Growth and Characterization of Epitaxial Oxide Thin Films

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It cannot be stolen by thieves, Nor can it be taken away by kings. It cannot be divided among brothers and, It does not cause a load on your shoulders. If spent, It indeed always keeps growing. The wealth of knowledge is the most superior wealth of all!

Contents

5.1 Introduction

Preface	i
Summary	ii
Acknowledgements	iii
Chapter 1 Introduction 1.1 Background 1.2 Present Work 1.3 Outline References	1 1 3 4
Chapter 2 Epitaxy and Epitaxial Oxide Thin Films 2.1 Epitaxy 2.2 Epitaxial Oxide Thin Films <i>References</i>	6 6 14
 Chapter 3 Experimental Details 3.1 Substrate Preparation 3.2 Deposition 3.3 Thickness Measurements 3.4 Epitaxial Growth Characterization Techniques 3.5 Other Characterization Methods 	28 28 29 34 34 39
References Chapter 4 Background of WO ₃ and WO ₃ Thin Films 4.1 Introduction 4.2 Studies on Bulk Tungsten Oxide 4.3 WO ₃ Thin Films 4.4 Observations of Superconductivity 4.5 Present Work	42 42 46 49 50 53
Chapter 5 Results and Discussion of WO ₃ Films	56

56

5.2	Films on SrTiO3 (100)	57
5.3	Films on R-plane Sapphire	66
5.4	Heat Treatment	72
5.5	Optical Microscopy	73
5.6	Results of Transport measurements	75
5.7	Discussion on the Transport Measurement Results	77
5.8	Summary	77
F	References	

Chapter 6 Ferroelectricity and Ferroelectric Thin Films		79
6.1	Introduction	79
6.2	Principles of Ferroelectricity	81
6.3	Basic Principle of Operation of a Ferroelectric Memory Cell	88
6.4	Characteristics of a FRAM Memory Material	90
6.5	Issues for Integration of Ferroelectric Capacitors	91
6.6	Electrode Materials for FRAMs	91
6.7	Ferroelectric Thin Film Materials	94
6.8	Present Work	106
R	eferences	

Chapter 7 Epitaxial SrBi ₂ Ta ₂ O ₉ Films with c-axis Orientation	112
7.1 Introduction	112
7.2 Film Deposition and Characterization	115
7.3 X-ray Diffraction Results and Discussion	115
7.4 SEM and EDS Results	122
7.5 Morphological Studies	124
7.6 Ferroelectric Measurements	130
7.7 Summary	132
Reference	

Chapter 8 Epitaxial SrBi ₂ Ta ₂ O ₉ Films of Non-c-axis Orientation	133
8.1 Introduction	133
8.2 Film deposition	134
8.3 X-ray Diffraction Results and Discussion	134
8.4 Morphological Studies	140
8.5 Summary	143
References	

Chapter 9 SrBi ₂ Ta ₂ O ₉ Films of a-/b-axis Orientation	144
9.1 Introduction	144
9.2 Films on TiO ₂ (110)	144
9.3 Films on LaSrAlO ₄ (110)	154
9.4 Deposition of SrBi2Ta2O9/Sr2RuO4/LaSrAlO4 (110) Heterostructures <i>References</i>	166

Chapt	er 10 Conclusions and Further Work	176
10.1	Conclusions on WO3 Thin Films	176
10.2	Conclusions on SrBi2Ta2O9 Thin Films	177
10.3	Suggestions for Further Work	179

Appendix A	Glazer octahedral tilt system	180
References		

Preface

This Dissertation contains the work carried out in the Department of Materials Science and Metallurgy, University of Cambridge between October 1998 and December 2001 under the supervision of Dr. Z. H. Barber. I certify that, except where indicated, the work described is, to the best of my knowledge, original and has been carried out without any collaboration. No part of this dissertation has previously been submitted for any qualification at this or any other university or other establishment.

The content of this dissertation does not exceed 60,000 words.

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Some of the work carried out during past three years has been published as follows:

- 1. A. Garg, J. A. Leake, and Z. H. Barber, Epitaxial Growth of WO₃ Films on SrTiO₃ and R-Sapphire, *J. Phys.*: *D*, *Appl. Phys.*, 33 (9), 1048 (2000)
- 2. A. Garg, S. Dunn, and Z. H. Barber, Growth and Characterization of Epitaxial SrBi₂Ta₂O₉ films on SrTiO₃ (110) Substrate, *Integrated ferroelectrics*, 31 (1-4), 13 (2000)
- A. Garg and Z. H. Barber, Growth of Extremely Smooth Epitaxial SrBi₂Ta₂O₉ films on SrTiO₃ Substrates, Workshop proceedings of the Ferroelectrics 2000 UK, eds. Neil Alford and Eric Yeatman, 11-14 April 2000, Cirencester, UK (an *IOM Communications* publication)
- 4. C. Christou, A. Garg and Z. H. Barber, Vapour-Phase Oxidation During Pulsed Laser Deposition of SrBi₂Ta₂O₉, *Journal of Vacuum Science and Technology-A*, 19 (5), 2061 (2001)
- 5. **A. Garg** and Z. H. Barber, Pulsed laser deposition of epitaxial SrBi₂Ta₂O₉ films with controlled orientation, accepted for publication in *Ferroelectrics*
- 6. Z. H. Barber, C. Christou, K.-F. Chiu and A. Garg, The measurement and control of ionization of the depositing flux during film growth, accepted for publication in *Vacuum*
- 7. A. Garg, S. Lloyd and Z. H. Barber, Epitaxial Growth of Fully a-/b-axis Oriented SrBi₂Ta₂O₉ Films, accepted for publication in *Integrated Ferroelectrics*

Summary

Epitaxial oxide thin films are used in many technologically important device applications. This work deals with the deposition and characterization of epitaxial WO₃ and $SrBi_2Ta_2O_9$ (SBT) thin films on single crystal oxide substrates. WO₃ thin films were chosen as a subject of study because of recent findings of superconductivity at surfaces and twin boundaries in the bulk form of this oxide. Highly epitaxial thin films would be desirable in order to be able to create a device within a film without patterning it, by locally creating superconducting regions (e.g. twins) within an otherwise defect free film by reducing or doping the film with Na. Films were deposited by reactive magnetron sputtering at various temperatures on single crystal SrTiO₃ (100) and R-sapphire substrates. X-ray diffraction studies showed that the optimised films were highly (001) oriented, quality of epitaxy improving with decreasing deposition temperature. AFM studies revealed columnar growth of these films. Films were heat treated with Na vapour in order to reduce or dope them with Na. Low temperature measurements of the reduced films did not show existence of any superconductivity.

SBT is a ferroelectric oxide and its thin films are attractive candidates for non-volatile ferroelectric random access memory (FRAM) applications. High structural anisotropy leads to a high degree of anisotropy in its ferroelectric properties which makes it essential to study epitaxial SBT films of different orientations. In this study, SBT films of different orientations were deposited on different single crystal substrates by pulsed laser ablation. Highly epitaxial c-axis oriented and smooth SBT films were deposited on SrTiO₃ (100) substrates. AFM studies revealed the growth of these films by 3-D Stranski-Krastanov mode. However, these films did not exhibit any ferroelectric activity. Highly epitaxial (116)-oriented films were deposited on SrTiO₃ (110) substrates. These films were also very smooth with root mean square (RMS) roughness of 15-20 Å. Films deposited on TiO₂ (110) were partially a-/b-axis oriented SBT films were deposited on LaSrAlO₄ (110) substrates. Films deposited at non-optimal growth temperatures showed the formation of many impurities. Attempts were also made towards depositing Sr₂RuO₄ films on LaSrAlO₄ (110) substrates, which can act as a bottom electrode for ferroelectric SBT films.

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stopped inviting me even after knowing how much I ate. A big thanks to cricket teams of Materials Science and St. John's MCR, for amazing matches, for after-match beer, and gossip. I discovered my ability as a 'promising' off spinner during past three years after my knee injury. A final thanks to my office mates Cliff, Mike, Moon-Ho and Yee and all other group members who always maintained a lively atmosphere in the office and lab respectively. One of the thursday evening at Free Press can not be forgotten when me and some 'others' were thrown out of the pub for our supposedly 'RUDE' behaviour.

My parents have not seen much of me during last ten years as I have been studying away from the home. I can never repay their debt in anyway for their incessant love, affection and support. I love you very much. Late *Badi Mausi* and *Mausaji* have also been been the same to me forever and I would like to pay my gratitude to them, which is never sufficient. My brothers Apurva and Rajat and sister Shilpi have also missed me equally and I also missed their love, affection and many fun moments with them. I love you all very much. I also missed my dear *dost*, Amit, who is always like a brother to me.. His friendship is a precious jewel to me.

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A sad moment in the end was sudden death of *Badi Mausi*.. I could not even go to India for her cremation, thanks to delays due to bureaucracy in the Home office who didn't issue my visa in time as if I was an illegal immigrant.

AaSalYa gaga Kûnbaj⁄a , idsablar 2001

Chapter 1 Introduction

k:m;[y;v;;i0;k:;rst;em; f:1 (;uk:d;c;n; = m; k:m;f:1 ht;B;t<m; t;es;y;;Cstv;k:m;1[; =47= X1 mdB;g;v;t;g;1t;;, a0y;;y; 2

On action alone be thy interest, Never on its fruits. Let not the fruits of action be thy motive, Nor be thy attachment to inaction.

Sri Bhagavad Gita, Chapter 2, Verse 47

1.1 Background

Thin films show different physical properties than the bulk materials because of many factors such as smaller size of the crystallites and in particular many crystallographic defects such as dislocations, vacancies, stacking faults, grain boundaries and twins. Epitaxial thin films have attracted the attention of the research community throughout the world for a long period of time because of their often superior properties over polycrystalline thin films. There have been numerous efforts on the development of electronic solid state devices based on epitaxial thin films and it has been recognised that for most technological applications, these devices show better performance and extended life than those based on polycrystalline films. This difference arises primarily due to the presence of crystallographic defects such as high angle grain boundaries in the polycrystalline films which affect

the device performance adversely. Because of these factors, growth of epitaxial thin films has been found to be extremely beneficial in many Si-based device applications which incorporate semiconductors, superconductors, ferroelectrics or magnetic materials.

Although epitaxy was probably first observed in alkali halides grown on alkali halide crystals over a century ago the word epitaxy was introduced in the literature by French mineralogist L. Royer in 1928.¹ Epitaxy is a phenomenon of the oriented growth of one crystal over another which was originally observed in natural minerals where two crystals of different species grow together with certain crystallographic orientation relationship. This kind of observation led to the beginning of the experimental work on epitaxy in laboratories. The work progressed from the growth of alkali halides on alkali halides and mica, to metals on alkali halides, and then to metals on metals and non-metals. This early work on epitaxy is extensively reviewed by Pashley.² Later, in the 1950s, developments in the growth of semiconductor epitaxy provided a new dimension to the field of epitaxial growth. In more recent times, in particular in the 1990s, enormous attention has been paid towards development of complex metal oxide thin films e.g. superconducting oxides such as yttrium barium copper oxide (YBCO), ferroelectric oxides such as lead zirconium titanate (PZT), manganites such as lanthanum calcium manganese oxide (LCMO) and many more materials. These materials are used as very important components in various solid state devices such as Josephson junctions³, data storage devices⁴ or tunnel junctions.⁵ However these complex metal oxides are quite complicated to deposit with correct stoichiometry because quite often they contain more than two elements. The situation is aggravated at times due to one of the components being volatile in nature such as lead in PZT. It still remains a challenge to deposit these materials with correct stoichiometry at optimum device processing temperatures. Many deposition techniques have evolved over the years to deposit complex oxide films which are perfect, both chemically and structurally. Sputtering, Laser Ablation, Molecular Beam Epitaxy (MBE) and Chemical Vapour Deposition (CVD) are the most common techniques used to deposit epitaxial films. Thus, in order to be able to grow these complex oxide films in a reproducible manner with desired structure and stoichiometry, it is very important to study their deposition, structure, growth and properties in a detailed manner and then be able to predict the optimal conditions for a particular deposition technique.

Early studies on epitaxial thin film growth did not commence until the discovery of electron diffraction in 1927. Later X-ray diffraction (XRD) provided a new approach to the study of epitaxial

thin films in a different manner. Transmission electron microscopy (TEM) with electron diffraction and X-ray diffraction together can give very useful insight about the phase identification, compositional effects, structure determination, presence of crystallographic defects, orientation relationship and many other structural details. Other electron diffraction techniques such as reflected high energy electron diffraction (RHEED) and low energy electron diffraction (LEED) can give valuable information about the initial growth mechanisms and surface structure of the very thin films during growth in an in-situ manner. Scanning probe techniques such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) are very useful tools for morphological studies e.g. to study nucleation and growth phenomena, determination of surface roughness and other morphological parameters, surface structure and electronic states.

1.2 Present work

This work describes the study of thin film deposition and characterization of epitaxial oxide thin films of two kinds: tungsten oxide (WO₃) and strontium bismuth tantalum oxide (SrBi₂Ta₂O₉ i.e. SBT). The first part of the thesis deals with thin film deposition and characterization of epitaxial WO₃ thin films on various single crystal substrates by magnetron sputtering. WO₃ is an important oxide with some fascinating properties. Thin films of this material have been explored widely for their use in electrochromic devices⁶ and gas sensing devices.⁷ Recently there have been some reports of superconductivity in the reduced form of this oxide: low temperature superconductivity in the twin boundaries of this oxide at 3 K in Na heat treated WO_{3-x}⁸ and high temperature superconductivity at 92 K in Na doped surface of WO_{3-x}.⁹ This provided the motivation for trials of epitaxial deposition of WO₃ thin films on various single crystal substrates by magnetron sputtering. Epitaxial films are of significant interest in this regard because of possibility of fabricating superconducting devices e.g. tunnel junctions in a single crystal film without patterning or lithography.

The second part of the thesis is about the growth and characterization of epitaxial thin films of SBT, a candidate material for non-volatile ferroelectric random access memory (FRAM) applications.¹⁰ The term non-volatility implies that the information is retained in the memory device even if the power is lost. These memories are non-volatile as compared to the volatile dynamic random access memories (DRAMs), work faster and at lower operating voltages (< 5 V), and are radiation hard.⁴,¹¹ However, high degree of anisotropy in the ferroelectric properties of SBT requires SBT films to be deposited in an epitaxial fashion in order to study the effect of film orientation on ferroelectric properties. Present

work deals with the deposition of epitaxial SBT thin films by pulsed laser ablation on various single crystal oxide substrates to study the structural and morphological aspects of the films.

1.3 Outline

Various aspects of epitaxial oxide thin films are discussed in Chapter 2. It briefly elucidates the basic aspects of epitaxial growth and the techniques which can be used to characterize epitaxial films. The importance of epitaxial oxide thin films is discussed. It also summarises the past work on epitaxial oxide thin films. A number of additional topics such as different materials and their applications, their deposition techniques and the important issues to be tackled are discussed.

Chapter 3 describes about the experimental details of both processing techniques: sputtering and laser ablation, and characterization techniques: X-ray diffraction, atomic force microscopy, scanning electron microscopy, transmission electron microscopy and electrical characterisation.

Basic aspects of WO_3 and background about the past work done on WO_3 in both thin film and bulk form are discussed in detail in Chapter 4. This explains briefly about the structural and electrical properties of WO_3 .

Chapter 5 presents the results and discussion of the WO_3 thin films on various substrates. Results of low temperature transport measurements on the heat treated film are also presented and discussed.

Chapter 6 discusses various fundamental aspects of ferroelectricity, and explains the importance of ferroelectric thin films. Emphasis has been paid towards the structure and growth of $Pb(Zr,Ti)O_3$ and SBT thin films.

Chapter 7, 8 and 9 present the results obtained on SBT films of various orientations on different single crystal substrates. These results are discussed in detail and are compared with contemporary work.

Finally, Chapter 10 gives the conclusions.

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- ¹⁰ C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, and J.F. Scott, *Nature*, **374**, 627 (1995)
- ¹¹ P.K. Larsen, R. Cuppens and G.A.C.M. Spierings, *Ferroelectrics*, **128**, 265 (1992)

Chapter 2 Epitaxy and Epitaxial Oxide Thin Films

This Chapter discusses briefly the important aspects of epitaxy and oxide thin films. Section 2.1 deals with some fundamental aspects of epitaxy. Section 2.2 is a summary of past work done on epitaxial oxide thin films, their main deposition methods and important issues. Most of the references in this chapter are quoted with respect to superconducting and ferroelectric oxides. These oxides exhibit quite similar behaviour in their deposition methods and growth modes, as most of them are chemically quite complex, oxygen sensitive and possess similar perovskite tetragonal structure.

