^2 \exp(-B / V) \quad (4-7)$$

where

$$A = 1.42 \times 10^{-6} \times \frac{\alpha \times \beta^2}{d^2 \times \phi} \times \exp\left(\frac{10.4}{\phi^{1/2}}\right) \quad (4-8)$$

and

$$B = 6.44 \times 10^7 \times d \times \phi^{3/2} / \beta \quad (4-9)$$

In equation (4-7), (4-8), and (4-9), I is field emission current in units of A, V is the applied voltage in units of V, d is distance between anode and cathode in units of cm, α is the area from which emission of electrons takes place in units of cm², ϕ is effective work function in units of eV, and β is called the field enhancement factor.

The electric field at the tip apex can be substantially enhanced with field enhancement factor β as shown in equation 2-6.

As demonstrated in Figure 4-21, the F-N plot exhibits the straight line with different slopes at high voltages. The straight line suggests that the electron emission is controlled by tunneling through a potential barrier. The field enhancement factor β of Si tip arrays could be deduced using equation (4-9). Assuming the tunneling barrier height of Si to be 4.3 eV (corresponding to the work function of *n*-type silicon with 2 $\Omega\cdot\text{cm}$ resistivity), the enhancement factor β could be estimated to be 110 from the F-N slope (*FNSL*) in Figure 4-21 (a).

On the other hand, the β could also be estimated from using the curvature of the Si tip as the following equation [48-49],

$$\beta = h / r \quad (4-10)$$

where r is the emitter-tip radius, and h is the tip height. Taken $h=1.5\ \mu\text{m}$, $r=20\ \text{nm}$ for Si tip from the SEM photograph shown in Figure 4-22, the value of β factor is estimated to be 75. The estimated values of β factor are close from two methods.

4.2.3.2 Effective work function

The effective work functions of Si tip arrays coated with BST thin films annealed at different temperatures are estimated. The slope of the F-N plot *FNSL* is deduced from Figure 4-21 (b). Since the SEM pictures of Figure 4-22 indicate that the sharpness of silicon tips are not altered by BST coating with the thickness of 30 nm and 90 nm, it is

reasonable to assume that the BST-coated Si tips and the bare silicon tips have the same field enhancement factor β . As a result, the effective work function of the BST-coated tips can be calculated from the ratio of the F-N slope $FNSL$ of BST-coated silicon tip to uncoated silicon tip as [122]

$$\phi_{BST} = \phi_{Si} (FNSL_{BST} / FNSL_{Si})^{2/3} \quad (4-11)$$

According to the F-N slope $FNSL$ and Si work function of 4.3 eV, the values of the effective work function are estimated as 4.1, 3.4, 2.3, 2.6, and 2.7 eV for BST-coated Si tips annealed at 600, 650, 700, 750, and 800 °C, respectively. The effective work functions of Si tips coated with BST films with different thicknesses are also deduced using above equation 4-11. It is found the value of the effective work function of BST coated Si tips is dependent on the coating film thickness, of 2.9, 2.3, 2.5, and 3.3 eV for sample with thickness of 15, 30, 60, and 90 nm, respectively. Table 4-3 lists the values of the estimated effective work function from the slopes of F-N plot.

Correlated to the J - E characteristic, the sample with the smallest effective work function exhibits the best improvement in field emission. It suggests that the improvement in electron emission originates from the lowering of work function with BST coatings.

Figure 4-21 F-N plot of field emission from Si tip arrays and BST-coated Si tip arrays (a), Si tip arrays coated with BST thin films annealed at different annealing temperatures (b), Si tip arrays coated with BST thin films with different thicknesses (c).

(a)

(b)

(c)

Figure 4-22 Scanning electron micrographes (SEM) of uncoated (a), 30-nm-thick (b), and 90-nm-thick (c) BST-coated Si tip arrays.

Table 4-3 The threshold field, the fluctuation of emission current density, the ratio of the F-N plot slope ($FNSL_{BST}/FNSL_{Si}$), the effective work function of BST coated Si tip arrays as a function of annealing temperature and film thickness.

Annealing temperature (°C)	Thickness of BST (nm)	Threshold field (V/ μ m)	Fluctuation	$FNSL_{BST}/FNSL_{Si}$	ϕ_{BST} (eV)
600	30	28.5	0.55	0.93	4.1
650	30	27	-	0.69	3.4
700	15	27	0.30	0.57	2.9
700	30	19	-	0.40	2.3
700	60	23	-	0.46	2.5
700	90	28	0.35	0.65	3.3
750	30	22.5	-	0.48	2.6
800	30	25.2	0.62	0.50	2.7

4.2.4 Field emission mechanism

The microstructure and electronic properties of BST thin films, and field emission properties of BST coated Si tip arrays have been systematically studied. It is revealed that the BST coated Si tip arrays show considerable improvement in field emission. The threshold field could be lowered substantially from 36 V/ μ m for bare Si tip arrays to about 19 V/ μ m for BST-coated Si tip arrays. The mechanism and enhancement of field emission of BST coated Si tip arrays are discussed in this part. A comparison of the different types of BST thin films is presented to clarify the relationship among microstructure, electronic properties and field emission behavior.

It is well known that field emission process from a wide band gap thin film on Si tip arrays includes the critical three steps of supplying electrons to the thin film, transporting them through the bulk to the surface, and emitting them into vacuum, based on the proposed model shown in Figure 2-7. It is believed that these steps are influenced by the microstructure and electronic properties of BST coating, which will be demonstrated below from the effect of annealing temperature and the impact of thickness.

(a) Effect of annealing temperature

The field emission behavior of 30-nm-thick BST coated Si tip arrays shows the annealing temperature dependence. The sample annealed at 700 °C has the lowest threshold field, while the samples annealed at lower (≤ 650 °C) or higher (≥ 750 °C) temperature can not further improve the field emission behavior. Analysis of the emission data using the F-N plot suggests that the electron emission is dominated by tunneling through a potential barrier; and the improvement in electron emission originates from the lowering of effective work function with the BST coatings. It is found that the sample with the low effective work function exhibits enhanced emission behavior.

Correlated to the microstructural features, it is shown that the crystallinity of perovskite structure is improved for the BST thin film annealed from 600 to 700 °C

and then degraded due to the severe interfacial reaction above 750 °C. Some small grains near the surface region of the 30-nm-thick BST film annealed at 700 °C are observed from the TEM images and also demonstrated by studying XPS Ba 3d_{5/2} core level spectra. On the other hand, it is found that the oxygen vacancy concentration increases for the 30-nm-thick BST thin films annealed from 600 to 750 °C and decreases above 750 °C. The decrease of oxygen vacancy concentration at the high annealing temperature may be associated with the severe interfacial reaction. It is known that the oxygen vacancies donate electrons, resulting in an *n*-type conductivity in the BST thin films. The variation of the oxygen vacancy concentration could lead to the shift of the Fermi level in BST films. Correspondingly, it is found that the Fermi level shifts up for the BST films with increasing annealed temperature from 600 to 750 °C, and then moves back slightly after annealed at 800 °C.

The increasing Fermi level of in the BST films annealed from 600 to 700 °C would improve the supply of conduction electrons to the emitting surface and also yield a lower tunneling potential barrier at the surface ($\phi = E_{\text{vacuum}} - E_f$) [122]. The low potential barrier increases the possibility of electrons with given energy tunneling into vacuum from the BST film surface. This conclusion supports the findings from the F-N analysis that the effective work function tends to decrease with the increase of the annealing temperature from 600 to 700 °C as shown in Table 4-3, and accordingly the emission behavior is improved. The Fermi level continuously shifts upward with

further increasing annealing temperature to 750 °C, but there is the severe interfacial reaction between BST and Si. The interfacial products may influence the supply of electrons from Si to BST film and also result in the degrading crystallinity of the BST film. Therefore, the increase of the effective work function for the BST coated arrays annealed at 750 °C is indicated in Table 4-3 and the degrading emission behavior is found. Downward shift of Fermi level and severer interfacial reaction is observed when sample annealed at 800 °C. Continuously increasing effective work function and degrading emission behavior are consequently displayed. From the study of the effect of annealing temperature, it is concluded that the promising candidate for field emission applications is the BST coating with reduced interfacial reaction, well-developed perovskite structure, increased oxygen vacancy concentration and upwards-moved Fermi level, which benefit the critical three steps of field emission process.

(b) Effect of thickness

From the emission current density-electric field (J - E) characteristics, it is found that the thickness of the BST thin film also impacts the field emission behavior of coated silicon emitter arrays. The threshold field is decreased with increasing thickness of BST coating. Analysis of the emission data implies that the 30-nm-thick BST coated Si arrays has the lowest effective work function.

In contrast to BST films, the thickness-dependent emission behaviors were also reported in carbon-based material. Generally, there are three major trends reported, including monotonic increase [12] or decrease [4] of the threshold field with film thickness and U-shape dependence of the threshold field on film thickness [123-124]. However, independence of electron emission on carbon-based material coating thickness was also reported [12,125]. These different trends are believed to originate from their different microstructure, doping, and surface condition, which could result in different thickness-dependent field emission mechanisms. For the BST thin films, it is found that the film thickness influences the microstructural development of the sol-gel films. In turn the corresponding three steps of field emission process would be affected by the microstructural evolution as discussed below.

The microstructure study shows that the crystallinity of BST thin films is improved with the increasing film thickness. The 15-nm-thick BST film reveals an amorphous structure. With the increasing film thickness above 30 nm, the BST films exhibit non-uniform and are composed of two-layer structure, i.e., amorphous layer on the bottom and then polycrystalline layer on it. The enhanced emission behavior from 15 to 30-nm-thick coating could be related to the perovskite structure in the surface region. However further increasing film thickness leads to the degrading emission behavior. The BST films with thickness of 60 and 90 nm exhibit higher crystallinity with randomly oriented polycrystalline grains. The improved perovskite structure for

thicker BST film could result in an increase in dielectric constant [126] and decrease the penetrating field in the film correspondingly [49]. The decrease in the penetrating field and the increase in electron transportation distance in the thicker film could limit the supply of the emitted electrons. Accordingly degraded emission behavior is observed for the BST film with thickness of 60 and 90 nm. Structural investigations suggest that the thickness dependence originates from the microstructural evolution features in the BST films. It is indicated that the emission behavior is governed by surface property for very thin film, and then dominated by the electron transportation in the bulk region for the thicker film.

CHAPTER FIVE

FIELD EMISSION OF $(\text{Ba},\text{Sr})_{1-x}\text{La}_x\text{TiO}_{3+y}$ COATED SI TIP ARRAYS

The field emission properties of the sol-gel BST coated Si tip arrays have been discussed in Chapter 4. The sol-gel BST coated Si tip arrays have demonstrated substantial enhancement of field emission with lower threshold field and improved emission current stability compared with bare Si tip arrays. It is found that the enhanced field emission is highly correlated with the microstructure and electronic properties of the BST coating. The film with perovskite grains in surface region is desired to achieve low threshold electric field. The enhancement of field emission is attributed to oxygen vacancies in the BST thin film. The oxygen vacancies donate electrons into the system and result in *n*-type conductivity of the thin film. The Fermi level of the BST film shifts upward with the increasing oxygen vacancy concentration and leads to enhanced field emission. The *n*-type doped films with perovskite structure could be achieved via not only controlling non-stoichiometric composition but also introducing transition metal dopants. The typical transition metal dopant such

as La^{3+} or Nb^{5+} is usually employed to substitute $\text{Ba}^{2+}(\text{Sr}^{2+})$ or Ti^{4+} sites in BST films respectively. La^{3+} substitution of $\text{Ba}^{2+}/\text{Sr}^{2+}$ sites in the lattice could introduce electrons into the conduction band of BST [88,94]. Tokura and co-workers [94-95] have extensively studied the mixed-crystal system $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ($0.1 \leq x \leq 1$). They found that La^{3+} substitution of Sr^{2+} makes $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ metallic with $0.1 \leq x \leq 1$, while the samples with $x \leq 0.1$ show some carrier localization effect, perhaps due to poor shielding of the impurity (La^{3+}) potential by low carrier density [98]. It is suggested that the BST thin film with La substitution should be a promising candidate as a coating material on Si tip arrays to further enhancement of field emission properties. Therefore, we extend our field emission studies to Si tip arrays coated with $(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_{3+y}$ (BSLT with $0.1 \leq x \leq 1$) thin films. Moreover, to understand BSLT properties is an important step for the realization of the field emission mechanism of this application of ferroelectric thin films.

