

**To my parents**

*Chang-Ou Ryu*  
*and*  
*Jeong-Sook Sohn*

## **Acknowledgments**

I wish to express my sincere and deepest gratitude to my academic advisor Prof. Seshu B. Desu for his constant help, personal attention, inspiring guidance, suggestions and encouragement given to me during the period of research, without which it would not have been possible for me to complete this work. I also would like to express my sincere appreciation to Dr. Reynolds who has encouraged me and has given me invaluable advice on the academic as well as personal matters throughout the whole period of study.

I wish to give special thanks to Dr. Joshi, Dr. In Kyeong Yoo and Prof. Kwangbae Lee. Dr. Joshi has been here for two year as a post-doctor. During that period, he allowed tremendous time for discussion about my research, many chapters of this dissertation were completed by the dedication of his effort. Dr. Yoo has given me spiritual rest whenever I feel difficulties in study and school life. Prof. Lee helped me at the later stages of this work and continued to encourage me to complete my study here.

I am also thankful to Mr. June-Key Lee who became one of my best friends during graduate work. He taught me how to think positively for the matters in the path of life. I also thank Mr. Yoon-Jong Song, now became Dr. Song, for his friendship in the laboratory. Xubai Zhang and Yongfei Zhu helped me to complete my dissertation by providing valuable data. My thanks are also due to all the members of our research group, especially, Victor, Sukku, Vedula, Chandra and Kaza.

I would like to take opportunity to thank Dr. Claus who has accepted serving as my thesis committee member, also, Jason, in the Multimedia Lab, who helped me to finish writing this dissertation.

I am also indebted to my brother Si-Ok, and brother-in-law Dr. Kwon for their interest and best wishes. Thanks to my wife, Seung-Ah, for her patience, encouragement.

**Sang-Ouk Ryu**

## Table of Contents

Chapter 1. Introduction	1
1.1 Ferroelectric memories and its basic operation	1
1.2 Materials and problem definition	8
1.3 Objectives and approach to the problems	13
1.4 Presentation of results	15
1.5 References	19
Chapter 2. Modified metalorganic solution deposition technique	21
2.1 Introduction	21
2.2 Selection of precursors and synthesis method	22
2.3 Properties of SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> ferroelectric thin films prepared by a modified metalorganic solution deposition technique	27
2.3.1 Abstract	27
2.3.2 Introduction	27
2.3.3 Experimental procedure	28
2.3.4 Results and Discussion	29
2.3.5 Conclusions	35
2.3.6 References	38
Chapter 3. Fabrication and characterization of (1-x)SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -xBi <sub>3</sub> TaTiO <sub>9</sub> layered structure solid solution thin films for FRAM applications	40
3.1 Abstract	40
3.2 Introduction	41
3.3 Experimental procedure	42
3.4 Results and Discussion	43
3.4.1 Properties of (1-x)SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -xBi <sub>3</sub> TaTiO <sub>9</sub> thin films as a function of x	44
3.4.2 Properties of 0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> thin films	53
3.4.3 Integration of 0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> thin films on metal-oxide electrodes	58
3.5 Conclusions	63
3.6 References	64

Chapter 4. Properties of optimized compositional $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9\text{-}0.3\text{Bi}_3\text{TaTiO}_9$ thin films	66
4.1 Thickness dependent properties of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9\text{-}0.3\text{Bi}_3\text{TaTiO}_9$ thin films	66
4.1.1 Abstract	66
4.1.2 Introduction	66
4.1.3 Experiment	67
4.1.4 Results and Discussion	68
4.1.5 Conclusion	72
4.1.6 References	73
4.2 Thermal stability of ferroelectric $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9\text{-}0.3\text{Bi}_3\text{TaTiO}_9$ thin film	75
4.2.1 Abstract	75
4.2.2 Introduction	75
4.2.3 Experimental procedure	76
4.2.4 Results and Discussion	77
4.2.5 Conclusion	84
4.2.6 References	84
Chapter 5. Discharging current-voltage characteristics of ferroelectric thin films	86
5.1 Abstract	86
5.2 Introduction	86
5.3 Experiment	87
5.4 Results and Discussion	88
5.4.1 Analysis of charging current	88
5.4.2 Leakage current mechanism of ferroelectric thin film capacitors	94
5.5 Conclusions	96
5.6 References	100
Chapter 6. Low temperature processed $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9\text{-}0.3\text{Bi}_3\text{TaTiO}_9$ thin film fabricated on multilayer electrode-barrier structure for high density ferroelectric memories	102
6.1 Abstract	102
6.2 Introduction	102
6.3 Experiment	104
6.4 Results and Discussion	105
6.5 Conclusions	109