2.1 Epitaxy

This section attempts to provide a brief description of epitaxy, its types, growth mechanisms of epitaxial thin films, defects in epitaxial films and their characterization techniques.

2.1.1 Introduction

Epitaxy, ideally, refers to formation of a single crystal film on the top of a single crystal substrate and subsequent evolution of a specific crystallographic orientation relationship between the film and the substrate as growth commences. The specific orientation relationship is governed by the crystal systems and lattice parameters of the two phases. There can be more than one orientation relationship in case of deviation from the single crystalline structure of the film. We can classify epitaxy into two basic types: *Homoepitaxy* and *Heteroepitaxy*. Homoepitaxy is the simplest form of epitaxy and refers to the state when both the film and the substrate are of the same material. Deposition of single crystal

Si on Si wafer is the most common example of homoepitaxy. This is an important practice in the semiconductor industry, for example in bipolar and MOS transistors. On the other hand, heteroepitaxy is related to the situation when film and substrate are of dissimilar materials, for example metal film on an alkali halide substrate. In practice, heteroepitaxy is the most general form of epitaxy in various technological applications such as semiconductors, superconducting devices, ferroelectric memories or optoelectronic devices.



FIGURE 2.1 Schematic illustration of lattice matched, strained, and relaxed epitaxy; from ref. [1].

The concept of matching of lattice parameters between the film and the substrate is an important aspect of epitaxy. In homoepitaxy, since both the film and the substrate are composed of the same material, there is no lattice strain at the film-substrate interface. However, in heteroepitaxy, there is generally a lattice parameter mismatch between the film and the substrate and thus the interface can be strained or relaxed depending upon the magnitude of the difference (see Fig. 2.1). This also results in an interface whose energy (γ_I) is greater than zero in most cases. This interface energy consists of mainly two terms: interface energy due to the formation of a new interface and elastic strain energy due to lattice mismatch and difference between modulus of the film and the substrate. A film can achieve a state of preferred orientation or may not exhibit any preferred orientation in such a way that it leads to the minimization of γ_I . The fundamental criterion for epitaxy is defined by the lattice mismatch f, which can be written as

$$\mathbf{f} = (\mathbf{a}_{\mathrm{f}} - \mathbf{a}_{\mathrm{s}})/\mathbf{a}_{\mathrm{s}} \tag{2.1}$$

where a_f and a_s are the lattice parameters of the film and the substrate. Ideally, for high quality epitaxy of the film, the lattice mismatch should be as small as possible (in general less than 10%).² There are many ways in which heteroepitaxial growth of films can take place. The most common example is the matching of lattice parameters which is schematically shown in Fig.2.2. Lattice matching can be as simple as simple cube on cube relationship (Fig. 2.2 (a)), or film planes can be rotated by 45° with respect to the substrate plane (Fig. 2.2 (b)), or (111) plane of the film can align with (001) plane of the substrate (Fig. 2.2 (c), e.g. Pt/Si(100)). There are a few instances where epitaxy is not restricted to the cases of low lattice parameter mismatch e.g. metals such as silver and nickel have been grown on heated rocksalt surfaces where the misfit was as big as 38%.² In these cases, twinning has been found to play an important role in accommodating misfit and still maintaining an epitaxial relationship. It should be noted whatever the mechanism of epitaxy is, minimization of interface energy governs its existence.

Another way to avoid large misfit strain, at least along the interface, is by tilting of growth planes of the film relative to the substrate plane by an angle.³ It can be seen from Fig 2.3, growth direction of film is at an angle α to the substrate normal where $\cos \alpha = k(1+f)$ where k is a positive constant. It can be seen from this equation that f should be negative i.e. film lattice parameter should be smaller than the substrate. Many hcp rare earths and metals grown on bcc (211) metal substrates have been shown to hold this relationship.



FIGURE 2.2 Various schemes of lattice match epitaxy; (a) when lattice parameters of films and the substrate are almost equal, (b) 45° rotation, and (c) (111) plane of films aligns with (001) substrate plane.



FIGURE 2.3 Schematic representation of the epitaxy by tilting of growth direction of the film relative to the substrate plane; from ref. [4].

2.1.2 Growth Mechanisms of Epitaxial Thin films

The study of growth mechanisms of epitaxy was not done in a proper way until the discovery of electron diffraction in the 1930s. Subsequently evolution of characterization techniques like STM, RHEED, and LEED made significant contributions to the knowledge of epitaxial growth of different materials. In addition to the earlier reviews on epitaxial growth^{2,5}, recently Pashley⁶ has written a review on the epitaxial growth mechanisms dealing with the theoretical aspects. Several crucial factors, both physical and chemical, such as lattice misfit, energy considerations, nature of bonding etc. have their own influence in giving rise to a particular film growth mode. However the considerations in these growth modes are valid only if there are no chemical reactions at the film-substrate interface, alloying and its effects, or other changes at the film-substrate interface which could be due to electron bombardment or dissociation during the film growth.

In general, epitaxial growth can be the result of any of the following three modes of growth':

- 1. Frank-Van der Merwe Growth (Layer by Layer Growth),
- 2. Volmer-Weber Growth (3-D Nucleation), and
- 3. Stranski-Krastanov (SK Growth, Mixed mode)

2.1.2.1 Frank-Van der Merwe Growth (Layer by Layer Mode)

Monolayer growth is essentially the formation of a continuous, complete, and single layer of atoms as shown in Fig. 2.4 (a). In this growth mode, initially one monolayer thick islands of atoms form and then they intergrow to form a single, continuous layer before significant clusters are developed on the next film layer. The driving force for this mode of growth is the reduction in the total surface energy i.e.

$$\gamma_{\rm I} + \gamma_{\rm F} \le \gamma_{\rm S} \tag{2.2}$$

where γ_I , γ_F , and γ_S are the interface, film and substrate surface energies respectively. For a case of deposition of a film on a clean surface of the same material, $\gamma_I = 0$ and $\gamma_F = \gamma_S$, and equation (2.2) is satisfied. For deposition of films on dissimilar substrates, this growth mode is favoured strongly for low misfits (i.e. low γ_I), in the presence of strong bonding between the film and the substrate (or negative heat of mixing) which implies low interfacial energy, low film surface energy and high substrate surface energy. It is also necessary to take elastic strain energy into account which increases with number of monolayers. This is done by replacing γ_I with γ_{IN} where N is the number of

monolayers. After the initial formation of a monolayer, subsequent monolayers grow on the top of each other until a critical film thickness is reached.⁸ At this stage dislocations begin to form and result in the commencement of strain relief. This phenomenon progresses as the film growth continues.



FIGURE 2.4 Film growth modes: (a) Layer by layer (Frank-Van der Merwe); (b) Island (Volmer-Weber); and (c) Stranski-Krastanov; from ref. [4].

2.1.2.2 Volmer-Weber Growth (Island Mode)

Volmer-Weber growth mode prevails in the circumstances when the energy reduction criterion as shown in equation (2.2) is not followed i.e.

$$\gamma_{\rm I} + \gamma_{\rm F} > \gamma_{\rm S} \tag{2.3}$$

The schematic of this kind of growth is shown in Fig. 2.4 (b). The nucleation of 3-D nuclei takes place either by surface diffusion or by direct impingement of atoms, often at active sites such as crystal defects, atomic steps or impurities. These sites act as a means for reducing the activation energy for nucleation or bonding of the nuclei to the substrate. The nucleation of this type can be understood well by classical nucleation theory.^{9,10} According to these theories considering the capillarity model, a stable nucleus is of radius more than a 'critical radius' to fulfil the free energy criterion which is given by the following equation

$$\Delta G = r^2 (a_1 \gamma_F + a_2 \gamma_I - a_2 \gamma_S) + a_3 r^3 \Delta G_V \qquad (2.4)$$

where a_1r^2 , a_2r^2 and a_3r^3 are the area of nuclei exposed to vapour, contact area between substrate and the nuclei, and volume of nuclei respectively, and a's are geometric constants. ΔG_V is the volume free energy change upon formation of a nucleus and is negative in sign and it is directly related to the substrate temperature and the deposition rate. Nuclei having their radius less than the value at which ΔG is maximum, will spontaneously decompose or evaporate since that is the direction of reduction of free energy. So for a stable nucleus to form, its radius should be greater than a critical radius, r^* , at which $d(\Delta G)/dr$ changes it sign from positive to negative. The critical radius is calculated by differentiating the equation (2.4) w.r.t. r and the derivative, $d(\Delta G)/dr$, is equal to 0. and can be written as

$$\mathbf{r}^* = [-2(a_1\gamma_F + a_2\gamma_I - a_2\gamma_S)]/[3a_3\Delta G_V]$$
(2.5)

The formation of nuclei of radius greater than a critical radius occurs until further nucleation is not possible as the energy situation of growth becomes more favourable and growth of existing nuclei takes place by the addition of more atoms. Strain relief can take place at the interface by generation of misfit dislocations at the interface either before the islands' coalescence or after, depending upon the degree of pseudomorphism (pseudomorphism as defined by Finch and Quarrell¹¹, is the modification in the lattice spacing of an epitaxial deposit in the interface plane to match that of the substrate). Then the coalescence of islands may be either by selective deposition of atoms at some preferential sites on the existing islands due to minimization of total surface energy or by liquid like coalescence of formation of a compound island whose shape is similar to that of two islands before coalescence.⁶ In practice, increasing the deposition rate or decreasing the substrate temperature enhances this kind of nucleation. Temperature additionally controls the surface diffusion of the atoms.

2.1.2.3 <u>Stranski-Krastanov Growth (Mixed mode)</u>

In this kind of growth mode, as shown in Fig. 2.4 (c), the growth changes from monolayer to island after formation of one or two monolayers. This is believed to happen because of stress increase and thus strain relief after the formation of few monolayers due to mismatch in the lattice spacings. Normally, this growth mode tends to occur when the lattice misfit is more than about 2% and the contribution due to strain energy in equation (2.2) is larger than those from surface energies. This growth mode has been observed by scanning tunnelling microscope (STM) in YBa₂Cu₃O_{7-X} (YBCO)

thin films deposited on $SrTiO_3$ (100) substrates.¹² To improve the quality of epitaxy, 3-D type of growth mode should be avoided or suppressed as it leads to the formation of defects such as twins, stacking faults and increased roughness in the films

2.1.3 Factors to be Considered for Epitaxial Growth

The most important factor affecting epitaxy is the nature of the substrate. The substrate for the epitaxial films should essentially be a single crystal substrate. The choice of substrate is limited by various factors such as crystal symmetry, orientation, minimum lattice parameter mismatch, surface energy considerations, surface finish, chemical nature, coefficient of thermal expansion and most importantly, the application for which the film is being deposited. Substrate preparation is also an important step towards depositing epitaxial films. In many instances, surface contamination can lead to dramatic changes in the epitaxy. Complete discussion on this aspect can be found in the text books on thin film deposition.^{1,4,13}

Substrate temperature during the deposition also plays an important role in determining the epitaxy. In general for single components, the higher the deposition temperature, the better are the chances of achieving the epitaxy (see Fig. 2.5). This is due to the improved ad-atom mobility at the substrate surface. Increase in the substrate temperature may also lead to cleaning of the substrate by desorption of any contaminants. Epitaxial temperature (temperature at and above which epitaxial growth is favoured) is also affected by the deposition rate.¹⁴ Usually, as the deposition rate increases the epitaxial temperature are secondary ion bombardment during deposition (either external or inherent) and the presence of an electric field.¹⁴ Some of the factors, which can affect the epitaxial growth temperature of multi-component oxides, are stability of various phases of the different oxide components, diffusion characteristics of different film species on the substrate, and nature of deposition process.



FIGURE 2.5 Effect of temperature and deposition rate on epitaxy of Ge on Ge(111) substrate, from ref.[14].

2.2 Epitaxial Oxide Thin Films

2.2.1 Introduction

Although research into oxide thin films has continued since the 1960s, it was the discovery of high temperature superconductivity in 1986¹⁵, which provided a major impetus to the research in the field of multi-component complex oxide thin films. Consequently, many areas of interest have emerged such as ferroelectric devices, optoelectronic devices, CMR devices etc. (see Table 2.1). These oxides are the subject of scientific studies because they represent immense promise for the 21st century solid-state devices. Although in the past these materials have been used as bulk material for many applications, it is the thin film form of these oxides which makes them more attractive for various applications. For example, integration of semiconductor technology with epitaxial metal oxide thin films such as superconducting oxides is a very promising field of research for many device applications. Superconducting oxides such as YBCO (yttrium barium copper oxide) for SQUIDs¹⁶ or ferroelectric oxide such as PZT (lead zirconium titanate) for non-volatile memory applications¹⁷ show excellent potential in device applications.

In recent years, enormous amount of emphasis has been paid towards developing epitaxial metal oxide thin films, in order to develop devices, which show better performance over an extended life span as compared to the devices based on polycrystalline films. Significant progress has been made towards studying the growth mechanisms of the epitaxial thin films by various techniques such as RHEED, LEED, and STM.^{18,19,20,21} But there are some issues which are yet to be tackled effectively. One of them is the processing temperature, which needs to be of the order of 500°C or less, for processing to be compatible with the Si integrated circuit processing. Other issues to be dealt with are reproducibility of composition in complex oxide deposition, phase stability, high quality of epitaxy and atomic level flatness of the films whilst maintaining the commercial viability of the device.

In this chapter, emphasis has been paid towards the deposition processes for fabricating epitaxial oxide thin films, and major issues in the epitaxial oxide film growth.

Property	Materials	Application
High temperature	$YBa_2Cu_3O_7$, $Bi_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$	Power transmission,
superconductivity		Communications, Microwave
		Devices
Ferroelectricity,	$Pb(Zr_{x}Ti_{1-x})O_{3}, SrBi_{2}Ta_{2}O_{9}$	Memories, Data Storage
Piezoelectricity		Devices, Sensors, Actuators
Optics	Nb ₂ O ₅ -SiO ₂ -Na ₂ O-Ba ₂ O ₃ -TiO ₂	All optical switching devices
Magnetism	(La _X Ca _{1-X})MnO ₃ , Ferrites, Garnets	Magnets (hard and soft),
		Tunnel junctions
Thermal barrier	ZrO_2 , Al_2O_3	Heat resistant coatings e.g. for
coatings		heat exchangers

TABLE 2.1 Some important metal oxides and their applications

2.2.2 Film Deposition Techniques

Over the years various processes have been developed for the deposition of metal oxide thin films. Almost all of these deposition techniques can be broadly divided into two categories, namely physical vapour deposition processes (PVD) and chemical processes. PVD processes include laser ablation, sputtering, evaporation whilst chemical processes are chemical vapour deposition techniques (CVD), liquid phase epitaxy, sol-gel and metal organic deposition (MOD) and spin coating. There have been many extensive reviews on the deposition of epitaxial oxide films.^{22,23,24} The growth of epitaxial metal oxides on single crystal substrates usually requires temperatures higher than those in the processing of

semiconductor devices. It still remains a major challenge for most of the thin film processing groups to bring the deposition temperature down to acceptable limits. Ideally, a manufacturing process for fabricating metal oxide thin films should have:

- 1. the capability to produce highly oriented films in a reproducible manner at lowest possible deposition temperatures,
- 2. ability to produce stoichiometric films of complex compositions,
- 3. compatibility with the integrated Si circuit with respect to the deposition temperature,
- 4. ability to produce uniform thickness with good conformal coverage,
- 5. the ability to produce patterned and layered heterostructures in a reproducible way, and
- 6. should operate at low cost.

In this section, different processing techniques are discussed with primary emphasis on the sputtering and laser ablation processes.

2.2.2.1 Magnetron Sputtering

Sputtering is one of the effects in glow discharge processes when a surface is bombarded by energetic particles. In this process the target atoms are ejected by the bombardment of energetic species (usually inert gas ions) on it (refer to Fig. 2.6). The sputtered atoms travel through the plasma and undergo many collisions with the plasma species (electrons, neutrals, gas ions, and metals ions) and subsequently deposit on a strategically placed substrate. The substrate can be heated depending upon the nature of the deposition. Sputtering process can employ dc or rf power depending upon the electrical conductivity of the target. DC power can be used only for conducting targets where rf power can be used for both conducting and insulating targets. Usually a magnetic field (use of magnetron target) is employed to enhance the efficiency of plasma utilisation and sputter efficiency. This happens due to increased electron residence time in the plasma, improving the ion collision probability and thus larger discharge currents. Sputtering process using a magnetron is called *magnetron sputtering*. A complete description of glow discharge processes and their application to sputtering process can be found elsewhere.²⁵



FIGURE 2.6 Schematic of dc and rf sputter deposition, depicting the main features.