This chapter is divided into two sections. The first section introduces the preparation and characterization of BSLT thin films, including the study of thermal decomposition behavior of dried BSLT gel powders, the effect of La substitution on microstructure, chemical compound formation and electronic properties of the BSLT thin films. Then, the second section provides the studies of field emission properties of BSLT coated Si tip arrays, the analysis of emission data, and the discussion of La substitution effect on field emission mechanism.

5.1 Preparation and characterization of BSLT films

5.1.1 Thermal decomposition properties

The formulated BSLT ($x = 0.25$) gel was selected to study La substitution effect on thermal decomposition behavior by using the Perkin-Elmer thermogravimetric analyzer (TGA-7) and differential thermal analyzer (DTA-7). The temperature range was from room temperature to 900 °C and the heating rate was 2 °C/min.

Figure 5-1 illustrates the thermal decomposition behavior of BSLT ($x = 0.25$) gel. With increasing temperature, a significant weight loss is observed below 300 °C due to the evaporation of residual solvent in the xerogel. Then, two exothermic peaks at 316 and 396 °C appear successively in the DTA curve, corresponding to the decomposition of metal-organic precursors. The peak at 316 °C is attributed to the decomposition of the precursors of barium acetate, strontium acetate and lanthanum acetate, and the peak at 396 °C is attributed to the decomposition of the precursor of titanium butoxide. The weight gain is observed in TGA between 316 and 460 °C, associated to some oxygen absorption [127]. Then, the $(\text{Ba,Sr,L a})\text{TiCO}_x$ complex is formed. With further increasing temperature, a decreasing step is found in the TGA curve between 460 and 730 °C, accompanied by a small exothermic peak in the DTA curve. The weight loss has been identified as the decomposition of $(\text{Ba,Sr,L a})\text{TiCO}_x$ complex to transfer first to a metastable pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ phase, and then to a perovskite $\text{A}_2\text{B}_2\text{O}_6$ (or ABO_3) phase.

Figure 5-1 TGA and DTA curves of BSLT ($x = 0.25$) gel precursor.

Based on the results of thermal decomposition analysis, the temperatures of heat treatment processes were determined. During the BSLT thin film deposition, the pyrolyzed processes at 200 and 400 °C were chosen for heat-treating after each layer of BSLT film coated on substrate to dry the solvent and burn off the bound organic components. After all the layers were coated, the films were annealed at 700 °C and 750 °C, respectively.

5.1.2 Microstructure of BSLT thin films

The influence of substitutional La concentration on the microstructure of sol-gel derived BSLT thin films was studied using XRD and TEM techniques. The

microstructure information is of vital importance in understanding the field emission mechanism of BSLT coated Si tip arrays.

5.1.2.1 X-ray diffraction

The X-ray diffractometer measurement was carried out using the Rigaku system with $\text{Cu } K\alpha$ ($1.54 \text{ \AA}$) radiation source. The scanning angle range was from 20° to 60° in 2θ with a scan rate of $2^\circ/\text{min}$. A small glazing angle fixed at 0.5° was used to ensure that the diffraction intensity mostly came from the thin films.

In previous microstructure study of BST, it was found that the microstructure is dependent on film thickness and annealing temperature. BST thin film annealed at 700°C has well-developed perovskite structure. A considerable improvement of field emission is revealed accordingly. Whereas, an additional $(\text{Ba,Sr})_2\text{TiSi}_2\text{O}_8$ phase appears due to the interfacial reaction between BST thin films and Si substrate when the sample is annealed above 750°C . The interfacial reaction impedes the development of BST perovskite structure, and a degraded emission behavior is displayed correspondingly.

The TGA and DTA results indicate that the perovskite structure of BSLT ($x = 0.25$) film should be developed at higher annealing temperature than 730°C . In this work, we will firstly investigate the microstructure of BSLT ($x = 0.25$) thin films annealed at 750°C with different thickness as shown in Figure 5-2. Then we will study the

effect of La concentration on the microstructure of BSLT ($0 \leq x \leq 1$) films annealed at 700 and 750 °C as shown in Figure 5-3 and 5-4, respectively. Apparently, the diffraction patterns indicate that the microstructure evolution is strongly dependent on the film thickness and the La concentration.

Figure 5-2 shows the XRD patterns of BSLT ($x = 0.25$) thin films deposited on Si substrate with thickness of 15, 30, 60, and 90 nm, followed by annealing at 750 °C. It is revealed that the thickness-dependent structural evolution of BSLT ($x = 0.25$) films is similar to that of the BST films. There are no obvious diffraction peaks of perovskite structure in the BSLT thin films with thickness of 15 and 30 nm, while perovskite phase is easily identified for the film with thickness of 60 nm. With increasing films thickness to 90 nm, the perovskite peak intensity increases and the peak width decreases, indicating improvement of film crystallinity. However, a small difference of crystallinity between BSLT ($x = 0.25$) and BST film that the 30-nm-thick BSLT film shows slightly stronger diffraction peaks of perovskite structure than that of 30-nm-thick BST film.

Since the diffraction peaks are not obvious for the very thin film, the 90-nm-thick BSLT ($0 \leq x \leq 1$) films were used to investigate the influence of La concentration on microstructure of the samples annealed at 700 and 750 °C.

Figure 5-3 shows the XRD patterns of BSLT ($0 \leq x \leq 1$) thin films deposited on Si substrate with thickness of 90 nm and annealed at 700 °C. The peaks of perovskite phase can be indexed for the samples with $x = 0$ and 0.1, whereas the diffraction peaks of perovskite structure become weaker and the diffraction peaks of pyrochlore structure appear with increasing La concentration to $x = 0.25$ and 0.5. With further increasing La concentration to $x = 0.75$ and 1, there is a broad peak at around $2\theta = 29.9^\circ$, which is related to pyrochlore phase formation [128]. The previous DTA and TGA results indicate that higher annealing temperature is required to achieve perovskite structure for the samples with high La concentration.

Figure 5-4 shows the XRD patterns of BST ($x = 0$) thin films annealed at 700 °C and BSLT ($0.1 \leq x \leq 1$) thin films annealed at 750 °C. The thickness of the films is about 90 nm. The diffraction peaks of perovskite structure can be easily indexed for samples with $x \leq 0.75$. As discussed in the previous chapter, there is an additional $(\text{Ba,Sr})_2\text{TiSi}_2\text{O}_8$ phase appearing for the BST film annealed at 750 °C, owing to the interfacial reaction between BST and Si substrate. However, such phase is not found for BSLT films ($0.1 \leq x \leq 1$) annealed at 750 °C as shown in Figure 5-4. It can be concluded that the interfacial reaction is effectively suppressed with La substitution in Ba/Sr sites. On the other side, the diffraction peaks of the perovskite phase become broad and shift to the higher degree with increasing La concentration from $x = 0$ to 0.75, which could be related to the degraded crystallinity of perovskite phase and the

lattice contraction as Ba/Sr sites are replaced by La, respectively. In particular, the peaks of the pyrochlore phase are observed in the sample with $x = 0.75$, which is a mixture of perovskite and pyrochlore phase. With further increasing La concentration to $x = 1$, only pyrochlore phase $\text{La}_2\text{Ti}_2\text{O}_7$ was observed by XRD. The $\text{La}_2\text{Ti}_2\text{O}_7$ phase has been known to form perovskite layer structure build up of corner-shared TiO_6 octahedra bonded together by the interlayer La cation [72-73], which is a ferroelectric film with very high coercive fields and Curie temperatures [74].

Figure 5-2 X-ray diffraction patterns of sol-gel BSLT ($x = 0.25$) thin films with different thicknesses annealed at 750 °C for 1 hour.

Figure 5-3 X-ray diffraction patterns of sol-gel BSLT ($0 \leq x \leq 1$) thin films with thickness of 90 nm annealed at 700 °C for 1 hour.

Figure 5-4 X-ray diffraction patterns of the sol-gel BST thin film annealing at 700 °C, and BSLT ($0.1 \leq x \leq 1$) thin films annealed at 750 °C for 1 hour. The thickness is about 90 nm.

5.1.2.2 TEM image

The microstructure of the sol-gel derived 30-nm-thick BSLT ($x = 0.25$) thin film is selected to be investigated using the Philips CM 200 FEG transmission electron microscope (TEM) to understand the effect of La substitution. This is due to BSLT ($x = 0.25$) thin film coated arrays shows the best enhancement of field emission which will be presented later.

Figure 5-5 shows the cross-section view of the 30-nm-thick BSLT ($x = 0.25$) thin film annealed at 750 °C. Apparently, the BSLT film is non-uniform and composed of two-layer structure in the film (shown in insets), an amorphous layer on the bottom and then a surface polycrystalline layer on it, which exhibits high crystallinity of perovskite structure. In addition, it is noted that there is an interface layer between BSLT and Si substrate, which could be attributed to interfacial reaction between BSLT and Si at high annealing temperature. The thickness of the interface layer is about 3 nm. Furthermore, a high-resolution TEM image shown in Figure 5-6 exhibits the lattice structure of the BSLT ($x = 0.25$) film annealed at 750 °C with thickness of 30 nm. The interplanar distance of (110) is about 0.272 nm, which is consistent with a value of 0.278 nm, deduced from XRD result.

Figure 5-5 Cross-section view of the sol-gel BSLT ($x = 0.25$) thin films annealed at 750 °C. The insets show two-layer structure in the film.

Figure 5-6 TEM bight-field image for the lattice structure of BSLT ($x = 0.25$) annealed at 750 °C with thickness of 30 nm.

5.1.3 X-ray photoelectron spectroscopy characterization

From the XRD and TEM investigations, it is revealed that the microstructure of BSLT thin film is strongly dependent on substitutional La concentration. The films exhibit perovskite structure ABO_3 at low La substitution level ($0.1 \leq x \leq 0.5$). At high La concentration ($0.75 \leq x \leq 1$) a pyrochlore phase $\text{A}_2\text{B}_2\text{O}_7$ is formed. Also it has been found that La substitution with La in BST films would suppress the interface reaction with Si substrate. On the other side, it is believed that the electronic structure of the BSLT thin films could also be influenced by the substitutional La. This is because La^{3+} , substituting of $\text{Ba}^{2+}/\text{Sr}^{2+}$ sites in the lattice, acts as donor to introduce electrons into the system [88].

In this section, the BSLT films of 30 nm thick are investigated because they exhibit the enhancement of field emission which will be discussed in next section. Firstly, the variation of oxygen vacancy concentration due to La substitution is estimated from the O 1s core level spectra. Secondly, the shift of the Fermi level due to the variations of oxygen vacancy and La substitution concentration is studied through core level and valence band spectra. Finally, the crystallinity information of BSLT thin films with different La concentrations is obtained from the studies of Ba $3d_{5/2}$ core level spectra.