6.6 References	112
VITA	114

## List of Figures

Figure 1-1. Unit cell of $ABO_3$ type perovskite structured material	4
Figure 1-2. A typical ferroelectric hysteresis loop	5
Figure 1-3. Schematic of the read/write operation in a ferroelectric memory cell	7
Figure 1-4. Proposed ferroelectric memory cell device configuration	9
Figure 1-5. Unit cell structure of bismuth layered oxide	11
Figure 1-6. Degradation of capacitor structure due to high temperature annealing of ferroelectric thin film	14
Figure 1-7. SBT and BTN crystal structures	16
Figure 1-8. Curie temperature( $T_c$ ) and Polarization( $P_s$ ) dependence for bismuth layered family	17
Figure 2-1. Fabrication of bismuth layered structure thin films	26
Figure 2-2. X-ray diffraction patterns of $SrBi_2Ta_2O_9$ thin films annealed at various temperatures for 30 min	30
Figure 2-3. AFM photograph of $SrBi_2Ta_2O_9$ thin film annealed at 750 °C for 30 min	32
Figure 2-4. Dielectric constant and dissipation factor as a function of frequency for $SrBi_2Ta_2O_9$ thin film annealed at 750 °C for 30 min	33
Figure 2-5. Hysteresis loop of 0.25- $\mu$ m-thick $SrBi_2Ta_2O_9$ film annealed at 750 °C for 30 min	36
Figure 2-6. Decay in remanent polarization as a function of number of bipolar switching cycles	37
Figure. 3-1. X-ray diffraction patterns of (a) $(1-x)SrBi_2Ta_2O_9-xBi_3TaTiO_9$ thin films annealed at 750 °C for one hour as a function of x and (b) $0.7SrBi_2Ta_2O_9-0.3Bi_3TaTiO_9$ thin films annealed at various temperatures for one hour.	45
Figure 3-2. AFM photographs of $(1-x)SrBi_2Ta_2O_9-xBi_3TaTiO_9$ thin films annealed at 750 °C for one hour	46
Figure 3-3. AFM photographs of $0.7SrBi_2Ta_2O_9-0.3Bi_3TaTiO_9$ thin films	48
Figure 3-4. Dielectric constant ( $\epsilon_r$ ) and Dissipation factor ( $\tan \delta$ ) of $(1-x)SrBi_2Ta_2O_9-xBi_3TaTiO_9$ thin films	49
Figure 3-5. Remanent polarization ( $P_r$ ) and Coercive field ( $E_c$ ) of $(1-x)SrBi_2Ta_2O_9-xBi_3TaTiO_9$ thin films	50
Figure 3-6. Normalized percentage of decay in (a) remanent polarization after $10^{10}$ cycles of bipolar switching and (b) retained charge after $10^6$ s. for $(1-x)SrBi_2Ta_2O_9-xBi_3TaTiO_9$ thin films	52