Reactive sputtering can used to prepare alloys or compounds, solid solutions, or a mixture. Reactive sputtering in a mixture of oxygen and argon has been a very important process for the deposition of oxides since the 1970s. Among one of the earlier studies, a mixture of argon (Ar) and oxygen (O_2) was used to deposit SiO₂ films from elemental Si target by reactive sputtering.²⁶ Application of RF sputtering facilitated the use of an oxide as the starting material and target, but given the variation in the sputter yields of different elements, the resulting films were not found to be stoichiometric.

Growth of oxides by sputtering involves different regimes depending upon the sputtering conditions. Work has shown that the nature of growth species changes from atomic to molecular as the sputtering gas pressure increases.²⁷ One major problem encountered in the sputtering of oxides is the resputtering of the growing film by negative ions and reflected neutrals^{28,29}, leading to morphological changes e.g. formation of various features such as pits, ripples, cones and craters on the film surfaces. Presence of these morphological changes was found to be dependent on a number of factors including deposition rates, flux and energy of bombarding ions, and the average angle of incidence of

bombarding ions. These studies also predicted that resputtering can be minimised by thermalising (reducing the energy of energetic species originating from the target) the energetic species in the plasma either by sputtering in high pressure environment or by off-axis sputtering. The issue of whether to use an oxide target or an elemental target is quite complex. Some of the considerations in selecting a particular target are target purity, deposition rates, and stoichiometry related issues.

Interdependence of various parameters makes this process quite complex. The main issues which are to be addressed are stoichiometry control, epitaxy, nature of the substrates (can involve use of buffer layers), and oxygen activity during the deposition.³⁰ It has been studied that given the condition that all the factors, particularly temperature, partial pressure of oxygen and total pressure, are within reasonable control, sputtering can produce films with good structural quality and good composition control within an accuracy of 0.1%.³¹ Highly oriented oxide films can be grown with controlled stoichiometry and properties as shown by various groups for high T_c superconducting films^{32,33} and ferroelectric films.³⁴ However, one of the major drawbacks is slow deposition rate which makes this process quite expensive.

2.2.2.2 lon Beam Sputtering

Ion beam sputtering using ion beams to sputter the materials has been used in different forms to fabricate metal-oxide thin films. Previous use of this technique includes the use of multi-component PZT targets to fabricate its thin films.³⁵ But the process was carried out under poorly controlled processing conditions which led to many problems: (i) preferential sputtering of the target materials and subsequently a change in the target stoichiometry which also affects the film stoichiometry and (ii) preferential scattering of low mass ions (Ar) on heavier species (e.g. Pb, Zr) in the target surface leading to resputtering of the film as well as ion bombardment induced damage and incorporation of gases into the films.

Subsequently two modified versions of this technique were developed: multiple ion beam-multi-target (MIBERS)³⁶ and single ion beam multi target (SIBMT)³⁷ methods. Ion beams used in these processes were produced using Kaufman type ion source³⁸ which were directed at single elemental targets at suitable current density. In these techniques controlled bombardment of a growing film by low-energy ions can be used as an approach to modify the film growth process by affecting the mobility of adatoms and therefore its microstructure and properties.

This technique presents several advantages over conventional plasma sputtering technique:

- 1. independent control over ion current density and energy providing better control over sputtering and consequently in the film characteristics,
- 2. lowering of operating pressure which minimized effects such as resputtering of the film, film damage and gas incorporation,
- 3. better control over composition of the film by controlling the deposition rate of each element, and
- 4. ability to produce smooth and epitaxial films at lower substrate temperatures.

However the disadvantages are high cost, complexity and inability to operate at high working pressures.

2.2.2.3 Pulsed Laser Ablation

In this process, a pulsed laser beam is focussed onto the surface of a target at an oblique angle so that a substrate can be placed directly in front of the target surface (see Fig. 2.7). This focussing action produces a laser spot of high enough energy which can ablate the target material which subsequently deposits onto the substrate. A mixture of Ar and O₂ or pure O₂ gas is used for the deposition of oxides with a pressure range of 20-50 Pa in most cases. The interaction of the laser beam with the target surface gives rise to a powerful plasma-like bright plume which emanates perpendicular to the target surface. Most commonly used lasers are UV excimer lasers such as ArF (193 nm), KrF (248 nm), XeF (351nm) and as it can be seen from these lasers, the wavelength of the laser is controlled by lasing gas composition. KrF excimer laser is one of the most widely used lasers because of its high-energy laser pulse output.

This technique has been successfully employed for deposition of high Tc superconductors, ferroelectric thin films, and other oxide films. Basic concepts of laser ablation and its application for deposition of various materials can be found elsewhere.³⁹ Among some recent studies, laser ablation has been successfully used to produce epitaxial cuprate films by layer by layer growth mode.¹⁹ It was shown that low partial pressure of oxygen and high growth temperatures are crucial for this growth mode to occur, whilst high oxygen partial pressure results in films grown by 3-D island growth mode. Several reviews has been written on the growth of high T_c superconducting films^{23,40} and ferroelectric thin films.^{24,41}



FIGURE 2.7 Schematic design of the laser. ablation

The most important aspect of laser ablation is the presence of a low number of process variables as compared to other physical and chemical vapour processes. This makes the process relatively easy to control. The important parameters to be controlled are laser power density, substrate target distance, and ambient oxygen pressure.

Some of advantages of this process are

- 1. excellent control over stoichiometry using single-phase multielemental target,
- 2. efficient target use,
- 3. it can be easily coupled with in-situ growth monitoring methods such as RHEED,
- 4. it can work at high working pressures,
- 5. possibility of depositing multilayers,

- 6. possibility of depositing films at higher deposition rates, and
- 7. absence of bombardment effects on the growing film unlike in sputtering.

However despite all the advantages of this process, some of the issues like creation of small droplets or particulates⁴² and deposition on larger area substrates, are yet to be dealt with successfully.

2.2.2.4 MBE Processes

This process essentially involves evaporation of source material in a UHV environment and then deposition of the evaporated flux onto the substrate. Vacuum evaporation is a low energy process as compared to sputtering because energy of species reaching the substrate is very low, of the order of 0.5 eV. For deposition of oxides, reactive evaporation is a very important method. Reactive evaporation involves use of a reactive gas, O₂, to maintain the correct oxygen stoichiometry of the film material while using elemental sources and also while using a compound source to compensate the loss of oxygen during the evaporation. The critical factors involved in the evaporation processes are vacuum level and the background oxygen pressure (pO_2) which are instrumental in controlling the impurity level and stoichiometry of the film. Among one of the early efforts on reactive evaporation, deposition of TiO₂ and Si₂O₃ was successfully demonstrated.⁴³ Use of active oxygen has been shown to improve the film quality considerably. Epitaxial YBCO films have been deposited by MBE in the presence of an RF plasma discharge to generate reactive oxygen species at low temperatures (< 500°C) and improvement in film properties was observed.⁴⁴ Epitaxial DyBa₂Cu₃O_{6+x} films were grown by MBE and it was shown that by controlling the local nucleation rate and lateral growth rate, it was possible to achieve layer by layer growth.²⁰ These processes can produce films with controlled stoichiometry and better epitaxy but at the cost of low deposition rates (of the order of 5-10 nm/m). Although these methods are complex in nature and expensive, they offer advantage of in-situ growth monitoring by RHEED/LEED.

2.2.2.5 Chemical Vapour Deposition (CVD) Processes

In this process, precursor compounds are heated to convert them into vapour phase and are introduced into the heated reaction chamber where a source of O_2 is present. The reaction vapours and gas are flowed over a substrate, usually heated between 400-1000°C, produce the film species which subsequently deposit on the substrate as shown by Fig. 2.8. The residual gases and volatile products are pumped away from the system. Deposition temperature in CVD is limited by the temperature at

which chemical precursors dissociate and react to form the film compound. However its further innovations like metallo-organic chemical vapour deposition (MOCVD) and plasma enhanced MOCVD (PE-MOCVD) processes offer advantages of depositing films at relatively lower temperatures as compared to those employed in PVD processes. This is achieved either by the use of a plasma or metallo-organic precursors which can react at relatively low temperatures. CVD processes also have the advantage of depositing films over large area substrates. However these processes are complex in nature because of many process parameters to be controlled. Some other problems with these processes are control of composition, accurate knowledge of phase diagrams, toxicity of precursors. Also precursors for MOCVD process are particularly expensive which also limit the application of the process on a wide scale. There are several reviews existing on the CVD deposition of the high T_c superconductors^{45,46} and ferroelectric thin films.^{47,48}



FIGURE 2.8 Schematic diagram of metallo-organic chemical vapour deposition (MOCVD) deposition process; from ref. [48].

2.2.2.6 Liquid Phase Epitaxy (LPE)

In this process liquids are used to grow the films on a single crystal substrate in near-equilibrium processing conditions. It involves the precipitation of a crystalline phase as the film from a supersaturated melt onto a substrate which acts as both the template for epitaxy and a physical support for the film. Above liquidus temperature all the constituents dissolve into the liquid. However for film growth as the liquid cools down, some of the constituents precipitate out of the solution and grow epitaxially on a suitable substrate. The typical growth rates for this process vary between 1 to 10 μ m/min. LPE offers several advantages over other epitaxial deposition processes such as low-cost

operation, good control of composition and thickness, and faster deposition rates. However disadvantages can be poor surface finish, complications in chemistry for the case of complex ternary or higher order systems and presence of volatile elements. LPE could be an attractive process for making coated conductors based on YBCO films and is being extensively studied.⁴⁹

2.2.3 Major Issues

Even though thin film deposition of epitaxial metal oxides has been carried out since the 1960s and significant progress has been made on all fronts, yet there are some fundamental issues which are yet to be dealt with. To reduce the deposition temperature for depositing epitaxial films is the foremost challenge for most of the processing techniques, barring some chemical processes. Other aspects involve production of stable phases with precise composition and correct oxygen content, good structure and morphology of the films, high degree of desired orientation, and issues regarding the nucleation and growth of the films. Choice of device compatible and cheap substrates and deposition over larger area substrates are the main bottlenecks in the commercial success. The interdependence of various parameters, for example processing temperature and epitaxy, poses serious questions about the choice of optimum conditions. In this section, it has been attempted to briefly elucidate these problems and the on going efforts to handle them.

2.2.3.1 Deposition Temperature and Orientation

Most of the metal oxides require high temperature for epitaxial growth, usually growth temperatures being $0.7-0.8T_m$ which is very high when compared to epitaxial growth temperatures of metals and semiconductors which fall usually between $0.2-0.5 T_m$. These temperatures are very high when considering the processing compatibility with semiconductor circuit processing. The effect of deposition temperature is direct on the epitaxy, although it also depends upon the type of processes. Usually if the deposition temperature is lowered, then epitaxy deteriorates. But there are a few reports of deposition at lower temperatures by MOCVD processes⁴⁸ or evaporation processes⁴⁴ maintaining the desired orientation of the films. It has been shown for ion beam sputtered PZT films that bombardment of the growing film by low energy ions in ion beam sputtering and use of active oxygen species helps to reduce the crystallization temperature of PZT to some extent.³⁶ But it is still not possible to deposit films at lower temperatures (below 500°C), with desired epitaxy, in processes like laser ablation or sputtering.

2.2.3.2 Phase Stability and Stoichiometry Control

Because of the thin film growth processes in general being non-equilibrium in nature, it becomes very important to know about the phase evolution under a given set of process parameters and how a desired phase can be obtained if they are altered accordingly. This problem arises predominantly in terms of deposition temperature and oxygen activity. Most of the perovskite oxides are not only complex oxides, but they also have some specific oxygen level for desired properties e.g. superconducting oxides like YBCO. These complexities put enormous restriction on the processing conditions to produce the correct phase. The work of Feenstra *et al.*⁵⁰ on the effect of oxygen partial pressure and temperature on the stability of YBCO, gives a very good idea about operating windows for different processes.

Chemical complexity of these oxides also poses problems regarding the correct stoichiometry of the films. This is particularly difficult in sputtering because of the different sputter yields of different elements which cannot be controlled independently when using a compound target and due to resputtering effects on the growing film. This problem has been tackled by using multi-elemental targets.²⁴ Also each element has different collision cross section with the plasma species because of different atomic masses which leads to a complexity in the transport processes during sputtering. Laser ablation has emerged as one of the most promising processes to address this problem with considerable success by using single compound oxide target and it has been demonstrated successfully that films can be deposited without any loss of stoichiometry.⁵¹

2.2.3.3 Substrate Effects

Choice of substrate is a very important factor in the growing epitaxial oxide films. It has been a matter of great concern in growing superconducting and ferroelectric oxide thin films. SrTiO₃ (100) and MgO (100) have proven to be useful substrates for growing highly epitaxial films of YBCO. But moisture sensitiveness of MgO and high dielectric constant of SrTiO₃ makes them unattractive. They are also expensive. Numerous other substrates have been tried such as LaAlO₃, sapphire, NdGaO₃ etc. but the search is still on for the best which is inexpensive, should not react with the film at the film deposition temperature and should be able to give high quality epitaxial films with excellent properties.³⁰ Ferroelectric thin films such as PZT have been grown epitaxially on platinised Si wafers (Pt/SiO₂/Si) but films on Pt give very poor fatigue characteristics which is very important for ferroelectric memory devices. This problem has forced researchers to look for other alternative

electrodes such as LSCO, YBCO etc. but they have not yet fulfilled the promise because of some compromise required in other properties. These problems have been, to some extent, alleviated by the use of buffer layers. Buffer Layers act as intermediate layers between the substrate and film and minimise the various deleterious effects on epitaxy from factors such as mismatch in lattice parameters and coefficient of thermal expansion and interdiffusion of elements, and sometimes promote crystallisation of the film.⁵² Various materials have been used for this purpose such as cerium oxide (CeO₂) for YBCO⁵³, and strontium ruthenium oxide (SrRuO₃) for PZT⁵⁴ and resulted in remarkable improvement in the device performance.

2.2.3.4 Structure and Morphology

Structure of the epitaxial oxide thin films such as YBCO has been characterised by X-ray diffraction extensively and it has been found that the best films grown have rocking curve width of the order of $0.15 \cdot 20^{\circ}$.²³ This degree of orientation is acceptable but when compared to substrate, it shows that there is a lot of scope for further improvement. The better the epitaxy of the film, better is the surface roughness. STM studies reveal that films grown by layer by layer growth mechanism are smoother than the films grown by 3-D island growth mechanism.⁵⁵ Stoichiometry control has also an important role to play in controlling the film structure. It was shown that by controlling the chemical composition correctly, films can be grown by layer by layer growth mode and this could also lead to smoother surface.⁵⁶ The effect of atomic oxygen on the growth and surface roughness of YBCO films grown on SrTiO₃ (100) by MBE process, has also been studied.⁵⁷ It was concluded that in the presence of atomic oxygen and with careful control of process parameters (low pO₂ and low deposition rate), it is possible to grow epitaxial films by 2-D growth mechanism and achieve atomically flat surfaces. So there are challenges to produce epitaxial oxide films with smoother surfaces and perfect orientation which require careful control of processing conditions.

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Chapter 3 Experimental Details

This chapter describes the experimental procedures to fabricate and characterize both WO_3 and $SrBi_2Ta_2O_9$ films. Substrate preparation prior to the film deposition is discussed in the beginning of this chapter, followed by a brief account of the deposition processes of the films (sputtering and laser ablation) and then characterization techniques of films in the following sections.

3.1 Substrate Preparation

Some of the substrates required cleaning before the film deposition because they were cut from a disc which was mounted on a disc holder for cutting using wax. This wax leaves carbonaceous substances and other dirt particles on the surface of the substrate which can adversely affect the nucleation and growth processes during film growth and can also lead to the inclusions or formation of many impurities. Hence it was important to clean these substrates properly before they were put into the film deposition system. The procedure of cleaning is as follows:

The substrates were put into a bath of acetone and ultrasonically treated for about 10 minutes to remove the wax and dirt from the substrate surface. Then these substrates were washed once more by using acetone and finally by ethanol or propanol. It is important to give a final wash using propanol or ethanol because acetone tends to leave some spots on the surface of the substrate. After the final wash the samples were dried by compressed air or dry nitrogen.