Figure 5-7 shows the main peaks in the XPS survey spectrum of the BSLT ($x = 0.25$) thin film with thickness of 30 nm annealed at 750 °C. The peaks correspond to La, Ba, Sr, Ti, and O. Besides, there is a little amount of carbon due to surface contamination.

Figure 5-7 XPS survey spectrum of the sol-gel derived BSLT thin film ($x = 0.25$) annealed at 750 °C with thickness of 30 nm.

As is detailed in Chapter 4, equation 4-5 is used for a quantitative analysis of XPS data. Table 5-1 lists the surface composition obtained from high resolution spectra of La 3d, Ba 3d, Sr 3d, Ti 2p, and O 1s. It reveals that an atomic ratio of $\text{La}/(\text{La}+\text{Ba}+\text{Sr})$ is 0, 0.10, 0.24, 0.46, 0.73, and 1, corresponding to the film with $x = 0, 0.1, 0.25, 0.50, 0.75$ and 1, respectively. It is also exhibited that the atomic ratio of O/Ti

increases with La substitution of Ba/Sr sites in the films, which could be related to the decrease of oxygen vacancies in the films.

Table 5-1 Surface compositions (At%) of all BSLT ($0 \leq x \leq 1$) thin films obtained from XPS measurements.

x	La(%)	Ba(%)	Sr(%)	Ti(%)	O(%)	La/(La+Ba+Sr)
0.00	-	16.2	9.1	20.9	53.7	0.00
0.10	2.3	13.0	7.3	19.4	58.0	0.10
0.25	5.7	11.4	6.4	20.5	56.1	0.24
0.50	10.7	8.3	4.6	20.1	56.3	0.46
0.75	16.3	4.2	1.8	19.6	58.1	0.73
1.00	21.7	-	-	19.1	59.2	1.00

The high resolution O 1s XPS spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations are given in Figure 5-8. A good fitting is obtained to the peak shape as indicated in the figure. It is remarkable that all O 1s spectra can be fitted with two peaks at binding energies of about 530.0 and 532.0 eV. The peak at low binding energy of 530.2 eV, denoted by $\text{O}_{(1)}$, is assigned to oxygen in the lattice. And at high binding energy of 532.2 eV, denoted by $\text{O}_{(2)}$, is reported to be adsorbed oxygen species and hydroxyl ion [109-112]. It has been reported that the adsorbed oxygen increases with the increase of the number of oxygen vacancies [109-112]. The change of oxygen vacancy concentration can be estimated from the variation of the area ratio of the two fitted O 1s peaks as shown in Table 5-2. It is

found that the area ratio of the $\text{O}_{(2)}$ to $\text{O}_{(1)}$ peaks decreases remarkably with La substitution in the films, which means the oxygen vacancy concentration is obviously reduced. It can be understood according to the principle of electroneutrality. Doping with higher-valence cation La in Ba/Sr site (A site) either increase the number of oxygen anions or decrease the oxidation state of Ti (B site) in the lattice of the perovskite ABO_3 [109]. However, from Ti $2p$ core level spectra, we found Ti^{4+} is stable in our films even with high La concentration. This will be discussed in detail later. Therefore, the addition of La at Ba/Sr (A site) site reduces the oxygen vacancy concentration in our thin films [86,109], as shown in the following equation

It is well known that both oxygen vacancy and La substitution can donate electrons into the system, resulting in n -type conductivity in perovskite BSLT thin films according to the following defect equation, respectively

The La substitution in the BST film can lead to the decrease in oxygen vacancy concentration and correspondingly the decrease in electrons donated by oxygen vacancies. On the other hand, the substitutional La dopants themselves donate electrons into the system. Therefore, it is expected that donated electrons are dominated by oxygen vacancies at low La concentration and then governed by

substitutional La at high La concentration. The variation of donated electrons could in turn induce the Fermi level shift [84,129].

Figure 5-8 XPS O 1s core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentration.

Figure 5-9 shows XPS Ti 2p core-level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations. There is a binding energy shift of Ti 2p_{3/2} peak. The shift in the peak is attributed to the Fermi level change [84,129] rather than chemical state change of Ti⁴⁺ [130-132]. It means La substitution of Ba/Sr site (A site) does not decrease the oxidation state of Ti (B site) in the perovskite ABO₃ lattice. The binding energy shift values of Ti 2p obtained from BSLT films with respect to that of the BST thin film ($x = 0$) are -0.2, 0.2, 0, -0.3, and -0.3 eV, corresponding to the BSLT films with $x = 0.10$, 0.25, 0.50, 0.75 and 1.00,

Figure 5-9 XPS Ti 2p core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentration. The shift in the peak is attributed to the Fermi level change of BSLT thin films.

respectively. It is found that the Fermi level shifts downward to 0.2 eV with low La concentration ($x = 0.1$) with respect to the BST film. It could be associated with a remarkable decrease of oxygen vacancy concentration with La incorporation; and correspondingly the electrons donated by oxygen vacancies are reduced when compared with the BST ($x = 0$) film. In fact, some researchers found that the films showed enhanced resistivity [91] or a large decrease in the leakage current [92] when the La substitution concentration was lower than 10 mol%, in comparison to undoped films. The large decrease in leakage current was associated with the formation of highly resistive layer and could be originated from compensation defect chemistry. The Fermi level of the film shifts upward with increasing La concentration

($x = 0.25$), which is attributed to the increasing doped electrons. It is believed that the doped electrons are dominated by La substitution at this high La concentration.

However, the Fermi level of the films shifts down again with further increasing La concentration ($x \geq 0.5$). The mechanism is not well known at the present time and is assumed to be related to the phase change or/and defects in structure owing to high La concentration. Using the criteria of electroneutrality, high concentration of La^{3+} ($x = 0.5$) could either decrease the oxidation state of B (Ti) or increase of the number of oxygen anions in the lattice. But neither Ti^{3+} nor Ti^{2+} is found in Ti 2p core level spectra for sample with $x \geq 0.5$. On the other hand, oxygen anion has relatively large radius, the oxygen ion could not exit in such a lattice as an interstitial anion in perovskite structure [109]. It is possible that there exists other phase which has increasing number of oxygen anions in lattice. In fact, the pyrochlore phase of $\text{A}_2\text{B}_2\text{O}_7$ is indicated for the samples with $x \geq 0.75$ in XRD results. Other mechanism to maintain electroneutrality is probable that a certain number of metal ions are missing from the lattice, forming cation vacancies. Due to the stabilizing action of BO_6 octahedra in the perovskite structure of ABO_3 , A site vacancies are possible in the lattice. In fact, it is well known that the perovskite structure of ABO_3 can tolerate significant amounts of vacancies of A- and O-sites, still retaining the perovskite or the deformed-perovskite structure. The vacancies at A site may be possible for the sample with $x = 0.5$. The electrons could not be effectively doped into the films with high La

concentration ($x = 0.5$) in either case of the increasing number of oxygen anions in lattice or vacancies at A sites. With further increasing La concentration ($x \geq 0.75$), the Fermi level of the films continuously shifts downward. From the previous XRD results, the perovskite phase ABO_3 accompanied the pyrochlore phase $\text{A}_2\text{B}_2\text{O}_7$ can be observed for the sample with $x = 0.75$, and only pyrochlore phase is exhibited for the sample with $x = 1$. It is found that the electrons could be doped in the films due to La substitution of Ba/Sr sites in perovskite structure, while the electrons can not be doped in the films due to the appearance of the pyrochlore phase $\text{A}_2\text{B}_2\text{O}_7$. Therefore the Ti 2p peak shifts down continuously with increasing La concentration above $x \geq 0.5$, which is dominated by the downward shift of the Fermi level.

Figure 5-10 shows XPS valence band spectra from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentration. The valence band extends from about 2 to 9 eV below the Fermi level and is derived primarily O 2p states. The valence band and the conduction band consist of O 2p orbital and Ti 3d orbital respectively in either perovskite [82] or pyrochlore structure [77]. This is because the highest filled and the lowest empty A site (Ba, Sr, and La) orbital are significantly farther away from E_F than the O 2p and Ti 3d levels [82,88]. The band gap of the well-crystallized SrTiO_3 and $\text{La}_2\text{Ti}_2\text{O}_7$ is reported to be 3.3 eV [81] and 3.29 eV [77], respectively. The binding energy of valence band maximum (E_{VBM}) could be determined by extrapolating the leading edge of the valence band spectrum to its base line [114]. The E_{VBM} (shown in

Table 5-2) of BSLT films with $x = 0, 0.10, 0.25, 0.50, 0.75$, and 1.00 is about $2.6, 2.2, 3.0, 2.6, 2.1$ and 2.1 eV, respectively. Namely, it means the Fermi level of sample with $x = 0.25$ shifts away from the valence band maximum (VBM) and the Fermi level of other samples shifts close to the VBM with respect to the BST ($x = 0$) film. The main reason of these phenomena is attributed to the shift of the Fermi level due to La substitution.

Figure 5-10 XPS valence-band spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentration.

Moreover, XPS Ba $3d_{5/2}$ core level spectra are obtained to study La concentration effect on the development of polycrystalline perovskite grains in sol-gel BSLT films ($0 \leq x \leq 0.75$). Figure 5-11 shows Ba $3d_{5/2}$ core level spectra of BSLT films with different La concentration. All spectra obtained from films can be fitted with two

peaks at the low binding energy around 779.1 eV and the high binding energy around 780.5 eV, denoted by $\text{Ba}_{(1)}$ and $\text{Ba}_{(2)}$ respectively. The $\text{Ba}_{(1)}$ is assigned to Ba with 12-fold oxygen coordination representative of bulk stoichiometry, and $\text{Ba}_{(2)}$ could originate from uncoordinated Ba atoms in a different chemical state [115-116]. The observation of fully coordinated $\text{Ba}_{(1)}$ indicates the formation of bulk perovskite phase. Their $\text{Ba}_{(1)}/\text{Ba}_{(2)}$ intensity ratios, shown in Table 5-2, are estimated to be around 0.34, 0.05, 0.51, 0.32, and 0.09 for films with $x = 0, 0.1, 0.25, 0.50$, and 0.75 , respectively, and it shows that the BSLT film with $x = 0.25$ has higher crystallinity of perovskite structure than others

Figure 5-11 XPS $\text{Ba } 3d_{5/2}$ core level spectra obtained from the 30-nm-thick BSLT ($0 \leq x \leq 0.75$) thin films with different La concentration. Increased $\text{Ba}_{(1)}/\text{Ba}_{(2)}$ ratio indicates improvement in crystallinity of the BSLT thin films.