Figure 3-7. Leakage current density of $(1-x)\text{SrBi}_2\text{Ta}_2\text{O}_9-x\text{Bi}_3\text{TaTiO}_9$ thin films	54
Figure 3-8. Dielectric constant ( $\epsilon_r$ ) and Dissipation factor ( $\tan \delta$ ) of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-$ $0.3\text{Bi}_3\text{TaTiO}_9$ thin films	56
Figure 3-9. Hysteresis loop of $0.25\text{-}\mu\text{m}$ -thick $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ thin films annealed at (a) $650\text{ }^\circ\text{C}$ and (b) $750\text{ }^\circ\text{C}$ for one hour	57
Figure 3-10. Leakage current density vs. electric field characteristic of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-$ $0.3\text{Bi}_3\text{TaTiO}_9$ thin films	59
Figure 3-11. Fatigue characteristics of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ thin films	60
Figure 3-12. Normalized retention characteristics of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ thin films	61
Figure 3-13. Hysteresis loop of $0.1\text{-}\mu\text{m}$ -thick $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ thin films annealed at $650\text{ }^\circ\text{C}$ for one hour on $\text{Pt-10\%Rh/PtRhO}_x/n^+$ -poly Si substrate	62
Figure 4-1. Hysteresis loop of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ film with thickness of $80\text{ nm}$ at $2\text{ V}$	69
Figure 4-2. The AFM pictures of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ film with thickness of $80\text{ nm}$	71
Figure 4-3. Hysteresis loops of (a) $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ , (b) $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films measured at $25\text{ }^\circ\text{C}$ and $170\text{ }^\circ\text{C}$ , respectively and (c) $\text{Pb}_{1.1}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin film measured at $25\text{ }^\circ\text{C}$ and $140\text{ }^\circ\text{C}$	78
Figure 4-4. Temperature dependent (a) $2P_r$ and (b) $2E_c$ of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films at $5\text{ V}$	79
Figure 4-5. Temperature dependence of dielectric constant and loss factor of a $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-$ $0.3\text{Bi}_3\text{TaTiO}_9$ thin film at the frequency of $100\text{ kHz}$ with $10\text{ mV}$	81
Figure 4-6. A plot of (a) leakage current density ( $J$ ) vs electric field ( $\text{kV/cm}$ ) for a $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ thin film with temperature range $15 - 175\text{ }^\circ\text{C}$ and (b) $J/T^2$ vs $1/T$ at the electric field of $200\text{ kV/cm}$ for $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TaTiO}_9$ , $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Pb}_{1.1}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin films	82
Figure 4-7. Decay in $2P_r$ as a function of number of bipolar switching cycles at the temperature of $170\text{ }^\circ\text{C}$	83
Figure. 5-1. Effect of ferroelectric polarization on $J$ - $V$ curve	89
Figure 5-2. Schematic view of (a) components contributing $J$ - $V$ characteristics and (b) reversed step pulse bias	91
Figure 5-3. (a) Schematic view of relationship between dielectric relaxation current and	

discharging current in $J-t$ curve (b) $J-t$ characteristics of PZT thin film at 7V	92
Figure 5-4. $J_C$ -V and $J_D$ -V curves measured by means of 'reversed step-pulse' method at 25 °C and 75 °C in (a) PZT (b) SrBi <sub>2.1</sub> Ta <sub>2</sub> O <sub>9</sub> thin film capacitors.	95
Figure 5-5. Plots of $\ln(J_L/T^2)$ vs $1/T$ and $\ln(J_L/T^2)$ vs $E^{1/2}$ for test capacitors of (a) PZT and (b) SBT.	97
Figure 6-1. X-ray diffraction pattern of 0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> thin films deposited on electrode-barrier/n <sup>+</sup> -poly Si structure and annealed at 650 °C for 60 min.	106
Figure 6-2. AFM photograph of 0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> thin film deposited on Pt-Rh/Pt-Ph-O <sub>x</sub> /n <sup>+</sup> -poly Si structure and annealed at 650 °C for 60 min.	107
Figure 6-3. Dielectric properties of (a) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh and (b) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh/Pt-Ph-O <sub>x</sub> /n <sup>+</sup> -poly Si capacitors.	108
Figure 6-4. Ferroelectric hysteresis properties of (a) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh and (b) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh/Pt-Ph-O <sub>x</sub> /n <sup>+</sup> -poly Si capacitors.	110
Figure 6-5. Fatigue behavior of (a) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh and (b) Pt-Rh/0.7SrBi <sub>2</sub> Ta <sub>2</sub> O <sub>9</sub> -0.3Bi <sub>3</sub> TaTiO <sub>9</sub> /Pt-Rh/Pt-Ph-O <sub>x</sub> /n <sup>+</sup> -poly Si capacitors.	111

## List of Tables

Table 1-1. Key characteristics of candidate nonvolatile memory technologies	2
Table 1-2 Crystallinity and Chemistry Data of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Bi}_3\text{TaTiO}_9$	18
Table 2-1. Dependence of grain size, dielectric parameters, and ferroelectric properties on post-deposition annealing temperature.	34
Table 4-1. Electrical properties of $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9$ - $0.3\text{Bi}_3\text{TaTiO}_9$ thin films with different thickness	70
Table 5-1. Barrier height ( $W_b$ ) calculated for Schottky emission model	99