FIGURE 3.1 Schematic of sputtering deposition chamber.

3.2 Deposition

3.2.1 Sputtering

Reactive magnetron Sputtering was used to deposit WO_3 thin films from a tungsten target in an $Ar+O_2$ atmosphere. Details of the deposition system and processes are briefly explained in the following sections.

3.2.1.1 System

MK-7 system, which employs ultra high vacuum (UHV) environment, was used to deposit WO_3 films. Fig. 3.1 shows the essential features of the deposition set-up. This system uses a conventional rotary pump and a turbo molecular pump for evacuation. A Cu gasket was used in order to seal the flange to the deposition chamber. Overnight bakeout and subsequent liquid nitrogen cooling gives a vacuum of the order of 10^{-8} to 10^{-9} mbar as measured by a Mass Spectrometer.

3.2.1.2 Magnetron, Target and Flange

The target used was a metallic tungsten target of size 55x35 mm. Fig. 3.2 shows the main features of the magnetron. The tungsten target is screwed on the target holder directly above the magnetron. The magnetron is cooled by circulating water in order to avoid heating of the target during the deposition process.

The flange consists of magnetron, a heater which acts as substrate holder, and target shields. The substrate holder can be rotated in the horizontal plane in order to keep the substrates away from the target during pre-sputtering and can be moved up and down to change the target-substrate distance by means of a knob located on the top of the flange. Angular position of the knob indicates the substrate's position with respect to the target. Before loading the system, it was made sure that the target assembly is electrically isolated from the rest of the parts on the flange and chamber.



FIGURE 3.2 Schematic of magnetron

3.2.2 Pulsed Laser Ablation

Pulsed laser ablation was used to deposit SBT thin films. The deposition system was an UHV system using a conventional rotary pump and a turbo pump. The chamber design can be referred to Fig. 2.7 in Chapter 2. On the sides of the chamber are windows which are made to observe the laser plume, its position relative to the heater and position of the laser beam on the target. The flange is inserted from the top of the chamber and it contains a multi-target carousel with motor controlled rotation of targets.

The laser used was a KrF laser with wavelength of 248 nm. The laser unit was supplied by Lambdaphysik (Germany). The beam path was an enclosed pathway and beam's path was adjusted through mirrors and lenses to the target. The beam enters the chamber through a window and is directed towards the target at an oblique angle.

The targets used were $SrBi_2Ta_2O_9$ targets with varying Bi content, Sr_2RuO_4 targets to deposit bottom electrodes for ferroelectric films.

3.2.3 Heater

Design of a substrate heater was one of the major challenges encountered during the project. Initially, a flat strip resistive heater and substrate holder was used. The heater was made of Pt in the case of sputtering, and Fecroloy (Fe-Cr-Al alloy) in the case of laser abaltion. Fecroloy has a protective oxide coating of Al_2O_3 which makes this alloy oxidation resistant even at temperatures as high as 1200°C. However, this geometry of heater was not very good for achieving a uniform temperature on the sample surface and led to the formation of many impurity phases in the case of the films where strict temperature control was required to achieve pure film phase. Also, this heater melted due to the formation of hotspots at sharp points at substrate temperatures beyond 1000°C. A tube heater was constructed which is shown in the Fig. 3.3. The heater was brazed to copper connectors on the ends. This heater had several advantages over the flat strip heater. Firstly, radiation losses are minimized because of its curved shape which redirects the heat towards the sample surface leading to lesser difference between the heater and the sample surface. Also temperature was more uniform on the sample surface when it was in the lowest part of the heater. Temperature was measured using an optical pyrometer by matching the colour of the filament with the colour of the heater. The substrate temperature was 100°C lower than the heater temperature in the case of strip heater and 50°C in the

case of tube heater. This was verified by measuring the temperature at the substrate surface using a K-type thermocouple.



FIGURE 3.3 Schematic design of the tube heater.

3.2.4 Deposition Procedure

Sputtering

Cleaned substrates were placed on the substrate holder. After putting the flange onto the chamber, the chamber was evacuated till a vacuum better than 10^{-8} mbar was achieved after overnight baking. The chamber was then cooled by liquid N₂ in order to reach vacuum level of 10^{-9} mbar. Chamber degassing was checked by closing the gate valve. Degassing rate was approximately 10^{-9} mbar/s during all the runs. The heater was heated to the desired temperature and held at this temperature for 1 h in order to preheat the substrates and also to evaporate any volatile matter from the substrate surface. At the same time Ar and O₂ were filled in the gas reservoir in the desired ratio with a total pressure of 100 kPa or higher.

Then the gas was introduced into the system by opening the leak valve with gate valve 3-1/2 turns open and desired gas pressure was set by carefully controlling the flow of gas through both valves. It was ensured that the backing pressure did not exceed 6×10^{-2} mbar during the deposition process. Prior to deposition the substrates were maintained in a position where they were not directly below the target during pre-sputtering. Power was applied to the target to start pre-sputtering to remove the oxide layer and any contamination from the target surface. Pre-sputtering was carried out for 5-10 mins. After pre-sputtering was over, the power was set to the desired value and the substrate holder was rotated to the correct position just below the target, pulled up to a desired substrate-target

distance and then the shutter was removed. Deposition was carried out for the desired length of time. Immediately after the deposition time, the power was turned down to zero and gate valve was closed and chamber was filled with the gas mixture to cool the substrate in the Ar-O₂ atmosphere. The heater current was slowly reduced to zero in steps of 50°C/min. All the films were 0.75 μ m thick unless otherwise mentioned.

The deposition conditions used are summarised below:

Substrate Temperatures: 500 to 900°C,

Deposition Rate: 12.5 nm/min,

Gas Pressure: 1.8 Pa (approx.),

Gas Composition: 60%Ar-40%O₂,

DC Power: 13 W (370-380 kV, 30-35 mA), and

Target-substrate distance: 4 cm

Laser Ablation

After loading the target and substrates inside the chamber, the chamber was evacuated till a vacuum between 10^{-6} and 10^{-7} mbar was achieved after overnight baking. Note that the vacuum was poor as compared to that in the sputtering chamber because of the use of rubber gaskets. The heater was heated to the desired temperature and held at this temperature for 1 h in order to preheat the substrates and also to evaporate any volatile matter from the substrate surface. At the same time O₂ was filled in the gas reservoir with a total pressure of 100 kPa or higher. After preheating, O₂ was introduced into the system by opening the leak valve with gate valve 2-1/2 turns open and desired O₂ pressure was set by carefully controlling its flow through both valves. It was ensured that the backing pressure did not exceed 6×10^{-2} mbar during the deposition process.

During the preheating period, the laser energy was set to obtain the desired laser fluence (laser energy unit area, J/cm^2) on the target, and desired flowing O₂ pressure was set in the chamber. Targets were pre-ablated for 200 pulses before film deposition to remove any dirt and impurities from the target surface. Substrates were covered by a shield during pre-ablation. Final ablation was carried out at

selected laser repetition rate for desired number of pulses to get a particular thickness of the film. Substrate target distance was fixed at 6.5 cm for all the runs. Substrate temperature was varied between 600 to 1000°C.

3.2.5 Substrates

The substrates used were single crystal SrTiO₃ (100) and (110), TiO₂ (110), LaSrAlO₄ (110) and R ($10\overline{1}2$) plane sapphire (Al₂O₃).

3.3 Thickness Measurements

For film thickness measurements, a platinum (Pt) strip was placed across the centre of a substrate (Fig. 3.4) prior to the deposition. After the deposition, the Pt strip was removed, leaving a step in the film. The step height gives a measure of the thickness of the film, determined using a profilometer. The profilometer consists of a diamond tip that travels across the sample along its length, and vertical downward movement of the tip at the step gives a measure of the step height which represents the thickness of the film. The sensitivity of the profilometer was approximately 10 nm.



FIGURE 3.4 Schematic representation of the thickness monitor.

3.4 Epitaxial Growth Characterization Techniques

Epitaxial films have been characterized by various different methods, and some of the most commonly used techniques are diffraction methods using X-rays and electrons and microscopy techniques such as transmission electron microscopy and scanning probe microscopy. These techniques are discussed briefly in the following section:

3.4.1 X-Ray Diffraction

This section does not deal with the fundamentals of X-ray diffraction, rather it attempts to briefly summarize the techniques which can be used to characterize epitaxial thin films. X-ray diffraction is usually a post deposition method of measuring the quality of epitaxy of the films. Although there are many ways in which X-rays can be employed to characterize epitaxial films, we used three techniques to characterize our sample, namely 2θ scans, rocking curve analysis and film texture characterization by measuring the pole figures. The following section describes the principle and geometry of the goniometers used in these measurements.

3.4.1.1 20 Scans and Rocking Curve Analysis using Vertical Goniometer

First technique which is normally employed is a normal θ -2 θ scan of the film over a wide angular range which can give an idea about the degree of preferred orientation of the film. If the film is textured, then the diffraction pattern exhibits diffraction peaks from some planes of unusually high intensity rather than the peaks from other planes (as compared to the intensity ratios in the diffraction pattern of a polycrystal). In the extreme cases of good epitaxy, peaks from only one particular type of plane, (hkl), are observed. These intense peaks are from the planes which are preferentially oriented with the substrate plane. Following these scans, quality of epitaxy can be determined by carrying out rocking curve analysis or ω scans.

A Philips PW1710 single circle vertical diffractometer was used to carry out these scans. The diffractometer consisted of a Cu-K_{α} ($\lambda = 1.54056$ Å) X-ray source, many filters (e.g. Mo, Zr, Ni etc., Ni was used in the measurements carried out during this project), many combinations of divergence, receiving and anti-scatter slits. A reflection type configuration was used to carry out the measurements. Samples were mounted on a sample holder made from glass slides which use plasticine to fix the sample and also to level the sample with the sample holder such that sample surface is coincident with the axis of rotation of the goniometer. Any displacement by a distance D, in the sample surface from the centre of diffractometer (of radius R) will cause an error in the measurement of 20. This error can be expressed as¹

$$\delta(2\theta) = 2D(\cos\theta)/R \tag{3.1}$$

Although the diffractometer includes a graphite monochromator in the path of the outgoing beam, a Ni filter was also used in all the measurements to completely suppress the $Cu-K_{\beta}$ which was observed without it. Another important factor is choice of divergence and receiving slits. Narrow slits provide good resolution but irradiate a smaller area of the sample which, sometimes, could lead to incomplete information, particularly in the case of thinner films. Additionally, count time needs to be increased because of substantial reduction in the intensity of the X-ray beam. During 20 scans, larger slit widths can be used without compromising on the resolution limit of FWHM (full width half maximum) of 20 peak. However in the case of ω scans, narrow slits need to be used, particularly for highly epitaxial thin films.



FIGURE 3.5 The set-up of the vertical diffractometer. By coupling and decoupling ω and 2θ , a 2θ -scan or a ω -scan may be carried out.

One important aspect of the vertical diffractometer is to be able to carry out a θ -2 θ scan which involves coupling the rotation angle of the sample and detector in a 1:2 ratio whilst the position of the source beam remains fixed. In this way the angle made by the incident and outgoing beam with the sample surface, shown in Fig. 3.5, is θ . Because these angles are equal, only diffracting planes which are parallel to the sample surface are detected using such a method. It should be noted that it is possible to de-couple the 1:2 rotation ratio so the angles are no longer equal. In this case the angle between the incident beam and the sample surface is usually referred to as ω and the angle between incident and detected beam is still 2 θ , as shown in Fig. 3.5.

The decoupling of sample and detector angles can be used to carry out a rocking curve. The 2 θ position of the relevant reflection from {hkl} planes parallel to the sample surface is located using a θ -2 θ scan. The detector arm is then fixed whilst the sample is rotated in order to detect the reflection from planes with the same {hkl} indices which are in slightly different orientations. The sharper the

rocking curve (i.e. lower full width half maximum (FWHM), $\Delta \omega$, of the curve), the higher the crystalline perfection.

3.4.1.2 Texture Goniometer

Another means of determining the degree of texture in epitaxial films by X-ray diffraction is polefigure analysis, as reported by several authors.^{2,3} The texture goniometer is a Philips X'Pert system having an automated texture goniometer cradle. The sample is mounted on an Al stage and its height is adjusted with a retractable needle as a guide. The detector arm and sample stage move in the same way as in the vertical goniometer such that the texture unit can also be used to perform θ -2 θ scans and ω scans. However the resolution is not as good due to the different optical arrangement. The texture cradle which is mounted on the sample stage enables the sample to be rotated in the plane which is normal to both its surface and the plane containing the incident X-Ray beam (ψ scan, rotation about AA' axis) and also in its own plane (ϕ scan) (refer to the geometry shown in Fig. 3.6). The ϕ scan may be measured over the entire 360° range, but the ψ scan is limited upto 70° due to defocussing effects.¹ By measuring a series of ϕ scans at various ψ angles for a fixed 2 θ value of the chosen reflection, it is possible to measure the 3-D orientational distribution of the plane normals (known as poles). To produce a 2-D representation of the 3-D distribution the poles which lie on the surface of a sphere may be projected onto the equatorial plane, producing a pole figure. Two common projections used in this work are the Schmidt projection and the Wulff projection.



FIGURE 3.6 Geometry of goniometer for pole figure analysis.

The resolution in ϕ and ψ is limited by the optical arrangement. For a 0.45 mm receiving slit the instrumental broadening (FWHM) in degrees is¹:

$$\delta\phi \approx 0.90 / \sin\psi \tag{3.2}$$

$$\delta \psi \approx 0.55 \,/ \sin \theta \tag{3.3}$$

These are approximations which become inaccurate at small values of ψ and θ but are correct in situations for which they will be used in this work.

Note that the experiment has been carried out with different widths of receiving slits and no significant change to the broadening of these peaks is observed.

3.4.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is also an important tool to learn about the presence of orientation relationship between the film and the substrate, presence of misfit dislocations at the interface, presence of precipitates, stacking faults, twins, anti-phase boundaries (APBs) and low angle grain boundaries. Early work on the different electron diffraction methods to study epitaxy has been reviewed extensively.⁴ This work focussed mainly on study of diffraction patterns from epitaxial films which provided information on the film orientation and its orientation relationships with the substrate. Later TEM has also been used extensively to study the various defects in the epitaxial films and multilayers.⁵

In the present study, Dr. Stephen Lloyd performed TEM investigations on the cross section of selected samples to study the crystallinity of the film, and its orientation relationship with the substrate.

3.4.3 Scanning Probe Microscopy

Since the invention of scanning tunnelling microscopy (STM) in 1982⁶, STM and AFM (Atomic force microscopy) have proved to be extremely useful tools for the study of topographic features of epitaxial thin films, which give a direct insight into the growth processes. Both STM and AFM are truly local surface probing tools in the sense that they image individual atoms and do not rely upon long range order. In STM, a tip is brought extremely close to the sample surface so as to observe a

tunnelling current between the sample surface and the tip. The obvious disadvantage with STM is that it can be used only with a sample with conducting surfaces. Whereas in AFM, a scanning tip is attached to a cantilever arm whose deflection is measured using a low power laser, reflected upon a position sensitive diode array detector. These arms are typically made of Si with Si_3N_4 as the tip material. In the past, STM has been successfully used by several authors to study the growth of many semiconductors such as the growth of epitaxial Si.⁷ In oxide thin film growth, YBCO thin films have also been studied by STM and AFM and it was possible to observe the classical spiral assisted film growth mechanism.⁸

In the present study, atomic force microscopy (using Nanoscope III, Digital Instruments) was used in order to carry out the morphological studies such as study of nucleation and growth mechanisms and measurements of roughness of the grown films. AFM was operated in the tapping mode in order to avoid any damage to the film surface caused by the tip in contact mode. The tip (made of Si_3N_4 , tip radius = 0.1 µm) is mounted on a flexible cantilever and scans across the sample surface. After mounting the sample on the sample holder or stage, an applied voltage makes the cantilever vibrate and the tip is brought down close to the specimen where it interacts with the atoms on the sample surface. Tip height is maintained using a piezoelectric crystal in order to maintain a constant vibrational amplitude which is equivalent to the constant distance between the sample surface and the tip. The changes in voltage applied to maintain this constant distance translate into the topographical variation of the sample surface when it is scanned by the tip.

3.5 Other Characterization Methods

3.5.1 Optical Microscopy

Optical microscopy can be used for observing the presence of any surface features of about 1 micron size. A reflected polarized light optical microscope was used to examine the surface of WO_3 films before and after heat treatment to observe any changes in the colour of the surface and to observe any twins if present.