Table 5-2 Summary of the measured shift value of binding energy of Ti 2*p* core level, the $\text{O}_{(2)}/\text{O}_{(1)}$ ratio, the $\text{Ba}_{(1)}/\text{Ba}_{(2)}$ ratio, and the binding energy of valence band maximum (E_{VBM}) of BSLT thin films with different La concentration.

x	$\text{O}_{(2)}/\text{O}_{(1)}$	$\Delta E_{\text{Ti } 2p} \text{ (eV)}$	$E_{VBM} \text{ (eV)}$	$\text{Ba}_{(1)}/\text{Ba}_{(2)}$
0	0.76	-	2.6	0.34
0.1	0.54	-0.2	2.2	0.05
0.25	0.35	0.2	3.0	0.51
0.5	0.31	0.0	2.6	0.32
0.75	0.19	-0.3	2.1	0.09
1	0.26	-0.3	2.1	-

In this part, XPS has been applied to study the chemical compound formation and the electronic structure of the 30-nm-thick BSLT ($0.1 \leq x \leq 1$) thin films. It is found that the oxygen vacancy concentration decreases with La substitution. With respect to the BST ($x = 0$) thin film, the Fermi level shifts down for BSLT sample with $x = 0.1$ ascribed to the decreasing oxygen vacancy concentration, shifts up for BSLT sample with $x = 0.25$ attributed to the increasing La substitution level, and shifts down again for BSLT samples with $x \geq 0.5$ which may be associated with the formation of the second pyrochlore phase. The Ba 3*d*_{5/2} core level spectra give information of crystallinity of perovskite phase in surface region of the BSLT films.

It is clear that microstructure and electronic structure of the BSLT films are strongly dependent on the substitutional La concentration. The films exhibit the perovskite structure at low La substitution level ($0.1 \leq x \leq 0.5$) and the pyrochlore phase appearing at high La concentration ($0.75 \leq x \leq 1$). Furthermore, The La substitution in BST films would suppress the interfacial reaction with Si substrate. The 30-nm-thick BSLT ($x = 0.25$) thin films exhibits high crystallinity of perovskite structure in the surface region. XPS study indicates that the oxygen vacancy concentration decreases with La substitution. With respect to the BST ($x = 0$) thin film, the Fermi level shifts down for BSLT sample with $x = 0.1$ ascribed to the decreasing oxygen vacancy concentration, shifts up for BSLT sample with $x = 0.25$ attributed to the increasing La substitution level, and shifts down again for BSLT samples with $x \geq 0.5$ which may be associated with the second pyrochlore phase appearing. The above information could provide convincing demonstration to understand the field emission properties of BSLT coated Si tip arrays which will be discussed in the next section.

5.2 Field emission properties of Si tip arrays coated with BSLT thin films

It is found that the sol-gel BST coated Si tip arrays have demonstrated substantial enhancement of field emission. In order to further improve emission behavior, *n*-type doped coating is achieved by using La substitution in BST films. Field emission properties of Si tip arrays coated with BSLT thin film with different La concentrations

are investigated in this section. The effect of La concentration on J - E characteristic is provided firstly. Next the field emission stability is presented. The effective work function of BSLT coated Si tips is deduced using the F-N plot in the third part. Lastly the La effect on field emission mechanism is discussed.

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

Figure 5-12 illustrates the influence of annealing temperature on field emission of Si tip arrays coated with 30-nm-thick sol-gel derived BSLT with $x = 0.25$ thin films annealed at 700 and 750 °C. It is obvious that the field emission characteristic of the BSLT coated silicon tip arrays shows annealing temperature dependence. The threshold electric field is about 28.5 V/ μm for the arrays coated with 30-nm-thick BSLT ($x = 0.25$) layer annealed at 700 °C, while it is lowered to about 15 V/ μm for the sample annealed at 750 °C. Correlated to the previous microstructure findings, the BSLT ($x \geq 0.25$) thin film annealed at 700 and 750 °C is pyrochlore and perovskite structure respectively. It demonstrates that the coating with perovskite structure improves the field emission behavior of Si tip arrays. The n -type thin film could be achieved with La substitution Ba/Sr sites in the perovskite structure. Accordingly, the following samples with La substitution were annealed at 750 °C to investigate the effect of La concentration and the impact of thickness on field emission.

Figure 5-13 shows the effect of La concentration on field emission of Si tip arrays coated with 30-nm-thick sol-gel derived BSLT ($0 \leq x \leq 1$) thin films. The sample with $x = 0$ (BST) is annealed at 700 °C and the other samples are annealed at 750 °C. It is clear that BSLT ($x = 0.25$) coated Si tip arrays show the best emission behavior compared with others. The threshold electric field could be lowered from 36 V/ μm for bare Si arrays to 15 V/ μm for BSLT ($x = 0.25$) coated Si arrays. Moreover, it demonstrates that the emission characteristics of the BSLT coated Si arrays are strongly dependent on the La concentration. The values of threshold field are about 19, 21.5, 15, 17, 25, and 30.5 V/ μm , corresponding to the Si tip arrays coated with BSLT film with $x = 0, 0.1, 0.25, 0.5, 0.75$ and 1, respectively. The BSLT coatings with appropriate La concentration ($x = 0.25$ and 0.50) show the improvement of field emission of Si tip arrays with respect to BST ($x = 0$) coating, while the coatings with lower or higher La concentration could degrade the emission behavior.

In addition, the thickness effect on field emission of Si tip arrays coated with BSLT ($x = 0.25$) thin film annealed at 750 °C is investigated as shown in Figure 5-14. The BSLT-coated Si arrays demonstrate enhancement of field emission and their threshold field is much sensitive to BSLT film thickness. The values of threshold field are estimated about 22.7, 15, 18 and 18.2 V/ μm corresponding to the BSLT ($x = 0.25$) thin film with the thickness of 15, 30, 60 and 90 nm respectively. It is shown that the 30-nm-thick BSLT film has the lowest threshold field for field emission. In early

study, BST coatings also show a U-shape dependence of the threshold field on film thickness.

Figure 5-12 Field emission of Si tip arrays coated with 30-nm-thick sol-gel BSLT ($x = 0.25$) thin film annealed at 700 and 750 °C.

Figure 5-13 Field emission of Si tip arrays coated with 30-nm-thick sol-gel BSLT ($0 \leq x \leq 1$) thin films annealed at 750 °C. The arrays coated with BSLT ($x = 0.25$) yield the optimal emission performance.

Figure 5-14 Field emission of Si tip arrays coated with sol-gel BSLT ($x = 0.25$) thin films annealed at 750 °C with different thicknesses. The arrays coated with 30-nm-thick BSLT film show the optimal emission performance.

5.2.2 Field emission stability

Stabilities of emission current density of Si tip arrays coated with 30-nm-thick sol-gel BSLT ($0 \leq x \leq 1$) thin films are investigated as shown in Figure 5-15. The sample with $x = 0$ (BST) is annealed at 700 °C and the other samples are annealed at 750 °C. As stated previously, the initial current density was maintained around several $\mu\text{A}/\text{cm}^2$ for all samples and the applied electric field was then kept in constant during the measurement. Compared with bare Si arrays, the current densities of BSLT ($0 \leq x \leq 1$) coated arrays are stable and maintained at the same order during the measurement. The average emission current density J_{average} , standard deviation ΔJ , and fluctuation f

$(f=\Delta J/J_{\text{average}})$ are determined for these arrays. Si tip arrays coated with BST ($x = 0$) or BSLT ($x = 0.25$) film display a smaller fluctuation of 0.30 compared with the bare Si arrays with large fluctuation of 1.4. The emission stability is also influenced by the La concentration. The fluctuations of BSLT coated arrays with $x = 0, 0.1, 0.25, 0.5, 0.75$, and 1 are 0.30, 0.43, 0.30, 0.34, 0.43, and 0.51 respectively, which are listed in Table 5-3. Moreover, the stability of emission current density of Si arrays coated with 30-nm-thick sol-gel BSLT thin film ($x = 0.25$) annealed at 750 °C was studied for 12-hour measurement as shown in Figure 5-16. A small fluctuation of 0.37 is exhibited. It demonstrates that BSLT coated Si arrays is a promising electron source for cold cathode.

Figure 5-15 The emission current density stabilities of bare Si arrays (a), and Si arrays coated with BSLT thin films with $x = 0$ (b), 0.1 (c), 0.25 (d), 0.5(e), 0.75 (f), and 1 (g).

Figure 5-16 The emission current density stability of Si arrays coated with 30-nm-thick BSLT thin film ($x = 0.25$) for 12-hour measurement.

5.2.3 Analysis of emission data

It is found that the BSLT thin film coated Si tip arrays show substantial enhancement in field emission shown in J - E characteristics (Figure 5-13 and 5-14). The F-N equation [26-27], $I = AV^2 \exp(-B/V)$, is applied to analyze these emission data in this part. The effective work function of BSLT coated Si arrays is deduced using the F-N plot [11,19,121-122]. The detailed principle using the F-N plot has been stated in the early section 4.2.3.

Figure 5-17 The F-N plot of filed emission from bare Si tip arrays and Si tip arrays coated with 30-nm-thick BSLT ($0 \leq x \leq 1$) thin films with different La concentrations.

Figure 5-17 shows the F-N plot of the BSLT-coated Si tip arrays. The F-N plot yields the straight line with different slopes at high voltages. The straight line suggests the electron emission is controlled by tunneling through a potential barrier. Since the influence of the thickness on the sharpness of Si arrays could be omitted as shown in early SEM picture of Figure 4-20, the field enhancement factor β of BSLT coated Si tip is assumed to be the same as that of the bare Si tip. According to the F-N slope ($FNSL$) and Si work function of 4.3 eV (corresponding to the n-type silicon of 2 $\Omega\cdot\text{cm}$ resistivity), the effective work function of BSLT coated Si tips can be deduced by equation 4-11 and their values are estimated as 2.3, 3.2, 2.0, 2.2, 2.5 and 3.2 eV for Si tips coated with BSLT film with $x = 0, 0.10, 0.25, 0.50, 0.75$, and 1 respectively, as

listed in Table 5-3. Correlated to the J - E characteristics, the sample with a low effective work function reveals a small threshold electric field. It suggests that the improvement in field emission originates from the lowering of effective work function with BSLT coatings.

Table 5-3 The threshold field, the fluctuation of emission current density, the ratio of F-N plot slope ($FNSL_{BST}/FNSL_{Si}$), the effective work function of BSLT coated Si tip arrays as a function of La concentration.

x	Threshold	Fluctuation	$FNSL_{BST}$	ϕ_{BSLT}
	field ($\text{V}/\mu\text{m}$)		/ $FNSL_{Si}$	(eV)
0.00	19	0.30	0.40	2.3
0.10	21.5	0.43	0.64	3.2
0.25	15	0.30	0.31	2.0
0.50	17	0.34	0.37	2.2
0.75	25	0.43	0.44	2.5
1.00	30.5	0.51	0.63	3.2

5.2.4 La substitution effect on field emission mechanism

In summary, the field emission properties of Si tip arrays coated with BSLT with $0.1 \leq x \leq 1$ thin films have been systematically studied in this work. It is found that the BSLT coating with appropriate La concentration ($x = 0.25$) shows the improvement of field emission of Si tip arrays with respect to the BST ($x = 0$) coating. The threshold field can be lowered from 19 $\text{V}/\mu\text{m}$ for arrays coated with BST ($x = 0$) film to about 15 $\text{V}/\mu\text{m}$ for arrays coated with BSLT ($x = 0.25$) film. No

obvious improvement of field emission has been observed for coatings with lower ($x = 0.1$) and higher ($x \geq 0.75$) La concentration. The electron emission behavior shows La concentration dependence.

As discussed early, field emission from Si tip arrays coated with a wide band gap thin film is a three-step process, including supplying electrons to the thin film at the Si/film interface, transporting them through the bulk to the film surface, and emitting them into vacuum. These steps could be affected by the microstructure and electronic properties of BSLT coating with different La concentrations. The mechanism and enhancement of field emission of BSLT coated Si tip arrays are discussed in this part.