3.5.2 Scanning Electron Microscopy

This technique is useful for monitoring the surfaces with grain size above ~10 nm and for carrying out the composition analysis using electron dispersive scan (EDS) over a selected area. In the present case this technique was mainly performed to carry out the EDS analysis of the SBT films. The microscope used was JEOL JSM-5800LV. It was generally operated at 20 kV. Samples were coated with gold (upto 2-3 nm thick) to avoid any charging effects which could be present due to the non-metallic nature of the samples.

3.5.3 Ferroelectric Measurements

Ferroelectric measurements were made in the Earth Sciences Dept. using a Sayer-Tower circuit TF Analyser 2001, supplied by Aixacct. Hysteresis (P-E) measurements were carried out at different frequencies and voltages.

3.5.4 Heat Treatment

Heat treatment of WO_3 thin films was carried out by Alison Aird in the Earth Sciences Department. Samples were heat treated with Na at various temperatures for different periods. Na and the sample were kept in a quartz tube which was then evacuated and sealed. Then these sealed tubes were placed inside the furnace at the desired temperature for required length of time.

3.5.5 R-T Measurements

Transport measurements on WO₃ and Sr₂RuO₄ films were made in different stages. First the samples were tested on a 4-point probe which can measure the resistance of the films down to 4.2 K. These temperatures were attained by inserting the probe into a liquid Helium dewar. Temperature is measured by means of a calibrated carbon glass thermometer. If the samples were found to be metallic (only for WO₃ samples), then they were further tested using *Heliox* which can measure the transport properties down to 300 mK, which is achieved by the use of He³. The resistance is measured by passing a constant current (1-100 μ A) and measuring the voltage across the film. For establishing the contact between the film and the probe, a photoresist lift-off mask was patterned on the sample surface. Deposition of gold on the exposed area of the sample provided the gold contact pads, each of dimension 1x1 mm². Connection to a substrate holder was required for probe measurements which

was made by wire bonding between the gold contacts on the films and the copper pads on the substrate holder.

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Chapter 4 Background of WO3 and WO3 Thin Films

This chapter briefly explains the structural details of tungsten oxide, its many forms and transitions. Other variants of this oxide such as its oxygen deficient form, and doped tungsten oxide are also explained. It has been shown that these changes lead to many interesting properties in this oxide, such as superconductivity, electrochromic phenomenon, gas sensing ability etc. and these can be applied in various applications. This chapter also deals with WO₃ thin films and reviews the past work done in this field, particularly of relevance to epitaxial films.

4.1 Introduction

Tungsten trioxide (WO₃) is an important $5d^0$ transition metal oxide with some interesting electrical and optical properties. The structure of WO₃ is similar to the ABO₃ perovskite type of structure where tungsten atoms occupy the B cation site which is octahedrally surrounded by oxygen atoms, forming corner shared octahedra. The cube corners (i.e. A site) remain vacant as shown in Fig. 4.1. This vacant site is occupied by another ion in the case of ternary oxides e.g. Na in Na_XWO₃, also called tungsten bronzes. Its ideal structure is equivalent to the cubic ReO₃ type of compounds. However in practice, the cubic symmetry of tungsten oxide is no longer stable which is primarily attributed to the tilting of WO₆ octahedra and subsequent displacement of the tungsten atom from its centre in an antiferroelectric arrangement. These kinds of crystallographic distortions are responsible for at least five phase transitions in WO₃ over a range of temperatures. When WO₃ is heated from 0 K to 1700 K, the phase transitions occur in a sequence: monoclinic \rightarrow triclinic \rightarrow monoclinic \rightarrow orthorhombic \rightarrow tetragonal. These transitions are summarised in Table 4.1.



FIGURE 4.1 Crystal Structure of WO₃.

Most of these transitions have been found to be first order, which can result in large hysteresis effects and coexistence of phases over fairly wide temperature ranges. Hence, reports of T_c for each phase transition have varied widely in the literature. Factors such as impurities, non-stoichiometry and crystal size, due to the existence of surfaces, have been shown to affect T_c .^{1,2} Also, there may be a difference in T_c between surface and interior regions of larger crystals.

Phase	Structure	Temperature range (K)
α_1	Tetragonal (P4/nmm)	Above 1170
-	a = 5.2955 Å, c = 3.9293 Å at 1190 K	
α_2	Tetragonal (P4/ncc)	1000-1170
	a = 5.2742 Å, c = 7.8467 Å at 1040 K	
β	Orthorhombic (Pmnb)	600-1170
•	a = 7.341 Å, b = 7.570 Å, c = 7.754 Å at 750 K	
γ	Monoclinic $(P2_1/n)$	290-600
	$a = 7.306 \text{ Å}, b = 7.540 \text{ Å}, c = 7.692 \text{ Å}, \beta = 90.88^{\circ} \text{ at room}$	
	temp.	
δ	Triclinic (P $\overline{1}$)	230-290
	$a = 7.309 \text{ Å}, b = 7.5165 \text{ Å}, c = 7.6811 \text{ Å}, \alpha = 88.81^{\circ},$	
	$\beta = 90.985^{\circ}, \gamma = 90.985^{\circ}$ at room temp	
ε	Monoclinic (Pc)	Below 230
	$a = 5.2771 \text{ Å}, b = 7.1555 \text{ Å}, c = 7.6630 \text{ Å}, \beta = 91.76^{\circ} \text{ at } 10 \text{ K}$	

TABLE 4.1 Phase Transitions^{*} in $WO_3^{3,4,5}$

*Note that these transitions temperature exhibit hysteresis effects and are not in universal agreement in the literature.

Fig. 4.2 shows the structures of the α_1 to ε phases of WO₃, and the distortions occurring during each phase transition. The α_1 phase occurs above 1170 K and possesses a tetragonal structure with space group P4/nmm. In this phase, positions of W atoms are arranged in a zigzag manner, but the octahedra are untilted. A second tetragonal phase, α_2 , is found at slightly lower temperatures of 1000 K to 1170 K. The α_1 to α_2 transition is tricritical (continuous) and non-ferroic i.e. without any ferroelectric transition.⁶ "Negative" tilting of the octahedra around the c axis results in doubling of the unit cell along c, and an octahedral tilt system of $a^{\circ}a^{\circ}c^{-}$ for α_2 . This octahedral tilt system has been defined by Glazer⁷ and is outlined in Appendix A. It should be noted that the labelling mentioned in Fig. 4.2 takes crystallographic axes into account when referring to a, b and c.



FIGURE 4.2 Structures of α_1 to ε phases and shape changes at each phase transition. Each picture highlights a main aspect of the structural change, as described in ref. [4]. The crystallography data used are given in Appendix A.

At 1000 K, the α_2 phase transforms to an orthorhombic β phase. This transition results in a doubling of the unit cell with a' = $\sqrt{2}a$ and b' = $\sqrt{2}b$. The transition is discontinuous in the x and y directions. Reproducible hysteresis behaviour has been observed between the heating and cooling curves. The β structure has W atoms off-centre in the yz plane, but centred along x. The octahedra are sheared in the yz plane.

The β to monoclinic γ transition is tricritical. The γ phase has octahedral tilt system a a c⁺. At room temperature, a mixture of the γ and triclinic δ phases can exist. The δ phase has space group P $\overline{1}$ and octahedral tilt system a b c⁻. At 230 K, the δ phase transforms to the monoclinic ε phase, involving the loss of an inversion centre. This transition is thus centric to acentric, and ε -phase shows ferroelectric behaviour.⁸ The δ - ε transition is the only one of the phase transitions which involves no change in the octahedral tilt system. However, significant changes in W atom positions occur, which result in enhancement of long-short bond alteration along [110] ε (or [100] δ). Long-short bond alteration occurs in the x and y directions, but the distortion alters in direction from layer to layer. In the ε phase, the shifts in the -z direction are larger than the shifts in the +z direction, causing a net polarization.

Some other researchers have claimed to find additional discontinuities at around 40 K, 65 K, 130 K and 1500 K by studies of DTA, heat capacity and resistivity.^{9,10,11} Despite extensive neutron diffraction experiments at low temperature, no new phases have been found.^{3,12}

Tungsten oxide has been studied extensively, both in the bulk and the thin film form because of its useful properties. Following sections discuss briefly its properties and applications in both forms, and about the observations of superconductivity in this oxide.

4.2 Studies on Bulk Tungsten Oxide

Tungsten oxide is a piezoelectric material at very low temperatures (below -50°C) and behaves as a semiconductor at temperatures above -52° C.¹³ Recent studies confirm the ferroelectricity in the low temperature phase, ϵ -WO₃.³ This material has been studied quite extensively because of its electrooptic properties also. It can incorporate metal ions such as Na⁺, Li⁺ and hydrogen as substitutional atoms in the A site to form tungsten bronzes. These bronzes and amorphous tungsten oxide, when irradiated by UV radiation, on application of an electric field, or when doped with protons of high mobility, display colour centres. This phenomenon has been attributed to the optical

transfer of the electrons from their self-induced potential wells to one of the neighbouring undistorted states (from W^{5+} to W^{6+}).¹⁴ This property is particularly useful in electrochromic devices. Another application of WO₃ has been found as a gas sensing material. The interactions of gases such as H₂S, NO, and NH₃ with this oxide induce changes in the electrical conductivity.¹⁵

4.2.1 Reduced Tungsten Oxide: WO_{3-x}

In practice, most WO₃ crystals are slightly oxygen deficient, and this very slightly reduced WO₃ has a similar structure to the completely unreduced material, with localised defects. Slightly surface reduced tungsten oxide can be produced by heating in vacuum at 500°C. WO₃ can be further reduced by heating it along with tungsten metal. Substochiometric structures tend to form, containing crystallographic shear planes (CS planes) and pentagonal tunnel structures, as shown in Fig. 4.3 and 4.4. The shear structures contain blocks of corner-sharing octahedra which share some octahedral edges with other similar blocks. Shear structures can also be produced by replacing some of the tungsten (VI) ions with tantalum (V) ions. At first, CS planes in the {102} orientation are formed. As the oxygen loss increases, the CS plane concentration increases. At WO_{2.93}, shear planes in the {103} orientation are also formed, up to WO_{2.85}. Then, the tunnel structures WO_{2.82} and W₁₈O₄₉ (WO_{2.72}) develop.¹⁶ As oxygen loss increases further, reduction to WO₂ can occur.



FIGURE 4.3 CS phases and tunnel structures. (a) CS planes (from ref. [16]). (b) Pentagonal columns of edge shared WO₆ octahedra are shown in a $(x \frac{1}{2} z)$ section of $W_{18}O_{49}$, highlighted in grey. The structure also contains empty hexagonal channels(from ref [17]).



FIGURE 4.4 Transmission electron microscope images of {102} CS planes (A) and pentagonal columns (B); from ref. [18].

4.2.2 M_xWO₃

 WO_3 can react with protons or metal ions, e.g. Na^+ , Li^+ , K^+ , ammonium ions or hydrogen, to form tungsten bronzes. The reaction is:

WO₃ + xA
$$\rightarrow$$
 A_xWO₃ $0 \le x \le 1$ A=H, Na, K, Li, etc

Intercalation of these ions into monoclinic WO_3 results in structural phase transitions firstly to tetragonal, then to cubic forms. Associated with the transition is a change in colour, from yellow/green WO_3 to firstly a blue colour, followed by a red/yellow colour. It is believed that the reaction mechanism involves the injection of both ions and electrons, resulting in the formation of W^{5+} sites.

<u>Na_xWO₃</u>

At very low values of x the Na_xWO_3 adopts low symmetry structures similar to undoped WO_3 .¹⁹ The structure of the fully saturated $NaWO_3$ (shown in Fig. 4.5) is similar to that of WO_3 , with sodium occupying the 12-fold co-ordinated 'A' sites in the perovskite structure. At intermediate compositions, non-stochiometric sodium tungsten bronzes of formula Na_xWO_3 are formed.^{20,21}



FIGURE 4.5 Structure of NaWO₃. The central atom (white) is W, the atoms on the faces (black) are O, and the corner atoms (grey) are Na.

Two separate tetragonal phases of Na_xWO₃ are known in this intermediate range. The tetragonal II bronze (TII) has x up to 0.2 and is dark blue in colour. The TII phase has P4/nmm symmetry, the same as the high temperature α_1 WO₃ phase, although the lattice parameters of a = 5.2492 Å and c = 3.8953 Å at x = 0.1²² are smaller than in the α_1 phase. The tetragonal I bronze (TI) is relatively light blue in colour, with 0.2<x<0.5. The TI phase has a = 12.097 Å; c = 3.754 Å for x = 0.33 and a = 12.150 Å; c = 3.769 Å for x=0.48.²³ In the TI phase superconductivity has been observed with a T_c of up to 3 K.²⁴

Electronic properties of WO₃ and its oxygen deficient form have been a subject of study because the charge transport in these oxides can shed some light on the possible pairing mechanism in high-temperature superconductors, namely Bose condensation of pre-formed bipolaron charge carriers. The motion of charge carriers in this oxide is neither by motion of free electrons nor by diffusive flow of ions. This rather happens by the formation of bi-polarons.²⁵ The characteristics of these bi-polarons make this oxide an interesting subject of study for its transport properties.²⁶

4.3 WO₃ Thin Films

WO₃ thin films have been studied since the late 1970's because of their applications in electrochromic devices such as electronic displays²⁷ and later for gas sensing applications.²⁸ Early efforts on the deposition of WO₃ were made by vacuum evaporation of WO₃ powder. Later films were also deposited by CVD processes²⁹, and sputtering.³⁰ But most of these studies were limited to the deposition of amorphous thin films and their electrical and optical characterisation. Later, Kaneko *et*

 $al.^{31}$ studied the effects of deposition conditions on the film properties in the films which were sputter deposited at varying total gas pressure and oxygen concentrations at 200°C. They concluded that amorphous and crystalline films prepared at a high total pressure had better electrochromic properties than those deposited at low pressure. Among some of the early work on deposition of epitaxial WO₃ thin films, Kobayashi *et al.*³² studied *rf* sputtered WO₃ films on MgO (100) and sapphire substrates at different oxygen concentrations in the sputtering gas at 450°C and determined the necessary oxygen concentration to deposit epitaxial WO₃ thin films on. Recently Legore *et al.*³³ have studied the growth processes in these films. They grew the WO₃ films by *rf* magnetron sputtering and direct electron beam evaporation. The films grown at room temperature were amorphous and post annealing in O₂ induced the formation of polycrystalline films. Epitaxial growth of tetragonal phase on r-sapphire takes place at 600°C in ultra high vacuum electron beam evaporation. They also showed that epitaxial films exhibit higher electrical conductivity and better gas sensing properties than polycrystalline films. Tagstrom and Jansson³⁴ studied CVD deposited epitaxial WO₃ films on r-plane sapphire. They determined the structure of the films as monoclinic confirmed by Raman spectroscopy.

4.4 Observations of Superconductivity

Superconductivity in bulk WO₃ was first observed in the tungsten bronzes at very low temperatures.^{35,36,37} The transition temperature (T_c) for these materials varies from 0.5 K for Na_{0.3}WO₃ to 6.6 K for Rb_{0.3}WO₃. It has also been found that hexagonal tungsten bronzes are more conducive to be superconducting than the tetragonal ones. The cubic perovskite structure is not superconducting at all. The observation of superconductivity is hence associated with the linking of oxygen octahedra in such as way that they produce a noncubic symmetry (tetragonal or hexagonal) after doping with cations. However this condition applies only for d-band materials. These were the first few reports on low temperature superconductivity observed in these materials.

After a very long gap, very recently Aird and Salje³⁸ discovered low temperature superconductivity at 3 K (at zero field) in the twin walls of reduced WO₃ (named as 'Sheet Superconductivity'). They reduced the WO₃ single crystals by Na vapour at 730 K in a quartz tube. The colour of the sample after the reduction was bluish. The reaction product was a non-superconducting matrix of tetragonal WO_{3-X} containing superconducting twin boundaries (see Fig. 4.6). These boundaries were regions along the original orthorhombic-tetragonal twin boundaries and were reduced slightly more than the matrix. These regions were found to be free of Na. The oxygen content along the twin boundaries was

slightly more than 2.9 and that in the matrix was 2.95.⁵ Another important aspect of this discovery was high values of critical field, H_{C2} , as shown in Fig 4.7.



FIGURE 4.6 Reduced crystal of WO_3 showing superconducting phase along domain boundaries (marked by black arrows), Scale Bar = 50 μ m; From reference [38].



FIGURE 4.7 Field dependence of resistivity of a reduced WO_{3-x} sample with mainly parallel domain walls; magnetic field values of 0 to 14.1 tesla were used; from reference [4].

Another very recent report is about the discovery of high temperature superconductivity³⁹ in Na doped WO₃. The authors showed that WO₃ single crystals with Na doped surface, with a composition of Na_{0.05}WO₃ exhibit a sharp diamagnetic step in the magnetization at about 91 K and a magnetic hysteresis below this temperature (see Fig. 4.8). During the transport measurements, they also observed a sharp decrease in the resistivity of the sample at around 91 K, with a sharp metal-insulator transition at about 100 K (see Fig. 4.9). These observations were attributed to the possible nucleation of a superconducting phase on the surface of WO₃ crystals. Interestingly the colour of the surface after doping was olive green, quite similar to the colour of the samples produced by Aird and Salje.³⁸ If this observation is true then this is the first non-cuprate oxide exhibiting superconductivity in this temperature range.



FIGURE 4.8 (a) Existence of sharp diamagnetic step in magnetisation at 91K, (b) Magnetic hysteresis below 91K; from reference [39].



FIGURE 4.9 Transport measurements using a current of 10 nA and in a voltage limited mode of 10 V for H=0 Oe and 10^4 Oe; from ref. [39].

4.5 Present Work

 WO_3 thin films were chosen as a subject for this study because of recent discovery of low and high temperature (~3 K and ~90 K) superconductivity in the bulk form of this oxide in reduced and sodium doped states respectively. Interest grew in depositing single crystal thin films of this material which when reduced or doped with Na can give rise to fascinating properties.

The present work is about deposition and characterization of epitaxial WO₃ thin films. Single crystal films are of particular interest due to the possibility of creating locally superconducting regions in the form of defects such as thin twin boundaries (few nm) upon doping or reducing the film with Na, in an otherwise single crystal film without having large scale crystallographic defects such as large angle grain boundaries. This can lead to the formation of many exciting devices (e.g. a tunnel junction formed by a very thin superconducting twin wall in conducting matrix or film), obviating the need of patterning and lithography. Also, the use of this oxide would allow us to make these device structures relatively easily because of the chemical simplicity of WO₃ as compared to the present generation of high T_c superconducutors such as YBa₂Cu₃O_{7- δ} (YBCO) which are very complex oxides and are difficult to fabricate.

Attempts were made to grow epitaxial thin films of WO_3 on single crystal substrates of $SrTiO_3(100)$ and R-plane sapphire at different temperatures. The deposited films were then characterized by XRD for phase identification and texture determination. AFM was performed for morphological characterization. The films were then heat-treated with Na for different times at various temperatures. Transport measurements were carried out on the heat treated films to observe any existence of superconductivity.

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Chapter 5 Results and Discussion of WO₃ Thin Films

This chapter presents the results of WO_3 films deposited on single crystal $SrTiO_3$ (100) and R-sapphire substrates. The films were characterized by optical microscopy, Raman spectroscopy, X-ray diffraction for structural characterization and atomic force microscopy for morphological studies. Films were heat treated with Na in order to reduce them or to dope with Na. Low temperature transport measurements were made on heat treated samples using a four point probe to observe any existence of superconductivity.

5.1 Introduction

 $SrTiO_3$ was chosen as a substrate because of very close lattice matching with WO_3 . To the best of my knowledge, there has been no report of the deposition of WO_3 films on $SrTiO_3$ (100). R-sapphire was chosen because it a cheaper and easily available substrate. Also, both $SrTiO_3$ and R-sapphire are electrical insulators, which is useful for gas sensing and other applications. $SrTiO_3$ possesses a cubic perovskite structure and its lattice constant is 3.905 Å and sapphire has a trigonal structure and its a and c lattice constants are 4.758 and 12.991 Å, respectively.

5.2 Films on SrTiO₃ (100)

5.2.1 Raman Spectroscopy

Raman spectroscopy was used as a tool for phase analysis of WO₃. Raman spectroscopy was performed in order to identify the phase unambiguously. With this technique, it is possible not only to identify different oxides but also to detect intercalated H₂O. Raman scans of two WO₃ films, deposited at 850 and 550°C respectively, and a bare SrTiO₃ (100) substrate are shown in Fig. 5.1 (a-c). All other films showed the similar kind of Raman traces. The films showed Raman shifts at 819, 699, 420, 374, 323, 300, 269, 193 and 147 cm⁻¹. A comparison of these values with those reported in literature^{1.2.3} shows that the film phase is room temperature monoclinic γ -WO₃. The main difficulty in getting reasonable intensity of the films' peaks was due to strong and very broad Raman shift peaks from the substrate between 100 to 1000 cm⁻¹ shown in Fig. 5.1 (c).







(b) WO_3 / $SrTiO_3$ (100), $T_d=550^{\circ}C$

FIGURE 5.1 Raman spectra of WO₃ films on SrTiO₃ (100) deposited at (a) 850 °C, (b) 550 °C and (c) of bare SrTiO₃ (100) substrate; the films were 0.75 μ m thick.

5.2.2 X-ray Diffraction Results and Discussion

θ-2θ scans of the films on (100) SrTiO₃ are shown in Fig. 5.2 and illustrate that the phase could be either monoclinic γ-WO₃ or orthorhombic β-WO₃. However Raman spectroscopy results confirmed it as a monoclinic γ-WO₃ phase. It can be observed from these X-ray scans that the (002) peaks of the films overlap with the (100) substrate peaks because of very similar inter-planar spacings. The reported 2θ positions for the (100) peak of SrTiO₃ and (002) peak of monoclinic WO₃ in the bulk form are 22.782° and 23.118° respectively.⁴ A low intensity separate film (020) peak can also be observed in Fig. 5.2. The (200) film peak was not seen in any of the films (2θ = 24.36°). It can be observed that all the film peaks were shifted to the left compared to their bulk values. The intensity of the (020) peak decreases as the deposition temperature decreases and is not seen at all in the film deposited at 500°C. There are no other film peaks present. These observations strongly suggest (001) plane epitaxy between WO₃ films and (100) SrTiO₃, meaning that the film planes are crystallographically aligned with the substrate planes. The disappearance of the (020) peak at lower temperature implies improved (001) epitaxy. These results show that it is possible to deposit epitaxial WO₃ films on (100) SrTiO₃ substrates at relatively low temperatures.

To confirm the presence of (001) epitaxy, pole figure analysis of the films was carried out using the (222) reflection which, if the films were epitaxial, would give a characteristic four-fold symmetry. The results are shown in Fig. 5.3 (a-e) and one can clearly see this four-fold symmetry confirming the (00l) epitaxy of the WO₃ films and strong in-plane alignment with the substrate. The angular spread of these poles was approximately 7-10°. This texture remains consistent in all the films deposited at temperatures down to 500°C. The pole figure analysis was also carried out with the (112) film reflection. These pole figures, as shown in Fig. 5.4, again confirm the presence of strong (001) crystallographic alignment of the film with the substrate and also show strong in-plane alignment. Fig. 5.4 (a) is the (112) pole figure of the film deposited at 850°C which is equivalent to the characteristic (112) pole figure of a cubic single crystal (with 12 poles). Interestingly, the number of poles between $\Psi = 60$ to 70° reduces as the deposition temperature decreases (Fig. 5.4 (b)) and are not seen at all in a film deposited at 500°C (figures 5.4 (c)). This is probably due to the decreased proportion of the (010) and (100) oriented material in the film as compared to the (001) oriented material upon reducing the deposition temperature. Presence of all the possible (112) poles in Fig. 5.4 (a) suggests that the film consists of some fraction of (100) oriented WO_3 (although not observed from the 2θ scan in Fig.5.2). This change is also evident from the Fig. 5.2 as the (020) peak

disappears at lower temperatures. These results again illustrate that the (001) epitaxy of WO₃ with (100) SrTiO₃ improves at the lower deposition temperatures.

The strong (001) texture in WO₃ films on (100) SrTiO₃ can be attributed to the good lattice matching between (100) SrTiO₃ and monoclinic γ -WO₃. The mismatch in the three crystallographic directions of the film with respect to the substrate plane i.e. along [100], [010] and [001] is 6.5, 3.5, and 1.5% respectively. From the lattice mismatches it is apparent that the plane with the lowest misfit with (100) $SrTiO_3$ is the (100) film plane, however our results show that the (001) film plane is preferentially aligned with the (100) substrate plane. This suggests that the (001) film plane is energetically stable on the (100) substrate plane despite a larger lattice mismatch as compared to (100) and (010) planes. Another interesting observation from Fig. 5.2 is the larger (002) plane spacing of the film than the bulk⁴ i.e. shift of (002) peaks towards lower 2θ . This is unexpected because, for the (001) plane of the film to align with the (100) plane of the substrate, a and b lattice parameters of the film have to stretch, resulting in a decrease in the (001) plane spacing i.e. shifting of (002) films peaks towards higher 20 value. Possible reason for this could be other stresses in the film such as thermal stresses due to mismatches between the coefficients of thermal expansion of the film and the substrate. However we could not determine these stresses because of lack of any data on the coefficient of thermal expansion for WO_3 . Another possible cause could be the internal stress in the thin films which are responsible for structural differences between the thin film and the bulk form of a material.

From the pole figure patterns, we attempted to find out the in-plane orientation relationship between the film and the substrate. A comparison of (222) pole figure of the films (see Fig. 5.3 (a-e)) and (111) pole figure of the substrate (see Fig. 5.3 (f)) illustrates the perfect alignment of the films with the substrate which is evident from the poles lying at the same positions as the poles from the substrate. This is an indication of the (001) film plane aligning very well with the substrate cube plane, with [100] and [010] directions of the film parallel to the cube directions of the substrate. This epitaxy can be schematically represented as shown in Fig 5.5. This is presumably the preferred configuration with minimum free energy. Hence, we can deduce that the in-plane orientation relationship exhibited by these films with the substrate is: $[110]_{WO_3} \parallel <110>_{SrTiO_3}$ and $[010]_{WO_3} \parallel <010>_{SrTiO_3}$.



FIGURE 5.2 θ -2 θ scans of the films deposited on SrTiO₃ (100) substrate at various deposition temperatures. The films were 0.75 μ m thick.



FIGURE 5.3 (2 2 2) pole figures of the WO₃ films deposited on (100) SrTiO₃ substrate at (a) 850, (b) 725, (c) 650, (d) 575, (e) 500 °C; and (f) (111) pole figure of the substrate; (Scale: each ring corresponds to ψ =10° on the Wulff net).



(a)









FIGURE 5.4 (112) pole figure confirming the presence of (001) texture for the films on (100) $SrTiO_3$ deposited at (a) 850, (b) 575, and (c) 500 °C; (Scale: each ring corresponds to $\psi = 10^{\circ}$ on the Wulff net).


FIGURE 5.5 Schematic of probable epitaxial relationship in $WO_3 ||$ SrTiO₃ (100), the lattice mismatches in [100], [010] and [001] direction are 1.5, 3.5, and 6.5%. (dark circles represent (100) mesh of SrTiO₃ and open squares denote the square mesh of γ WO₃ (001).

5.2.3 Atomic Force Microscopy

Fig. 5.6 shows the AFM micrographs of the two 0.75 μ m thick WO₃ films on SrTiO₃ (100) deposited at 850 and 500°C respectively. The morphology of the films suggests that films grow in a columnar fashion. The roughness of these films was of the order of 9 and 5 nm respectively. This decrease in the film roughness with decreasing deposition temperature is an indication of the improvement in the film epitaxy which is also supported by XRD observations (see section 5.2.2). The lateral size of the columns was approximately same in both cases; about 150-200 nm. This shows that the lateral diffusion of film species on the film surface is not influenced by decrease in the deposition temperature.



FIGURE 5.6 AFM images of 0.75 μ m thick WO₃ films on SrTiO₃ (100) deposited at different temperatures; (a) 850 and (b) 500 °C.

5.3 Films on R-plane Sapphire

5.3.1 X-ray Diffraction

The films deposited on R-plane sapphire were also crystallographically aligned with the substrate as illustrated by the θ -2 θ scans shown in Fig. 5.7. The phase present could be either orthorhombic β -WO₃ or monoclinic γ -WO₃, based on the angular positions of peaks. Raman spectroscopy again confirmed the phase as monoclinic WO₃. It can be observed from the XRD scans that the films are strongly (001) oriented, which is revealed by the very strong (002) peaks. However one can also observe the presence of weaker (020) and (200) peaks. (002) peak broadening can also be seen upon decreasing the temperature.

To confirm the presence of (001) texture, (2 2 2) pole figure analysis of these films was carried out. These pole figures, as shown in Fig. 5.8 (a-d), reveal perfect four-fold symmetry at approximately Ψ =55° with an angular spread of 6-7° which is an indication of very strong (001) texture and very good in-plane alignment. To illustrate the orientation relationship between the WO₃ films and the Rplane sapphire substrate, we have superimposed the $(11\overline{2}0)$ pole figure (or $(10\overline{1}2)$ standard projection) of sapphire onto the (222) pole figure (or (001) standard projection) of the WO_3 films maintaining the relative positions; see Fig. 5.9 (three digit and four digit notations represent film and substrate planes respectively). This illustrates that the films deposited on R-plane sapphire exhibit an orientation relationship of $[1\bar{1}0]_{WO_3} \parallel [0\bar{1}0]_{Sapphire}$ and $[110]_{WO_3} \parallel [21\bar{1}]_{Sapphire}$. The lattice matching of the monoclinic phase with R-plane sapphire can also be understood from the schematic diagram, shown in Fig. 5.10, depicting the relative atomic positions. In this case, the square mesh formed by the diagonals of the R-plane sapphire matches almost perfectly with the (001) WO_3 . The mismatches are 4.2, 7.1, and 8.5% along [100], [010] and [001] directions of WO₃. In this case, it is favourable for the (001) plane of WO_3 to align preferentially with the diagonals of the R-plane sapphire unit cell and this is also consistent with the 2 θ scans. The <110> directions of the film run parallel to the <010> and $<21\overline{1}>$ directions of the substrate, also shown by Fig. 5.9. Relatively higher lattice mismatch for the WO₃ films on R-sapphire than in the films on $SrTiO_3$ (100) and low mobility of film species at lower temperatures could be the reasons for peak broadening in the films deposited at lower temperatures.

These results indicate moderate quality epitaxy in the films deposited on R-plane sapphire. Low angular spread of the poles reveals that (001) epitaxy of WO_3 films is of higher quality on R-plane

sapphire than on (100) SrTiO₃. These results are consistent with the results of Kobayashi *et al.*⁵ who observed the epitaxy of WO₃ on R-plane sapphire at low temperatures and LeGore *et al.*⁶ who reported epitaxial deposition of WO₃ on R-plane sapphire at 600 °C, but no orientation relationship was reported. However, these results are not in full agreement with those of Tagtstrom and Jansson¹ who used a different deposition technique at lower deposition temperature. Although the equilibrium structure was monoclinic in both cases, the preferred orientation of the films differs. We find highly (001) oriented films whilst they found triplet peaks corresponding to the (100), (010) and (001) reflections with (0*k*0) peak of highest intensity. The higher quality of epitaxy on R-plane sapphire as compared with (100) SrTiO₃ is an interesting feature, suggesting that the lattice matching may not be the only criterion for epitaxy. Interfacial energy considerations may be favourable for the films on R-plane sapphire substrates as compared with (100) SrTiO₃.



FIGURE 5.7 XRD patterns of films deposited on R-sapphire at various deposition temperatures.



FIGURE 5.8 (222) pole figure of the films on *R*-sapphire deposited at (a) 850, (b) 725, (c) 650, (d) 575 °C; and (e) $(11\overline{2}0)$ pole figure of the substrate; (Scale: each ring corresponds to $\psi=10^{\circ}$ on the Wulff net).



FIGURE 5.9 Superimposition of (001) WO_3 and (10 $\overline{1}$ 2) *R*-sapphire standard projections in the relationship shown by pole figures ($o - WO_3$, \blacksquare - *R*-sapphire, *S* – substrate, and *F* – film).



FIGURE 5.10 Schematic diagram illustrating the epitaxy between $WO_3(001)$ (mesh of open squares, dimensions-7.3x7.5 Å) and *R*-plane sapphire (black circles).