Correlated to the microstructural features, it is revealed that the microstructure of the BSLT film is strongly dependent on La concentration. In XRD study, the films exhibit perovskite structure at low La substitution level ($0 \leq x \leq 0.5$) and pyrochlore phase at high La concentration ($0.75 \leq x \leq 1$). The degraded emission behavior of arrays coated with high La concentration ($0.75 \leq x \leq 1$) could be related to the appearance of the pyrochlore phase. Moreover, studies using TEM image and XPS Ba $3d_{5/2}$ core level spectra show that the BSLT ($x = 0.25$) film has the well-developed perovskite structure in the surface region and the suppressed interfacial reaction. It is believed that the interfacial structure at the back contact and the surface structure at front contact could affect the supply of electrons into the film and electron emission into

vacuum, respectively. In our studies, it is found that the improvement of the crystallinity of perovskite structure in the surface region and the decrease of the interfacial reaction for the BSLT film ($x=0.25$) could benefit the field emission process. It is consistent with the findings in the BST coatings.

Furthermore, the electronic structure studies using the photoelectron spectroscopy also support that the BSLT ($x=0.25$) film is a promising coating on Si tip arrays to achieve the improvement of electron emission behaviors. La^{3+} cations, substituting $\text{Ba}^{2+}/\text{Sr}^{2+}$ sites in the lattice, act as a donor-type dopant in the film. Nevertheless the Fermi level shifts downward (with a value of -0.17 eV) for the film with a low La concentration ($x=0.1$) compared with BST ($x=0$) film. It could be associated with the remarkable decrease of oxygen vacancy concentration with La incorporation and correspondingly the electrons donated by oxygen vacancies are reduced. Therefore, there is a degraded field emission behavior of BSLT ($x=0.1$) coated arrays. With an appropriate concentration of La incorporation ($x=0.25$), the Fermi level shifts upward with a value of 0.15 eV with respect to BST film. The up-shift of the Fermi level yields a lower work function ($\phi = E_{\text{vacuum}} - E_f$). The lowering potential barrier implicates the increasing possibility of electrons with given energy tunneling into vacuum from the emitting surface. This is consistent with the analysis of the emission data using the F-N plot. The BSLT ($x=0.25$) coated Si arrays show the lowest effective work function as given in Table 5-3 and they exhibit the best emission

behavior correspondingly. However, further increasing La concentration ($x \geq 0.5$) results in downward shift of the Fermi level in these films. It is possible that the new phase appears at high La concentration and accordingly the electrons could not be effectively doped into the films. Consequently, the increasing effective work function (shown in Table 5-3) and the degrading field emission behavior of BSLT ($x \geq 0.5$) coated Si arrays are revealed. From the above discussions, it is concluded that BSLT ($x = 0.25$) coating is the promising candidate for field emission applications with the reduced interfacial reaction, well-developed perovskite structure in surface region, and upwards-moved Fermi level, which benefit field emission process.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

In this thesis, ferroelectric $(\text{Ba}_{0.65}\text{Sr}_{0.35})\text{TiO}_3$ (BST) and $(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_{3+y}$ (BSLT with $0.1 \leq x \leq 1$) thin films have been fabricated on silicon tip arrays using the sol-gel technique for potential field emission applications. Characterizations of the thin films and field emission properties of the ferroelectric thin film coated Si tip arrays have been systematically studied. The field emission mechanism of BST and BSLT ($0.1 \leq x \leq 1$) coated Si tip arrays has been discussed by correlating to the microstructural features and electronic properties of the coatings. The main conclusion and recommendations are summarized as follows.

The sol-gel technique has been successfully employed to fabricate the ferroelectric BST and BSLT thin films. TGA and DTA have been used to identify the thermal

treatment route of the thin film deposition process. Two-step pyrolyzing procedures at 200 and 400 °C prior to post-annealing were performed and the thin films were annealed at selected temperatures.

The structural feature and the compositional analysis of the BST films have been investigated using XRD, TEM, SIMS, and FT-IR spectroscopy. The microstructure of BST film is strongly dependent on the annealing temperature. The BST thin films exhibit an amorphous phase when annealed at 600 °C, and the perovskite structure while annealed between 650 and 700 °C. Severe interfacial reaction occurs between Si substrate and BST film annealed above 750 °C. Moreover, the microstructure of BST thin films annealed at 700 °C shows thickness dependence. The crystallinity of perovskite structure is improved with the increase of BST film thickness. The 15-nm-thick BST film is amorphous in nature, and then the polycrystalline perovskite grains develop in the thicker film with an amorphous layer existing in the bottom region of film. SIMS depth profile shows that the BST/Si interface has a solid-state reaction layer of $(\text{Ba,Sr})\text{Ti}_x\text{Si}_y\text{O}_z$. The FT-IR spectroscopy indicates that the interfacial layer of samples annealed above 750 °C changes the chemical bonding configuration.

The formation of chemical compound and electronic structure of BST films have been studied using XPS technique. The Fermi level shifts up for BST films with increasing annealing temperature from 600 to 750 °C, and then moves back slightly after

annealed at 800 °C. the upward shift of the Fermi level from 600 to 750 °C is attributed to the increasing oxygen vacancy concentration in films, and the downward shift of the Fermi level at 800 °C is associated with the severe interfacial reaction. The crystallinity information of BST thin films with different thicknesses is obtained from the studies of XPS Ba $3d_{5/2}$ core level and valence band spectra. It provides the evidence of the structural evolution, and the results are consistent to the previous XRD and TEM results.

The BST coated Si tip arrays show substantial improvement of field emission compared with bare Si tip arrays. The threshold electric field could be lowered substantially from 36 V/ μm for bare Si tip arrays to about 19 V/ μm for 30-nm-thick BST coated Si tip arrays annealed at 700 °C. The emission behavior of BST coated Si arrays shows annealing temperature dependence, and the degraded field emission behavior is found at lower (≤ 650 °C) or higher (≥ 750 °C) annealing temperature. The thickness of BST coatings also affects the field emission properties significantly with U-shape dependence of the threshold field on film thickness. The 30-nm-thick BST thin film demonstrates the lowest threshold field for field emission. In addition, the BST coatings considerably improve the electron emission stability of Si tip arrays. Analysis of the emission data (J - E characteristic) using the F-N plot suggests that electron emission is controlled by tunneling mechanism, and the improvement in

electron emission originates from the lowering of effective work function with BST coatings.

The field emission mechanism of BST-modified Si tip arrays has been discussed based on the proposed model. It is found that the promising candidate for field emission applications is the BST film with high crystallinity of perovskite structure in surface region, decreased interfacial reaction, increased oxygen vacancy concentration and upwards-moved Fermi level. Meanwhile, the thickness dependence originates from the developed microstructural features in BST films. The increasing thickness of BST films could limit the supply of the emitted electrons.

In the case of BSLT ($0.1 \leq x \leq 1$) thin films, the effect of La concentration has been studied to optimize field emission properties. Based on XRD, XPS Ba $3d_{5/2}$ core level spectra and TEM investigation, it is found that the microstructure of BSLT film is strongly dependent on La concentration. The films exhibit perovskite structure at low La substitution level ($0.1 \leq x \leq 0.5$) and second pyrochlore phase at high La concentration ($0.75 \leq x \leq 1$). It is also found that La substitution in BST film suppresses the interfacial reaction with Si substrate. The 30-nm-thick BSLT ($x = 0.25$) thin film shows high crystallinity of perovskite structure in surface region.

XPS has been applied to study the chemical compound formation and electronic structure of the 30-nm-thick BSLT ($0.1 \leq x \leq 1$) thin films. The oxygen vacancy concentration decreases due to La incorporation according to the principle of electroneutrality. Since both oxygen vacancy and La substitution donate electrons into the system, it is expected that doped electrons are dominated by oxygen vacancies at low La concentration and then be governed by substitutional La at high La concentration. With respect to BST ($x = 0$) film, The Fermi level shifts down for BSLT sample with $x = 0.1$ ascribed to the reduced doped electrons due to decreasing oxygen vacancy concentration, shifts up for BSLT sample with $x = 0.25$ attributed to the increasing donated electrons owing to increasing La substitution level, and shifts down again for BSLT samples with $x \geq 0.5$ which may be associated with the pyrochlore phase.

The BSLT ($x = 0.25$) coated Si tip arrays show the best improvement in field emission compared with other samples. The threshold field can be lowered from 19 V/ μm for arrays with 30-nm-thick BST coating to about 15 V/ μm for arrays with 30-nm-thick BSLT ($x = 0.25$) coating. The sample also shows the improvement of electron emission stability with the fluctuation of 0.30. The emission behavior shows La concentration dependence, and lower ($x = 0.1$) or higher ($x \geq 0.5$) La concentration can not result in a further improvement of field emission. By the analysis of emission data (J - E characteristics) using the F-N plot, it is found that the

improvement in field emission originates from the lowering of effective work function.

Correlated to the microstructure and electronic structure, the BSLT ($x = 0.25$) film shows high crystallinity of perovskite structure in the surface region, suppressed interfacial reaction, and increasing Fermi level. Therefore, BSLT ($x = 0.25$) coated Si tip arrays show the enhancement of field emission.

A conformal, stable and n -type doped BST and BSLT ($0.1 \leq x \leq 1$) thin film coating on Si tip arrays can be achieved with simple sol-gel method. The sol-gel BST and BSLT coatings have been shown to be a practical way to improve field emission of Si tip arrays. The field emission properties are closely correlated to the microstructure and electronic properties of ferroelectric thin films.

6.2 Recommendations for future work

In this thesis, it is evident that the sol-gel derived BST and BSLT ($0.1 \leq x \leq 1$) ferroelectric thin films exhibit a good prospect for potential field emission device applications. The enhanced field emission properties of coated arrays sound obviously compared with that of uncoated arrays. Thus it is highly recommended to extend the work to two possible areas of further work. The first area is to successively investigate fundamental problems in order to fully understand field emission mechanism of BSLT

($0 \leq x \leq 1$) coated Si arrays. The second area is to use other deposition techniques to fabricate ferroelectric thin film coated Si tip arrays to further improve field emission properties.

In this thesis, Si tip arrays coated with sol-gel BST and BSLT ($0 \leq x \leq 1$) thin films exhibit relatively low threshold field and improved emission stability. The corresponding mechanisms are discussed. Whereas, there are still some fundamental problems remaining to be investigated to fully understand the field emission of ferroelectric thin film coating on Si arrays and these can be associated with the basic properties of the film. For understanding the back and front contacts, it involves the development of diagnostic technique to find out the local physical properties such as conduction/valence band offset between coatings and Si, work function, electron affinity, and geometrical feature of films and this may require techniques having analytical capability with nanoscale resolution. For understanding the mechanism responsible for charge transport in the film, one has to deal with the electronic properties of a rather complicated medium. Such a medium includes many irregularities in the film, as we have observed interface layer, amorphous and nanostructure polycrystalline structure in our thin films. These issues are actually challenges for theoretical and experimental research and also the frontier in the field of condensed matters physics.

Sol-gel technique has been demonstrated to be a very effective route for growing multi-element thin films with ease of stoichiometry control, and therefore La substitution in BST films can be well controlled. However, it requires a high post annealing temperature in order to achieve a perovskite structure, an ideal coating for field emission. The high-temperature process results in the solid-state interfacial reaction with Si diffusion into the film. The produced interfacial layer deteriorates the emission performance and thus reliability of the emitter. Therefore, it is recommended to employ other deposition methods such as CVD and sputtering technique to investigate the field emission of ferroelectric thin film coating on Si tip arrays. It is expected to obtain a *n*-type doped film with perovskite structure processed at a relatively low temperature, leading to a small amount of interface-reaction layer. In addition, these deposition methods could provide better coverage of coatings on Si tip arrays than sol-gel techniques. Some preliminary results using sputtering technique have been obtained [133].