5.3.2 AFM Results

Fig. 5.11 shows the AFM micrographs of the two 0.75 μ m thick WO₃ films on R-sapphire deposited at 850 and 500°C respectively. These films also showed the similar morphology as observed for the films on SrTiO₃ (100). The roughness of these films was of the order of 3-4 nm, the same for both cases. Another interesting aspect of these films is their lower roughness as compared to the films on SrTiO₃ (100). This could again be due to the better nature of film epitaxy on R-sapphire than on SrTiO₃ (100). The lateral size of the columns was approximately 250 nm for the films deposited at 850°C and 100-150 nm for the films deposited at 500°C.



FIGURE 5.11 AFM images of WO_3 films on R-sapphire deposited at different temperatures; (a) 850 and (b) 500 °C.

5.4 Heat Treatment

 WO_3 samples were heat-treated with sodium vapour in a quartz tube in order to reduce or dope the samples with sodium. These heat treatments were carried out by Alison Aird at the Department of Earth Sciences. Heat treatment conditions for some of the samples are listed in Table 5.1. Heat treatment time and temperature were varied to achieve different levels of reduction or doping.

No.	Substrate and preparation conditions	Heat-treatment conditions	Transport characteristics
1	R-Sapphire, T _d =650°C	5 m/400°C; 60 m/377°C	Semiconducting till 300 mK
2	R-Sapphire, T _d =650°C	30 m/470°C	Insulating
3	SrTiO ₃ (100), T _d =600°C	6 h/430°C	Semiconducting till 300 mK
4	SrTiO ₃ (100), T _d =650°C	95 m/372°C	Insulating
5	SrTiO ₃ (100), T _d =850°C	10 m /460°C	Insulating

TABLE 5.1 Summary of heat treatments and transport measurement results

T_d – Deposition Temperature

5.5 Optical Microscopy

5.5.1 As-deposited Films

Among as-deposited films, WO_3 films on $SrTiO_3$ (100) showed tweed structures viewed in a transmitted polarized light microscope which arises from the substrate. An example of this pattern can be seen in Fig. 5.12.



FIGURE 5.12 Optical micrograph of a WO_3 film deposited on $SrTiO_3$ (100) showing the tweed pattern. The width of the photo is approximately 500 μ m. The colour of the film was yellow.

An example of WO_3 film on R-sapphire is shown in Fig. 5.13. Films on R-sapphire did not show formation of any kind of tweed pattern when observed under polarized light microscope. The surface of the films was without any distinguishable feature.



FIGURE 5.13 Optical micrograph of a WO₃ film deposited on R-Sapphire showing a featureless surface. The width of the photo is approximately 750 μ m.

5.5.2 Heat Treated Samples

Upon heat treating with sodium vapour, a colour change was observed in the surface of the film. A micrograph of such film is shown in the Fig. 5.14. Films were also examined by scanning probe microscopy to measure the sodium and oxygen concentrations. It was generally found that the films were both reduced and incorporated sodium after heat treatment.



FIGURE 5.14 Optical micrograph of a WO_3 film on $SrTiO_3$ (100) after reaction with sodium vapour. A change in colour from yellow to blue was observed. The width of the photo is approximately 350 μ m.

Contacts were deposited onto these samples for low temperature measurements. Figure 5.15 shows an example of a film with gold electrical contact pads deposited onto the surface.



FIGURE 5.15 A WO₃ thin film with contacts deposited. The width of the photo is approximately 500 μ m.

5.6 Results of Transport measurements

In-plane transport measurements were made on all the samples which were heat treated. Some of the samples were found to be semiconducting down to 300 mK and some samples became extremely insulating while cooling down. Results for the films on both substrates are shown in Figs. 5.16-5.20 and are summarized in Table 5.1. No particular trend was observed between heat treatment temperature, time and transport properties. For samples 2 and 4, accurate measurements could not be carried out below 200 K and 50 K respectively because of high resistance.



FIGURE 5.16 R-T Characteristics of a WO₃ film deposited on SrTiO₃ (100) at 650 \degree and heat treated at 400 \degree for 5 m and then at 377 \degree for 60 m (sample 1).



FIGURE 5.17 *R*-*T* characteristics of WO₃ film on *R*-sapphire deposited at 650 °C and heat treated at 470 °C for 30 m (sample 2).



FIGURE 5.18 *R*-*T* Characteristics of a WO₃ film deposited on SrTiO₃ (100) at 600 $^{\circ}$ and heat treated for 6h at 370 $^{\circ}$ (sample 3).



FIGURE 5.19 Transport properties of a WO₃ film on SrTiO₃ (100) deposited at 650 $^{\circ}$ C and heat treated for 95 m at 372 $^{\circ}$ C (sample 4).



FIGURE 5.20 *R*-*T* Characteristics of a WO₃ film deposited on SrTiO₃ (100) at 850 °C and heat treated for 10 m at 460 °C (sample 5).

5.7 Discussion on the Transport Measurement Results

Transport measurements of the heat treated samples reflect the possibility that samples don't possess the precise levels of oxygen deficiency and sodium doping. Semiconducting nature of some samples suggests that the reduction level is high enough to produce the charge carriers to give rise to conduction. The insulating samples suggest that they are not reduced enough to give rise to presence of charge carriers which are essential for conduction. Superconductivity was not observed in any of the samples which shows that it was not possible to reduce or dope the samples with precise oxygen or sodium concentration.

5.8 Summary

Good quality epitaxial tungsten trioxide films were deposited on (100) $SrTiO_3$ and R-plane sapphire substrates by DC reactive magnetron sputtering at temperatures varying between 500 and 850°C. The equilibrium phase of the films was monoclinic γ -WO₃. It was found that films on both substrates were epitaxial, with [001] orientation along the growth direction. The epitaxy on R-plane sapphire was of higher quality than on (100) $SrTiO_3$, as indicated by the angular spread of poles in the pole figures, despite better lattice match with (100) $SrTiO_3$. The epitaxy does not degrade at deposition temperatures as low as 500°C, and the (001) alignment on (100) $SrTiO_3$ improves as the deposition temperature decreases. The films deposited on both (100) $SrTiO_3$ and R-plane sapphire maintained the same alignment with the substrate for all temperatures. The orientation relationship of the films deposited on (100) SrTiO₃ was $[110]_{WO_3} \parallel < 110 >_{SrTiO_3}$ or $[010]_{WO_3} \parallel < 010 >_{SrTiO_3}$ and those deposited on R-plane sapphire exhibited orientation relationships of $[1\bar{1}0]_{WO_3} \parallel [0\bar{1}0]_{Sapphire}$ and $[110]_{WO_3} \parallel [21\bar{1}]_{Sapphire}$.

In order to observe whether such films could show superconductivity, they were heat treated with sodium vapour to reduce them or to dope them with Na. Low temperature transport measurements showed that none of our samples exhibited any trace of superconductivity.

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Chapter 6 Ferroelectricity and Ferroelectric Thin Films

This chapter deals with the fundamental principles of ferroelectricity and its application to the working principle of a ferroelectric memory. It also summarises the candidate materials for ferroelectric random access memory applications (FRAM) and their properties. Special emphasis has been given to $Pb(Zr,Ti)O_3$ and $SrBi_2Ta_2O_9$. Both polycrystalline and epitaxial thin films deposited by various different processes are discussed.

6.1 Introduction

The idea to use ferroelectric materials as data storage devices dates back to early 1950s and onwards when researchers at various laboratories (e.g. IBM) conducted research on ferroelectric capacitors to replace existing ferromagnetic memories which were space consuming.¹ In a ferroelectric material, by using the two stable remanent polarization states $+P_R$ and $-P_R$ of a ferroelectric crystal at zero electric field, it is possible to store the information as '0' and '1' states of data required for Boolean algebra. However these early efforts on ferroelectric memories were unsuccessful because of higher operating voltage of the devices, poor control of switching threshold and lack of isolation of memory elements in the matrix. In the 1970s a major amount of research was focused towards the development of Sibased random access memory devices (RAM) and read only memory devices (ROM) such as Dynamic RAMs (DRAM), Static RAMs (SRAM), Electrically Programmable ROMs (EPROM), Electrically Erasable Programmable ROMs (EEPROM) which offered good performance at low cost

and reasonable compactness. Among these ROMs, DRAMs and SRAMs were volatile i.e. uninterrupted power supply was required to retain the data, whereas EPROMs and EEPROMs were non-volatile. However EPROMs and EEPROMs suffered from slower read and write speeds and a limited number of allowed write cycles as compared to their volatile counterparts DRAMs and SRAMs.

However, there was a renewed interest in ferroelectric memories again from the mid 1980s which is mainly because of improvement in the thin film deposition techniques.^{2,3,4,5} This permitted wafer scale integration of ferroelectric thin films as thin as 25 nm, lowering of operating voltages to as low as 1 V leading to reduced power consumption and a significant reduction in cost. A ferroelectric random access memory (FRAM) combines advantages of both volatile DRAM and SRAM and nonvolatile EPROM and EEPROM. A FRAM is nonvolatile like an EEPROM and EPROM, and can be accessed at higher speeds like a DRAM and SRAM (60 ns), and operates at lower voltages (< 5 V).^{6,7} Additionally FRAMs are radiation hard which makes them useful for military applications and satellite communication systems. Fig. 6.1 shows a plot of access time versus cost per bit developed and projected over a period of about 10 years. In 1988 (Fig 6.1 (a)), there were about 14 different kinds of digital electronic memories ranging from cheaper but slow and high density disks to the fast SRAMs. It was expected that by 1998 (Fig. 6.1 (b)), FRAM would eliminate core magnetic and bubble memory and other devices and thus would make the memory market more competitive. As of 1999 projection by NEC (Fig. 6.1 (c)), the future of FRAMs lies in the smart cards, audio memories, computers etc.

The following sections describe the phenomenon of ferroelectricity and working of a ferroelectric memory, properties required for a FRAM, candidate materials and present issues.



FIGURE 6.1 Cost per bit versus access time: (a) for various kinds of digital memory in use in 1988; (b) projections for 1998 made in 1989; (c) 1999 comparison by NEC; from ref. [6].

6.2 Principles of Ferroelectricity

This section should not be treated as a reference on ferroelectricity, which has been extensively reviewed by many authors.¹ Rather it attempts to provide a brief account of ferroelectricity principles and also describes the working of a ferroelectric memory. The phenomenon of ferroelectricity in ferroelectric materials is analogous to the ferromagnetism in ferromagnetic magnetic materials. Just as

the ferromagnetic materials exhibit a spontaneous magnetic moment at zero magnetic field, ferroelectric crystals also exhibit a spontaneous electric dipole moment per unit volume or polarization at zero electric field. This behaviour is observed below a certain transition temperature, named the Curie Temperature above which a ferroelectric phase converts into a paraelectric phase which always has higher symmetry than the ferroelectric phase and is in a non-polar state where dipoles are randomly oriented in crystal giving rise to zero polarization. In order to describe the essential feature of ferroelectricity, we assume a hypothetical model of a two dimensional crystal AB (which is oversimplified), shown in Fig. 6.2. The A ions which we assume carry a negative charge are located at the lattice points and B ions which carry a positive charge are located on the horizontal lines joining A ions. At equilibrium, B ions always lie closer to one of the two adjacent A ions than to the other. This situation can be explained in terms of potential between two adjacent A ions. There are two equilibrium positions in which a B ion can stay, but to change from one state to another, energy must be provided to overcome an energy barrier ΔE . Let us assume that at a given temperature T, all the B ions are closer to the A ions on their left and consider each AB group as an electric dipole. In this situation the structure can be visualized as the top two layers of fig 6.2 (a) and the assembly of dipoles can be expressed as the same rows in Fig. 6.2(b). In this state, the crystal is said to be spontaneously polarized: with a dipole moment per unit volume i.e. spontaneous polarization. The crystals exhibiting this property are called *pyroelectric* and the direction of spontaneous polarization is called the *polar axis*.



FIGURE 6.2 Schematic representation of structure and dipoles in a hypothetical 2-D crystal; from ref. [1].

6.2.1 Ferroelectric Domains

Alignment of dipoles in one of the polar directions may extend only over a region of the crystal and there can be different regions in the crystal with aligned dipoles which are oriented in many different directions with respect to one another. Regions of uniform polarization are called *domains*, and they are separated by a boundary from one another called a *domain wall*. Ferroelectric domain walls are much narrower than the domain walls in ferromagnetic materials. TEM observations have shown that ferroelectric domain walls are of the order of 1-10 nm.⁸ It should be noted that ferroelectric domain walls should not be confused with the grain boundaries in a polycrystalline material. Unlike grain boundaries, domain walls separate domains which are inclined to each other by angles which are governed by the crystal system of the ferroelectric. In a tetragonal perovskite material such as PbTiO₃, the direction of spontaneous polarization is along the c-axis of the ferroelectric tetragonal phase. In this material, the walls which separate domains with oppositely oriented polarization are called 180° walls (as shown in Fig. 6.3) and those separating the regions perpendicular to each other are called as 90° domain walls.⁹

The types of domain walls that can occur in a ferroelectric crystal depend upon the crystal structure and symmetry of both paraelectric and ferroelectric phases. In the rhombohedral phase of lead zirconate titanate, $Pb(Zr,Ti)O_3$, the direction of polarization develops along the (111) direction of the paraelectric cubic unit cell. This gives eight possible directions of spontaneous polarization with 180°, 71° and 109° domain walls. The criteria to derive the possible types of domain walls in a ferroelectric crystal can be found elsewhere.¹⁰

The driving force for the formation of domain walls is the minimization of the electrostatic energy of the depolarising field (E_d) and the elastic energy associated with the mechanical constraints arising due to ferroelectric-paraelectric phase transition. A depolarizing field, which is oppositely oriented to the direction of remanent polarization P_R , is caused due to the formation of a surface charge in the ferroelectric material at the onset of spontaneous polarization at the transition temperature. This depolarizing field will form whenever there is a non-homogeneous distribution of the spontaneous polarization (e.g. due to change in polarization at the grain boundaries or due to the fall-off of the polarization near the surface of ferroelectrics) and it can be very strong (of the order of MV/m), making the single domain state of the material energetically unfavourable. This electrostatic energy associated with the depolarizing field can be minimized by (i) splitting of the material into oppositely

oriented domains or (ii) compensation of the electrical charge via electrical conduction through the crystal.



Creation of 180° domain walls

FIGURE 6.3 Schematic representation of a 180° and 90° domain walls in a tetragonal perovskite crystal such as PbTiO₃; from ref. [9].

Formation of the domains may also be the result of mechanical constraints associated with the stresses created by the ferroelectric phase transition e.g. from cubic paraelectric phase to tetragonal paraelectric phase in PbTiO₃. Both 180° and 90° domains minimize the energy associated with the depolarising field but elastic energy is minimized only by the formation of 90° domains. Combination of both effects leads to a complex domain structure in the material with both 90° and 180° domain walls.

6.2.2 Ferroelectric Switching

Upon application of a DC electric field in the horizontal direction of Fig. 6.2, the dipoles which were already aligned in the field direction will remain aligned but those which are antiparallel will have a tendency to reorient themselves in the direction of electric field. Upon application of sufficiently large

electric field, their dipoles will be able to align themselves in the direction of applied field. This phenomenon of polarization reversal takes place by way of nucleation of favourably oriented domains and domain wall motion.



FIGURE 6.4 Characteristic hysteresis loops of a ferroelectric material.

If we assume that our hypothetical crystal has an equal number of positive and negative domains then the net polarization of the crystal will be zero. Upon application of an electric field E, initial polarization P increases linearly with the increasing electric field and the crystal behaves like a dielectric because the applied field is not large enough to switch any of the domains oriented opposite to its direction. A plot between P and E is shown in Fig. 6.4 and this linear region is shown as AB. Upon further increasing the electric field, oppositely oriented domains start to reorient themselves and polarization starts increasing rapidly (BC) until all the domains are aligned in the direction of the electric field i.e. reach a single domain state (CD) when polarization saturates to a value called *saturation polarization* (P_s). Upon decreasing the electric field, the polarization generally does not return to zero but follows path DE and at zero field some of the domains still remain aligned in the positive direction and the crystal exhibits a *remanent polarization* (P_R). To bring the crystal back to zero polarization state, a negative electric field is required (along the path EF) which is also called the *coercive field* (E_C). Further increase of electric field in the negative direction will cause complete reversal of all domains in the direction of field (path FG) and the loop can be completed by following the path GHD. This relation between P and E is called a ferroelectric hysteresis loop which is an important characteristic of a ferroelectric crystal. The principle feature of a ferroelectric crystal is not only the presence of spontaneous polarization but also the fact that this polarization can be reversed by application of an electric field.