AUTHOR'S PUBLICATIONS

Invited Talk:

- [1] X. F. Chen, W. G. Zhu, **H. Lu**, J. S. Pan, H. J. Bian, O. K. Tan, and C. Q. Sun, "Si Field Emitter Arrays Coated with Thin Ferroelectric Films", 5th Asian Meeting on Electroceramics (AMEC-5), Thailand, Dec. 2006, accepted (invited).

Journal Paper:

- [2] **H. Lu**, J. S. Pan, X. F. Chen, W. G. Zhu, and O.K. Tan, "Influence of annealing temperature on the band structure of sol-gel $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ thin films on n -type Si(100)", Appl. Phys. Lett., 88 (2006)132907.
- [3] **H. Lu**, X. F. Chen, W. G. Zhu, J. S. Pan, and O. K. Tan, "Annealing temperature effect on field emission of silicon emitter arrays with sol-gel $(\text{Ba}_{0.65}\text{Sr}_{0.35})\text{TiO}_3$ coatings", Ferroelectrics, 334 (2006) 253.
- [4] **H. Lu**, J. S. Pan, X. F. Chen, and W. G. Zhu, "Field emission of silicon emitter arrays coated with sol-gel $(\text{Ba}_{0.65}\text{Sr}_{0.35})_{1-x}\text{La}_x\text{TiO}_3$ thin films", J. Appl. Phys., 102 (2007) 014113.
- [5] X. F. Chen, **H. Lu**, W. G. Zhu, and O. K. Tan, "Enhanced field emission of silicon tips coated with sol-gel derived $(\text{Ba}_{0.65}\text{Sr}_{0.35})\text{TiO}_3$ thin film", Surf. &

Coating Technl., 198 (2005) 266.

- [6] X. F. Chen, **H. Lu**, H. J. Bian, W. G. Zhu, C. Q. Sun, and O. K. Tan, "Electron emission of silicon field emitter arrays coated with N-doped SrTiO₃ film", Journal of Electroceramics, 16 (2006) 419.
- [7] Y. K. Lu, W. Zhu, Y. Zhang, **H. Lu**, and R. Gopalkrishnan, "HfO₂Nano-thin Films Grown by Laser MBE for Gate Dielectric Application", NanoSingapore 2006: IEEE Conference on Emerging Technologies - Nanoelectronics - Proceedings, 2006, p 273-277.
- [8] **H. Lu**, X. F. Chen, J. S. Pan, and W. G. Zhu, "Thickness effect on field electron emission of silicon emitter arrays coated with sol-gel Ba_{0.65}Sr_{0.35}TiO₃ and (Ba_{0.65}Sr_{0.35})_{0.75}La_{0.25}TiO₃ thin films", Thin Solid Films, Submitted.

Conference Papers:

- [1] **H. Lu**, X. F. Chen, J. S. Pan, W. G. Zhu, and O. K. Tan, "Electron emission properties of (Ba_{0.65}Sr_{0.35})_{1-x}La_xTiO₃-coated Si field emitter arrays", 5th Asian Meeting on Electroceramics (AMEC-5), Thailand, Dec. 2006, accepted.
- [2] X. F. Chen, **H. Lu**, W. G. Zhu, and J. S. Pan, "Ferroelectric (Ba,Sr)_{1-x}La_xTiO₃ Thin Films on Si Arrays for Electron Field Emission", The 16th International Symposium on the Application of Ferroelectrics, Japan, Mar. 2007.

BIBLIOGRAPHY

- [1] R. H. Fowler and L. W. Nordheim, “Electron emission in intense electric fields”, Proc. Roy. Soc. (London) A, 119 (1928) 173.
- [2] C. Spindt, “A thin-film field-emission cathode”, J. Appl. Phys., 39 (1968) 3504.
- [3] D. Temple, W. D. Palmer, L. N. Yadon, J. E. Mancusi, D. Vellenga, and G. E. McGuire, “Silicon field emitter cathodes: Fabrication, performance, and applications”, J. Vac. Sci. Technol. A, 16 (1998) 1980.
- [4] O. Ternyak, R. Akhvediani, A. Hoffman, W. K. Wong, S. T. Lee, Y. Lifshitz, S. Daren, and E. Cheifetz, “Field electron emission from undoped, continuous, submicron-thick diamond films”, J. Appl. Phys., 98 (2005) 123522.
- [5] R. H. Baughman, A. Auvar, Zakhidov, and W. A. de Heer, “Carbon nanotubes-the route toward applications”, Science, 297 (2002) 787.
- [6] R. Z. Wang, H. Zhou, X. M. Song, B. Wang, H. Wang, and H. Yan, “Effects of phase formation on electron field emission from BN films”, J. Cryst. Growth, 291 (2006) 18.
- [7] J. Chen, S. Z. Deng, and N. S. Xu, “Field emission from crystalline copper sulphide nanowire arrays”, Appl. Phys. Lett., 80 (2002) 3620.
- [8] A. Ghis, R. Meyer, P. Ramband, F. Levy, and T. Leroux, “Sealed vacuum devices: Fluorescent microtip”, IEEE Trans. Electron Devices, 38 (1991) 2320.

Bibliography

- [9] K. L. Jensen, R. H. Abrams, and R. K. Parker, "Field emitter array development for high frequency applications", *J. Vac. Sci. Technol. B*, 11 (1993) 468.
- [10] S. H. Xia, J. Liu, D. F. Cui, J. H. Han, S. F. Chen, and L. Wang, "Investigation on a novel vacuum microelectronic pressure sensor with stepped field emission array", *J. Vac. Sci. Technol. B*, 15 (1997) 153.
- [11] V. V. Zhirnov, W. B. Choi, J. J. Cuomo, and J. J. Hren, "Diamond coated Si and Mo field emitters: diamond thickness effect", *Appl. Surf. Sci.*, 94/95 (1996) 123.
- [12] A. R. Krauss et al., "Electron field emission for ultrananocrystalline diamond films", *J. Appl. Phys.*, 89 (2001) 2958.
- [13] M. Y. Jung, D. W. Kim, S. S. Choi, Y. S. Kim, Y. Kuk, K. C. Park, and J. Jang, "Fabrication of a nanosize Si-tip coated with a thin diamond-like carbon film", *Thin Solid Films*, 294 (1997) 157.
- [14] T. Sugino, S. Kawasaki, K. Tanioka, and J. Shirafuji, "Electron emission from boron nitride coated Si field emitters", *Appl. Phys. Lett.*, 71 (1997) 2704.
- [15] B. V. Spitsyn, V. V. Zhirnov, A. N. Blaut-Bachev, L. V. Bormatova, A. F. Belyanin, P. V. Pashchenko, L. L. Bouilov, and E. I. Givargizov, "Field emitters based on Si tips with AlN coating", *Diamond and Related Materials*, 7 (1998) 692.
- [16] Y. J. Yoon, G. B. Kim, and H. K. Baik, "Effects of phase and thickness of cobalt silicide on field emission properties of silicon emitters", *J. V. Sci. Technol. B*, 17 (1999) 627.
- [17] W. A. Mackie, J. L. Morrissey, C. H. Hinrichs, and P. R. Davis, "Field emission from hafnium carbide", *J. Vac. Sci. Technol. A*, 10 (1992) 2852.
- [18] T. Xie, W. A. Mackie, and P. R. Davis, "Field emission from ZrC films on Si and Mo single emitters and emitter arrays", *J. Vac. Sci. Technol. B*, 14 (1996) 2090.

Bibliography

- [19] W. P. Kang, A. Wisitsora-at, J. L. Davidson, O. K. Tan, W. Zhu, Q. Li, and J. F. Xu, "Electron emission from silicon tips coated with sol-gel $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ ferroelectric thin film", *J. Vac. Sci. Technol. B*, 19 (2001) 1073.
- [20] W. P. Kang, A. Wisitsora-at, J. L. Davidson, O. K. Tan, W. Zhu, Q. Li, and J. F. Xu, "Effect of annealing temperature on the electron emission characteristics of silicon tips coated with $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ thin film", *J. Vac. Sci. Technol. B*, 21 (2003) 453.
- [21] W. Zhu, O. K. Tan, J. Ray, M. A. Imam, and X. F. Chen, "Sol-gel $(\text{Ba}_{0.67}\text{Sr}_{0.33})\text{Ti}_x\text{O}_y$ thin films for flat panel display application", *Integr. Ferroelectr.*, 49 (2002) 221.
- [22] G. Rosenman, D. Shur, Ya. E. Krasik, and A. Duaevsky, "Electron emission from ferroelectrics", *J. Appl. Phys.*, 88 (2000) 6109.
- [23] H. Riege, I. Boscolo, J. Handerek, and U. Herleb, "Features and technology of ferroelectric electron emission", *J. Appl. Phys.*, 84 (1998) 1602.
- [24] D. M. Smyth, "The defect chemistry of metal oxides", Oxford University Press, New York, 2000.
- [25] D. Temple, "Recent progress in field emitter array development for high performance applications", *Mater. Sci. Eng. R*, 24 (1999) 185.
- [26] R. Gomer, "Field emission and field ionization", American Institute of Physics, New York, 1993.
- [27] W. Zhu, "Vacuum microelectronics", John Wiley & Sons, New York, 2001.
- [28] I. Brodie and P. R. Schwoebel, "Vacuum electronic devices", *Proceedings of the IEEE*, 82 (1994) 1006.
- [29] K. L. Jensen and A. K. Ganguly, "Numerical simulation of field emission from silicon", *J. Vac. Sci. Technol. B*, 11 (1993) 371.
- [30] K. L. Jensen, "Improved Fowler–Nordheim equation for field emission from semiconductors" *J. Vac. Sci. Technol. B*, 13 (1995) 516.

Bibliography

- [31] K. L. Jensen and A. K. Ganguly, "Time dependent, self-consistent simulations of field emission from silicon using the Wigner distribution function", J. Vac. Sci. Technol. B, 12 (1994) 770.
- [32] K. R. Shoulder, "Microelectronics using electron-beam-activated machining techniques", Advances in Computers, 2 (1961) 135.
- [33] B. V. Spitsyn, L. L. Bouilov, and B. V. Derjaguin, "Vapor growth of diamond on diamond and other surfaces ", J. Cryst. Growth, 52 (1981) 219.
- [34] F. J. Himpsel, J. A. Knapp, J. A. Van Vechten, and D. E. Eastman, "Quantum photoyield of diamond (111)-A stable negative-affinity emitter", Phys. Rev. B, 20 (1979) 624.
- [35] I. L. Krainsky and V. M. Asnin, "Negative electron affinity mechanism for diamond surface", Appl. Phys. Lett., 72 (1998) 2574.
- [36] S. S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, "Self-oriented regular arrays of carbon nanotubes and their field emission properties", Science, 283 (1999) 512.
- [37] X. Xu and G. R. Brandes, "A method for fabricating large-area, patterned, carbon nanotube field emitters", Appl. Phys. Lett., 74 (1999) 2549.
- [38] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, "Synthesis of large arrays of well-aligned carbon nanotubes of glass", Science, 282 (1998) 1105.
- [39] E. J. Chi, J. Y. Shim, H. K. Baik, and S. M. Lee, "Fabrication of amorphous-carbon-nitride field emitters", Appl. Phys. Lett., 71 (1997) 324.
- [40] Y. X. Wang, Y. A. Li, W. Feng, W. Q. Li, C. H. Zhao, L. H. Liu, K. C. Feng, and Y. N. Zhao, "Influence of thickness on field emission characteristics of AlN thin films", Appl. Surf. Sci., 243 (2005) 394.
- [41] W. A. Mackie, J. L. Morrissey, C. H. Hinrichs, and P. R. Davis, "Field emission from hafnium carbide", J. Vac. Sci. Technol. A, 10 (1992) 2852.

- [42] Z. S. Wu, S. Z. Deng, J. Zhou, N.S. Xu, J. Chen, and J. Chen, "Needle-shaped silicon carbide nanowires: Synthesis and field electron emission properties", *Appl. Phys. Lett.*, 80 (2002) 3829.
- [43] C. J. Lee, T. J. Lee, S. C. Lyu, Y. Zhang, H. Ruh, and H.J. Lee, "Field emission from well-aligned zinc oxide nanowires grown at low temperature", *Appl. Phys. Lett.*, 81 (2002) 3648.
- [44] J. Chen, S. Z. Deng, N. S. Xu, W. X. Zhang, X. G. Wen, S. H. Yang, "Temperature dependence of field emission from cupric oxide nanobelt films", *Appl. Phys. Lett.*, 83 (2003) 746.
- [45] Y. H. Lee, C. H. Choi, Y. T. Jang, E. K. Kim, B. K. Ju, N. K. Min, and J. H. Ahn, "Tungsten nanowires and their field electron emission properties", *Appl. Phys. Lett.*, 81 (2002) 745.
- [46] J. Zhou, S. Z. Deng, N. S. Xu, J. Chen, and J. C. She, "Synthesis and field-emission properties of aligned MoO₃ nanowires", *Appl. Phys. Lett.*, 83 (2003) 653.
- [47] N. S. Xu and S. E. Huq, "Novel cold cathode materials and applications", *Mater. Sci. Eng. R*, 48 (2005) 47.
- [48] T. Utsumi, "Keynote address vacuum microelectronics: what's new and exciting", *IEEE Trans. Electron Devices*, 38 (1991) 2276.
- [49] N. S. Xu, J. C. She, S. E. Huq, S. Z. Deng, and J. Chen, "Theoretical study of the threshold field for field electron emission from amorphous diamond thin films", *J. Vac. Sci. Technol. B*, 19 (2001) 1059.
- [50] J. C. She, S. E. Huq, J. Chen, S. Z. Deng, and N. S. Xu, "Comparative study of electron emission characteristics of silicon tip arrays with and without amorphous diamond coating", *J. Vac. Sci. Technol. B*, 17 (1999) 592.
- [51] A. Zangwill, "Physics at surface", Cambridge University Press, Cambridge, 1988.

Bibliography

- [52] W. Zhu, G. P. Kochanski, S. Jin, L. Seibles, D. Jacobson, M. McCormack, and A. White, "Electron field emission from ion implanted diamond", Appl. Phys. Lett., 67 (1995) 1157.
- [53] Z. H. Huang, P. H. Cutler, N. M. Miskovsky, and T. E. Sullivan, "Theoretical study of field emission from diamond", Appl. Lett. Phys., 65 (1994) 2562.
- [54] Y. Muto, T. Sugino, J. Shirafuji, and K. Kobachi, "Electrical conduction in undoped diamond films prepared by chemical vapor deposition", Appl. Phys. Lett., 59 (1991) 843.
- [55] R. Schlessner et. al., "Energy distribution of field emitted electrons from diamond coated molybdenum tips", Appl. Phys. Lett., 70 (1997) 1596.
- [56] M. L. Yu, H. S. Kim, B.W. Hussey, T. H. Chung, and W. A. Mackie, "Energy distributions of field emitted electrons from carbide tips and tungsten tips with diamondlike carbon coatings", J. Vac. Sci. Technol. B, 14 (1996) 3797.
- [57] N. S. Xu and R. V. Latham, "Coherently scattered hot electrons emitted from MIM graphite microstructures deposited on broad-area vacuum-insulated high-voltage electrodes", J. Phys. D: Appl. Phys., 19 (1986) 477.
- [58] Y. D. Kim, W. Choi, H. Wakimoto, S. Usami, H. Tomokage, and T. Ando, "Direct observation of electron emission site on boron-doped polycrystalline diamond thin films using an ultra-high-vacuum scanning tunneling microscope", Appl. Phys. Lett., 75 (1999) 3219.
- [59] J. B. Cui, J. Ristein, and L. Ley, "Low-threshold electron emission from diamond", Phys. Rev. B, 60 (1999) 16135.
- [60] M. W. Geis et al., "Comparison of electric field emission from nitrogen-doped, type Ib diamond, and boron-doped diamond", Appl. Phys. Lett., 68 (1996) 2294.
- [61] S. R. P. Silva, G. A. Amaratunga, and K. Okano, "Modeling of the electron field emission process in polycrystalline diamond and diamond-like carbon thin films", J. Vac. Sci. Technol. B, 17 (1999) 557.

- [62] G. A. J. Amaratunga and S. R. P. Silva, "Nitrogen containing hydrogenated amorphous carbon for thin-film field emission cathodes", *Appl. Phys. Lett.*, 68 (1996) 2529.
- [63] J. D. Shovlin and M. E. Kordesch, "Electron emission from chemical vapor deposited diamond and dielectric breakdown", *Appl. Phys. Lett.*, 65 (1994) 863.
- [64] O. Groning, O. M. Kuttel, P. Groning, and L. Schlapbach, "Field emitted electron energy distribution from nitrogen-containing diamondlike carbon", *Appl. Phys. Lett.*, 71 (1997) 2253.
- [65] P. W. May, S. Hohn, M. N. R. Ashfold, W. N. Wang, N. A. Fox, T. J. Davis, and J. W. Steeds, "Field emission from chemical vapor deposited diamond and diamond-like carbon films: Investigations of surface damage and conduction mechanisms", *J. Appl. Phys.*, 84 (1998) 1618.
- [66] M. W. Geis, N. N. Efrenow, K. E. Krohn, J. C. Twichell, T. M. Lyszczarz, R. Kalish, J. A. Greer, and M. D. Tabat, "A new surface electron-emission mechanism in diamond cathodes", *Nature*, 393 (1998) 431.
- [67] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, "Introduction to ceramics", 2nd ed., John Wiley & Sons, Singapore, 1976.
- [68] T. M. Shaw, S. Troler-Mckinstry, and P. C. McIntyre, "The properties of ferroelectric films at small dimensions", *Annu. Rev. Mater. Sci.*, 30 (2000) 263.
- [69] A. I. Kingon, S. K. Streiffer, C. Basceri, and S. R. Summerfelt, "High-permittivity perovskite thin films for dynamic random-access memories", *Mater. Res. Soc. Bull.*, 21, No.7 (1996) 46.
- [70] R. E. Jones and S. B. Desu, "Process integration for nonvolatile ferroelectric memory fabrication", *Mater. Res. Soc. Bull.*, 21, No.7 (1996) 4655.
- [71] W. Zhu, O. K. Tan, Q. Yan, and J. T. Oh, "Microstructure and hydrogen gas sensitivity of amorphous (Ba,Sr)TiO₃ thin film sensors", *Sensor Actuator B*, 65 (2000) 366.

Bibliography

- [72] D. L. Polla and L. F. Francis, "Ferroelectric thin films in microelectromechanical systems applications", *Mater. Res. Soc. Bull.*, 21, No.7 (1996) 46.
- [73] P. M. Gasperin, "Ditatanate de Lanthane", *Acta Cryst. B*, 31(1975) 2129.
- [74] A. V. Prasadaraao, U. Selvaraj, S. Komarneni, and A. S. Bhalla, "Grain orientation in sol-gel derived $\text{Ln}_2\text{Ti}_2\text{O}_7$ ceramics ($\text{Ln}=\text{La}, \text{Nd}$)", *Material Lett.*, 12 (1991) 306.
- [75] S. Nanamatsu, M. Kimura, K. Doi, S. Matsushita, and N. Yamada, "A new ferroelectric: $\text{La}_2\text{Ti}_2\text{O}_7$ ", *Ferroelectrics*, 8 (1974) 511.
- [76] M. Kimura, S. Nanamatsu, K. Doi, S. Matsushita, and M. Takahashi, "Electrooptic and piezoelectric properties of $\text{La}_2\text{Ti}_2\text{O}_7$ single crystal", *Jpn. J. Appl. Phys.*, 11 (1972) 904.
- [77] M. Uno, A. Kosuga, M. Okui, K. Horisaka, and S. Yamanaka, "Photoelectrochemical study of lanthanide titanium oxide, $\text{Ln}_2\text{Ti}_2\text{O}_7$ ($\text{Ln}=\text{La}, \text{Sm}, \text{and Gd}$)", *J. of Alloys Compounds*, 400 (2005) 270.
- [78] R. C. Ewing, W. J. Weber, and J. Lian, "Nuclear waste disposal-porychlore ($\text{A}_2\text{B}_2\text{O}_7$): Nuclear waste form for the immobilization of plutonium and "minor" actinides", *J. Appl. Phys.*, 95 (2004) 5949.
- [79] F. Amy, A. Wan, A. Kahn, F. J. Walker, and R. A. McKee, "Band offsets at heterojunctions between SrTiO_3 and BaTiO_3 and $\text{Si}(100)$ ", *J. Appl. Phys.*, 96 (2004) 1601.
- [80] F. Amy, A. S. Wan, A. Kahn, F. J. Walker, and R. A. McKee, "Surface and interface chemical composition of thin epitaxial SrTiO_3 and BaTiO_3 films: Photoemission investigation", *J. Appl. Phys.*, 96 (2004) 1635.
- [81] S. A. Chambers, Y. Liang, Z. Yu, R. Droopad, J. Ramdani, and K. Eisenbeiser, "Band discontinuities at epitaxial $\text{SrTiO}_3/\text{Si}(001)$ ", *Appl. Phys. Lett.*, 77 (2000) 1662.

Bibliography

- [82] V. E. Henrich and P. A. Cox, "The surface science of metal oxides", Cambridge University Press, Cambridge, 1994.
- [83] M. Dawber, J. F. Scott, and A. J. Hartmann, "Effect of donor and acceptor dopants on schottky barrier heights and vacancy concentrations in barium strontium titanate", J. Eur. Ceram. Soc., 21 (2001) 1633.
- [84] S. W. Robey, L. T. Hudson, C. Eylem, and B. Eichirn, "Substitution-induced midgap states in the mixed oxides $R_x\text{Ba}_{1-x}\text{TiO}_{3-\delta}$ with $R=\text{Y}$, La , and Nd ", Phys. Rev. B, 48 (1993) 562.
- [85] M. Copel, J. D. Baniecki, P. R. Duncombe, D. Kotecki, R. Laibowitz, D. A. Neumayer, and T. W. Shaw, "Compensation doping of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films", Appl. Phys. Lett., 73 (1998) 1832.
- [86] Q. Zou, H. Ruda, B. G. Yacobi, and M. Farrell, "Microstructural characterization of donor-doped lead zirconate titanate films prepared by sol-gel processing", Thin Solid Films, 402 (2002) 65.
- [87] Y. Park, V. Choong, Y. Gao, B. R. Hsieh, and C. W. Tang, "Work function of indium tin oxide transparent conductor measured by photoelectron spectroscopy", Appl. Phys. Lett., 68 (1996) 2699.
- [88] N. Shanthi and D. D. Sarma, "Electronic structure of electron doped SrTiO_3 : $\text{SrTiO}_{3-\delta}$ and $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ", Phys. Rev. B, 57 (1998) 2153.
- [89] X. G. Guo, X. S. Chen, Y. L. Sun, L. S. Sun, X. h. Zhou, and W. Lu, "Electronic band structure of Nb doped SrTiO_3 from first principle calculation", Phys. Lett. A, 317 (2003) 501.
- [90] M. Copel, P. R. Duncombe, D. A. Neumayer, T. M. Shaw, and R. M. Tromp, "Metallization induced band bending of $\text{SrTiO}_3(100)$ and $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ " Appl. Phys. Lett., 70 (1997) 3227.
- [91] M. W. Cole, P. C. Joshi, and M. H. Ervin, "La doped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films for tunable device applications", J. Appl. Phys., 89 (2001) 6336.

Bibliography

- [92] S. Saha and S. B. Krupanidhi, "Large reduction of leakage current by graded-layer La doping in $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films", *Appl. Phys. Lett.*, 79 (2001) 111.
- [93] C. P. de Araujo, J. F. Scott, and G. W. Taylor, "Ferroelectric thin films: synthesis and basic properties", Gordon and Breach, New York, 1994.
- [94] A. Fujimori et al., "Doping-induce changes in the electronic structure of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$: limitation of the one-electron rigid-band model and the Hubbard model", *Phys. Rev. B*, 46 (1992) 9841.
- [95] A. Fujimori, Y. Tokura, and T. Arima, "Optical-conductivity spectra of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$: Filling-dependent effect of the electron correlation", *Phys. Rev. B*, 46 (1992) 11167.
- [96] R. Ramakumar, K. P. Jain, and R. Kumar, "Electron-correctlation effects on the properties of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ ", *Phys. Rev. B*, 50 (1994) 10122.
- [97] D. A. MacLean, H. N. Ng, and J. E. Greedan, "Crystal structure and crystal chemistry of the RETiO_3 perovskite: $\text{RE}=\text{La, Nd, Sm, Gd, Y}$ ", *J. Solid State Chem.*, 30 (1979) 35.
- [98] Y. Tokura, Y. Taguchi, Y. Okada, Y. Fujishima, and T. Arima, "Filling dependence of electronic properties on the verge of metal-mott-insulator transition in $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ", *Phys. Rev. Lett.*, 70 (2126) 1993.
- [99] X. F. Chen, W. Q. Lu, W. Zhu, S. Y. Lim, and S. A. Akbar, "Structure and thermal analysis on phase evolution of sol-gel $(\text{Ba,Sr})\text{TiO}_3$ thin films ", *Surf. & Coatings Technl.*, 167 (2003) 203.
- [100] M. K. Zhu, Y. H. Yang, X. H. Li, B. Wang, H. Wang, and H. Yan, "Preparation of $\text{Ba}_2\text{Si}_2\text{TiO}_8$ thin films by magnetron sputtering", *Microelectronic Engineering*, 66 (2003) 745.
- [101] U. Breuer, W. Krumpfen, and F. Fitsilis, "XRF and SIMS/SNMS analyses of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ dielectrics", *Anal. Bioanal. Chem.*, 375 (2003) 906.

- [102] V. P. Tolstoy, I. Chernyshova, and V. A. Skryshevsky, "Handbook of infrared spectroscopy of ultrathin films", John Wiley & Sons, New York, 2003.
- [103] S. S. A. Seo, H. N. Lee, and T. W. Noh, "Infrared spectroscopy of CaTiO_3 , SrTiO_3 , BaTiO_3 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films, and $(\text{BaTiO}_3)_5/(\text{SrTiO}_3)_5$ superlattice grown on $\text{SrRuO}_3/\text{SrTiO}_3(001)$ substrates", *Thin Solid films*, 486 (2005) 94.
- [104] K. Matsui, M. Taga, and T. Kobayashi, "Correlation between fourier-transform-infrared (FTIR) spectra and temperature dependence of dielectric properties of SrTiO_3 thin films", *Jpn. J. Appl. Phys.*, 32 (1993) L796-798.
- [105] E. J. H. Lee, F. M. Pontes, E. R. Leite, E. Longo, R. Magnani, P. S. Pizani, and J. A. Varela, "Effects of post-annealing on the dielectric properties of $\text{Au/BaTiO}_3/\text{Pt}$ thin film capacitors", *Materials Letters*, 58 (2004) 1715.
- [106] T. G. Mayerhofer and H. H. Dunken, "Single-crystal IR spectroscopic investigation on fresnoite, Sr-fresnoite and Ge-fresnoite", *Vibrational Spectroscopy*, 25 (2001) 185.
- [107] H. Lu, J. S. Pan, X. F. Chen, W. Zhu, and O. K. Tan, "Influence of annealing temperature on the band structure of sol-gel $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ thin films on *n*-type $\text{Si}(100)$ ", *Appl. Phys. Lett.*, 88 (2006) 132907.
- [108] J. F. Moulder, W. F. Stryckle, P. E. Sobol, and K. Bomben, "Handbook of X-ray Photoelectron Spectroscopy", Perkin-Elmer Corporation (Physical Electronics), 1992 (2nd edition).
- [109] Y. Wu, T. Yu, B. S. Dou, C. X. Wang, X. F. Xie, Z. L. Yu, S. R. Fan, Z. R. Fan, and L. C. Wang, "A comparative study on perovskite-type mixed oxide catalysts $\text{A}'\text{A}1-x\text{BO}_3-\lambda$ ($\text{A}' = \text{Ca}, \text{Sr}$, $\text{A} = \text{La}$, $\text{B} = \text{Mn}, \text{Fe}, \text{Co}$) for NH_3 oxidation", *J. Catal.*, 120 (1989) 88.
- [110] C. M. Pradier and C. Hinnen, "Structural and surface characterization of perovskite-type oxides; influence of A and B substitutions upon oxygen binding energy", *J. Mater. Sci.*, 33 (1998) 3187.

-
- [111] H. He, H. X. Dai, and C. T. Au, “An investigation on the utilization of perovskite-type oxides $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ ($\text{M} = \text{Co}_{0.77}\text{Bi}_{0.20}\text{Pd}_{0.03}$) as three-way catalysts. Appl. Catal. B: Environmental, 33 (2001) 65.
 - [112] K. Tabata, Y. Hirano, and E. Suzuki, “XPS studies on the oxygen species of $\text{LaMn}_{1-x}\text{Cu}_x\text{O}_{3+\lambda}$ ”, Appl. Catal. A: General, 170 (1998) 245.
 - [113] N. Shanthi and D. D. Sarma, “Electron structure of the electron doped $\text{SrTiO}_{3-\delta}$ and $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ ”, Phys. Rev. B, 57 (1998) 2153.
 - [114] S. A. Chambers, T. Droubay, T. C. Kaspar, M. Gutowski, and M. Van Schilfgaarde, “Accurate valence band maximum determination for $\text{SrTiO}_3(001)$ ”, Surf. Sci., 554 (2004) 81.
 - [115] L. T. Hudson, R. L. Kurtz, and S. W. Robey, “Surface core-level shifts of barium observed in photoemission of vacuum-fractured $\text{BaTiO}_3(100)$ ”, Phys. Rev. B, 47 (1993) 10832.
 - [116] V. Craciun and R. K. Singh, “Characteristics of the surface layer of barium strontium titanate thin films deposited by laser ablation”, Appl. Phys. Lett., 76 (2000) 1932.
 - [117] E. A. Kraut, R. W. Grant, J. R. Waldrop, and S. P. Kowalczyk, “Precise determination of the valence-band edge in X-ray photoemission spectra: application to measurement of semiconductor interface potentials”, Phys. Rev. Lett., 44 (1980) 1620.
 - [118] D. Ferrer, T. Tanii, I. Matsuya, G. Zhong, S. Okamoto, H. Kawarada, T. Shinada, and I. Ohdomari, “Enhancement of field emission characteristics of tungsten emitters by single-walled carbon nanotube modification”, Appl. Phys. Lett., 88 (2006) 033116.
 - [119] T. Sugino, S. Kawasaki, K. Tanioka, and J. Shirafuji, “Electron emission from boron nitride coated Si field emitters”, Appl. Phys. Lett., 71 (1997) 2704.

- [120] K. L. Ng, J. Yuan, J. T. Cheung, and K.W. Cheah, “Electron field emission characteristics of electrochemical etched Si tip array”, *Solid State Communications*, 123 (2002) 205.
- [121] B. W. Han, H. S. Lee, and B. T. Ahn, “Field emission characteristics of CoSi₂/TiN coated silicon emitter tips”, *Applied Surface Science*, 187 (2002) 45.
- [122] H. Lu, X. F. Chen, W. Zhu, J. S. Pan, and O. K. Tan, “Annealing temperature effect on field emission of silicon emitter arrays with Sol-gel (Ba_{0.65}Sr_{0.35})TiO₃ Coatings”, *Ferroelectrics*, 334 (2006) 253–261.
- [123] R. D. Forrest, A.P. Burden, S. R. P. Silva, L. K. Cheah, and X. Shi, “A study of electron field emission as a function of film thickness from amorphous carbon films”, *Appl. Phys. Lett.*, 73 (1998) 3784.
- [124] J. D. Carey and S. R. P. Silva, “Field emission from amorphous semiconductor”, *Solid-state Electronics*, 45 (2001) 1017.
- [125] J. P. Zhao, Z. Y. Chen, X. Wang, T. S. Shi, and T. Yano, “Thickness-independent electron field emission from tetrahedral amorphous carbon films”, *Appl. Phys. Lett.*, 76 (2000) 191.
- [126] M. C. Chiu, C. F. Cheng, W. T. Wu, and F. S. Shieu, “Effect of crystallinity on the dielectric properties of Ba_{0.5}Sr_{0.5}TiO₃ thin films”, *J. Electrochem. Soc.*, 152 (2005) F66.
- [127] J. H. Lee and Y. M. Chiang, “Pyrochlore-perovskite phase transformation in highly homogeneous (Pb,La)(Zr,Sn,Ti)O₃ powders”, *J. Mater. Chem.*, 9 (1999) 3107.
- [128] P. Du, I. M. M. Salvado, and P. M. Vilarinho, “Limits of formation of random grown perovskite and pyrochlore phases in sol–gel derived La modified lead zirconate titanate thin films”, *Thin solid films*, 375 (2000) 19.

Bibliography

- [129] Y. B. Zheng, S. J. Wang, A. C. H. Huan, C. Y. Tan, L. Yang, and C. K. Ong, “Al₂O₃-incorporation effect on the band structure of Ba_{0.5}Sr_{0.5}TiO₃ thin films”, Appl. Phys. Lett., 86 (2005) 112910.
- [130] S. A. Nasser, “X-ray photoelectron spectroscopy study on the composition and structure of BaTiO₃ thin films deposited on silicon”, Appl. Surf. Sci., 157 (2000) 14.
- [131] A. Azoulay, N. Shamir, E. Fromm, and M.H. Mintz, “The initial interactions of oxygen with polycrystalline titanium surfaces”, Surf. Sci., 370 (1997) 1.
- [132] K. Muralikrishna, M. Sharon, and M.K. Mishra, “Preparation and characterization of mixed oxides obtained from various molar mixtures of β -PbO₂ and TiO₂”, J. Phys. Chem. Solids, 57 (1996) 615.
- [133] X. F. Chen, H. Lu, H. J. Bian, W. Zhu, C. Q. Sun, and O. K. Tan, “Electron Emission of Silicon Field Emitter Arrays Coated with N-Doped SrTiO₃ Film”, J. Electroceram., 16 (2006) 419.