6.2.3 Crystal Systems

The phenomenon of ferroelectricity is also influenced by the crystal system of the ferroelectric material. Only non-centrosymmetric crystal systems which have unique polar axis/axes can exhibit ferroelectricity. A polar axis is the one which shows directionality, and none of the symmetry operations appropriate to the crystal class will switch this directionality. The value of spontaneous polarization is dependent upon temperature i.e. polarization changes as the crystal temperature changes and electrical charges can be observed on the faces which are perpendicular to the polar axis. This effect is called the *pyroelectric* effect. However not all the crystals with these characteristics show ferroelectricity i.e. not all of them show reversibility of spontaneous polarization on applying electric field. So, a ferroelectric crystal is a pyroelectric crystal with reversible polarization upon application of an electric field.

6.2.4 Poling of Ferroelectrics

Due to the complex set of elastic and electric boundary conditions at each grain, ferroelectric grains in ceramics and polycrystalline films generally split into many domains (see Fig. 6.5). If the direction of spontaneous polarization is distributed randomly though the material then the material will show zero net polarization and is non-polar. Such material will not be either pyroelectric or piezoelectric. Polycrystalline ferroelectrics can be brought into a polar state by application of a strong electric field (10-100 kV/cm), usually at elevated temperatures. By this process, domains in an individual grain can be reoriented in the direction of the applied electric field. This material will have a non-zero polarization even if all the domains do not reorient themselves completely. A single crystal that does not have domains is said to be in a single or monodomain state. This state can also be achieved by

poling the crystal. It should be noted that by definition poling of polycrystalline material is possible only in ferroelectric materials. A polycrystalline pyroelectric (nonferroelectric) or piezoelectric materials cannot be poled.



FIGURE 6.5 Illustration of the reorientation of domains in a polycrystalline ferroelectric material after poling; from ref. [9].

The polarization at zero electric field is known as remanent polarization (P_R) as mentioned earlier. Maximum remanent polarization that can be achieved in a polycrystalline ferroelectric material depends upon the available domain states. Based on theoretical calculations¹¹, in a ferroelectric with only 180° domains, maximum P_R is 0.25 P_S . In a tetragonal ferroelectric with six available domain states, maximum P_R is 0.83 P_S . In a rhombohedral ferroelectric with eight possible domain states, maximum P_R is 0.83 P_S . In an orthorhombic ferroelectric with 12 possible domain states, (P_R)_{max} = 0.91 P_S . However actual polarization is lower because of inability of all the domains to be completely reoriented due to complex set of boundary conditions and also some domains switch back to the original state after removal of the field. This may be because of the strain associated with dimensional changes in the sample upon poling.

6.2.5 Measurement of Hysteresis Loop

Ferroelectric hysteresis loops can be experimentally measured using a Sawyer-Tower circuit¹², using an *ac* field, and are observed on the screen of an oscilloscope. The circuit is shown schematically in Fig. 6.6. Horizontal axis uses the voltage across the crystal and a quantity which is proportional to the field across the crystal is plotted on this axis. The linear capacitor C_0 is connected in series with the crystal. In this configuration, the voltage across C_0 is proportional to the polarization of the crystal. This polarization is laid across the vertical plates of the oscilloscope. This circuit not only measures the hysteresis loop, it also quantifies the spontaneous polarization P_s and coercive field E_c .



FIGURE 6.6 Schematic representation of sawyer-tower circuit; from ref. [12].

6.3 Basic Principle of Operation of a Ferroelectric Memory Cell

Most of the ferroelectric materials which could be potential candidates for ferroelectric devices including memories are oxides such as Barium Titanate, Lead Titanate etc. and these are based on the perovskite ABO₃ structure. The crystal structure of the characteristic tetragonal perovskite unit cell is shown in Fig. 6.7, where A^{+2} ions occupy the corner of the unit cell, B^{+4} ion lies at the centre of the unit cell and O^{-2} ions stay at the face centres of the unit cell. Since the cubic phase is centrosymmetric, having no polar axis, there is no net spontaneous polarization in the crystal. However, structural distortion at the Curie temperature causes the structure to change to a non-centrosymmetric tetragonal structure, which then gives rise to a net dipole moment (or spontaneous polarization). Movement of the central atom, B, is the key to the ferroelectricity. It works as a switch and can be moved up or down relative to other ions by application of an electric field. This characteristic of the central atom gives rise to the hysteresis behaviour in a ferroelectric material as

shown in the Fig. 6.4. At zero field we have two stable states of polarization $+P_R$ and $-P_R$, arbitrarily defined as states '0' or '1'. Binary information in the form of '0' and '1' can be stored by moving this atom up or down. When the power is interrupted, the atom stays in its position thereby preserving the data in the memory device. This phenomenon can be termed as *nonvolatility* and this property of a ferroelectric can be utilized to make a memory device which is non-volatile, generally known as FRAM (ferroelectric random access memory) device. The movement of the central atom is very fast and it can be moved many times e.g for 10^{12} switching cycles.



FIGURE 6.7 A typical ABO₃ perovskite unit-cell e.g. PbTiO₃. Remanent polarization is zero when the structure is cubic (paraelectric phase) and it is non-zero in the ferroelectric phase which has tetragonal structure.

A typical memory cell is schematically shown in Fig. 6.8. In the current devices, the memory cells are arranged in a square matrix. Therefore, a 1-megabit memory cell will have 1000 rows (drive line) and 1000 columns (word line). To overcome the crosstalk problem between two neighbouring cells, each memory cell capacitor is isolated from its neighbours by means of a passgate transistor. Each bit is written by applying one half a short voltage pulse along a row and the other half along a column. In this state, pulses add up to switch the polarization state only at the particularly addressed cell. Two reading schemes for the FRAMs are being explored, namely^{6,13}: Destructive readout (DRO) where the information must be rewritten after every read operation and Nondestructive read out (NDRO) where information can read over and over again until the next write operation. DRO is the most likely used scheme in the present generation FRAMs because it closely resembles a DRAM. In DRO, the bit is

read when a positive switching voltage is applied to the memory cell in the same way as the writing voltage is applied. If the data is already stored as state '0' or $+P_R$, then only a linear nonswitching response is measured in the form of a voltage across as 10-50 ohm resistor. If the data was stored as state '1' or $-P_R$, a switching response greater than the linear response is measured because it contains the additional displacement current term dP/dt where P is the polarization. A sense amplifier then compares this response with that of a reference cell which is always polarized in $+P_R$ or state '0'.



FIGURE 6.8 Schematic diagram of a typical memory cell; from ref. [13].

6.4 Characteristics of a FRAM Memory Material

A FRAM memory should show

- 1. low electrical conductivity,
- 2. good leakage and breakdown characteristics,
- 3. large switching polarization, necessary to store larger amount of data,
- 4. a low switching time (5-200 ns) for faster devices,
- 5. higher Curie temperature, above 100°C,
- 6. good aging and retention characteristics,

- 7. fatigue resistance up to a minimum of 10^{12} switching cycles (fatigue is defined as rapid decay in the polarization with increase in the polarization reversal cycles during bipolar switching),
- 8. Low power consumption i.e. low switching voltage (1-5 V), and
- 9. good imprint characteristics (imprint is caused by development of an internal field in the ferroelectric capacitor which leads to a progressive shift of the hysteresis loop along the field axis).

6.5 Issues for Integration of Ferroelectric Capacitors in a Commercial Memory Technology

- 1. Development of an appropriate electrode technology,
- 2. A suitable ferroelectric thin film material,
- 3. A thin film deposition process which can be scaled up and which has capability to deposit thin films with good conformal coverage over nonplanar surfaces,
- 4. Suitable and compatible lithography and etching technology to produce submicron patterns with extreme precision, and
- 5. A fitting device integration process

6.6 Electrode Materials for FRAMs

In an integrated ferroelectric thin film memory, top and bottom electrodes are required to switch the memory device between two polarization states on the application of an electric field. Importance of electrodes cannot be underestimated because they greatly affect the performance of the device in terms of both microstructure and properties. This section discusses the selection criteria, and different types of electrode materials with their relative advantage or disadvantage over each other. Choice of an electrode material is governed by many factors which are summarized as follows¹⁴:

- sufficiently low electrical resistance,
- chemical compatibility with the underlying semiconductor and the ferroelectric,

- adequate adhesion to the ferroelectric film and other components in contact,
- morphological stability under processing conditions,
- ability to act as diffusion barrier, and
- ability to control the microstructure and properties of the ferroelectric.

Based on these criteria, they can be broadly divided into two categories of materials: metals and oxides. Most common ferroelectric materials such as PZT and SBT are deposited under highly oxidizing conditions so it becomes necessary for the bottom electrode to be stable under these conditions, and this is a major limiting factor upon the choice of electrode.

6.6.1 Metal Electrodes

Conducting metal electrodes have been the most popular choice because of the ease of deposition. Fig. 6.9 shows a plot between partial pressure of oxygen and temperature which shows the stability conditions of different metals as compared with their oxides. It is evident that the choice is limited to few noble metals such as Pt, Au or Ag. However Ag and Au react with the ferroelectric perovskites during their processing which limits their use. This makes Pt as the only feasible choice for electrode material. Pt has been extensively used as the bottom electrode for ferroelectric thin films. It has been deposited mainly by sputtering and e-beam evaporation. Usually Ti (and sometimes Ta) has been used as an intermediate layer to improve the adhesion between Pt and underlying SiO₂ layer. However Pt/Ti electrodes suffer from two major drawbacks: (i) formation of hillocks due to stress relief in Pt films which can lead to capacitor shorting and (ii) Pt/Ti interactions leading to alloy or compound formation such as TiO₂, Pt₃Ti, Ti₅S₃. This hillock and compounds formation can lead to significant changes in the morphology and microstructure of PZT film. Many aspects of Pt/Ti electrodes and interactions have been discussed in detail by Shareef and Kingon.¹⁴



FIGURE 6.9 Stability regime of many metal electrodes with respect to their oxide in the FRAM processing conditions; from ref. [14].

6.6.2 Oxide Electrodes

An alternative to Pt electrodes for FRAM applications has evolved in the form of conducting oxide electrodes. It was shown that PZT films deposited on $YBa_2Cu_3O_{7-\delta}$ (YBCO) bottom electrodes did not suffer from fatigue.¹⁵ This discovery fuelled the research into the direction of finding many more such types of electrodes. Besides YBCO, many kinds of conducting oxide electrodes have been used as bottom electrodes to deposit ferroelectric thin films: RuO_2^{16} , $SrRuO_3^{17}$, $La_{1-x}Sr_xCoO_3$ (LSCO)¹⁸, IrO_2 .¹⁹ Additionally oxide electrodes are morphogically stable during ferroelectric film processing and do not suffer from hillock formation. Besides, it is easier to fabricate epitaxial ferroelectric thin films on single crystal oxide substrates using a buffer layer of a conducting oxide as electrodes than on Pt coated Si wafers. However PZT films deposited on the conducting oxide electrodes exhibit comparatively lower resistivity and poorer leakage characteristics than the PZT films on Pt electrodes.¹⁴

The resistivities of some oxide electrodes are compared in Table 6.1. It can be observed that the resistivity of oxides is far greater than that of Pt which is approximately 1 $\mu\Omega$ -cm.²⁰ However conductivity of oxides can be improved up to a reasonable value by using a suitable processing technique. It has been shown that the thin film electrodes of LSCO can exhibit resistivities of the order of 100 $\mu\Omega$ -cm.

Material	Resistivity ($\mu\Omega$ -cm)	Processing Method
RuO ₂	50-90	CVD
RuO ₂	150-180	RF reactive sputtering
LSCO	100-200	Pulsed laser ablation
LSCO	200	PECVD
YBCO	600	Pulsed laser ablation
YBCO	450	Ion beam sputtering
SrRuO ₃	340	Off-axis sputtering ²¹
Sr ₂ RuO ₄	270	Pulsed laser ablation ²²

TABLE 6.1 Comparision of resistivities of various oxide electrode materials¹⁴

6.7 Ferroelectric Thin Film Materials

For FRAM device applications, an ideal candidate material should have the properties mentioned in section 6.4. Of many of the hundreds or even thousands of known ferroelectric materials, only few are suitable for switching applications and can be integrated into semiconductor technology. Research towards the development of memory materials has been going on since the 1950s. First generation materials were KNO_3^{23} , $Bi_4Ti_3O_{12}$ (in DRAMs and FEFETs)²⁴, $BaMgF_4$ (in FEFETs).^{25,26} In particular, KNO_3 thin films possessed very high remanent polarization and well defined coercive fields but its hygroscopic nature makes it incompatible with standard IC processing technology. A review of the ferroelectric properties of these materials can be read elsewhere.²⁷ Later, $Pb(Zr_x,Ti_{1-x})O_3$ (PZT) emerged as a promising candidate for these applications.^{6,28,29} However PZT films on metal electrodes suffer from fatigue (i.e. drastic loss in the remanent polarization) upon cyclic switching for 10^{10}

switching cycles. Also PZT films are not easy to fabricate with controlled stoichiometry because of the presence of lead because of its high volatility under PZT processing conditions. It also leads to severe processing complications including environmental hazard issues and contamination problems. PZT thin films and their electrical characteristics are discussed briefly in subsequent sections.

Bi layered perovskite oxides such as $SrBi_2Ta_2O_9$ (SBT) emerged as the next generation materials after PZT as SBT thin films do not suffer from fatigue on Pt coated Si substrates.³⁰ This paved the path for a new area of research into the field of ferroelectric memory devices. However there were some serious problems with SBT also, such as lower remanent polarization in the polycrystalline state. Also, high structural anisotropy in ferroelectric properties make it essential to grow highly epitaxial SBT films in an appropriate orientation, which is an important issue to be dealt with. The present study focuses on the growth of epitaxial SBT films in different orientations. SBT is discussed in detail in subsequent sections with respect to its crystal structure, properties, current research into SBT thin film deposition and unsolved issues with SBT thin films. Also, there is a long list of other Bi-layered perovskites which have been studied so far for FRAM applications. Some of them are BaBi₄Ti₄O₁₅³¹, Bi_{3.25}La_{0.75}Ti₃O₁₂³², and Ba₂Bi₄Ti₅O₁₈.³³

6.7.1 Pb(Zr_x,Ti_{1-x})O₃ (PZT) and PZT Thin Films

6.7.1.1 Introduction

PZT has been a widely studied material for FRAM applications for over a decade. Compositionally it is a solid solution of lead titanate (PT) and lead zirconate (PZ) and its structure and properties can be tailored by varying the stoichiometric ratios of PT and PZ. Pb(Zr_x ,Ti_{1-x})O₃ thin films show high values of remanent polarization (20-50 μ C/cm²), low values of coercive field (~50-70 kV/cm), a high Curie temperature (> 400°C) and show a clear dependence upon x with optimum ferroelectric properties obtained near the morphotropic phase boundary (x=0.52) with Ti rich compositions showing high coercive fields.³⁴

6.7.1.2 Growth of PZT Films

Early studies were focussed on PZT films deposited on Platinized Si wafers using many different processes such as sputtering, laser ablation, MOCVD and sol-gel. Processing of these films has been

studied in detail by many authors.³⁵ The major problem in PZT film synthesis has been the high volatility of lead at the PZT film's synthesis temperatures. This gives rise to the formation of oxygen vacancies in the PZT films which are detrimental to the fatigue performance of the capacitor. The role of oxygen vacancies in promoting fatigue is discussed in detail in the following sections. Films have been deposited at temperatures in the range of 500-700°C depending upon the process. It is generally observed that crystallization of perovskite PZT on Pt/Ti electrodes is preceded by the formation of a non-perovskite pyrochlore-type phase which can be deficient in lead and oxygen (e.g. $Pb_{2-\delta}(Zr,Ti)O_{7-x})$.

Sreenivas et al.⁵ successfully demonstrated the use of magnetron sputtering to deposit highly oriented PZT films with controlled stoichiometry and properties, using elemental targets of Pb, Zr and Ti. They showed that highly oriented growth of PZT is governed by three main mechanisms: (i) formation of a reproducible oxide layer on the target surface, (ii) stability of oxide species formed during transport through the plasma towards the substrate, and (iii) nucleation and growth of the film on the substrate surface. It has also been shown that formation of the perovskite phase is affected by the lead incorporation in the films which is governed by the kind of sputtering system affecting the efficiency of lead transport through the plasma. Ishida et al.³⁶ showed that in a diode sputtering system, use of higher gas pressure led to a slower or poor transport of lead from the target to the film, thus requiring a larger supply of lead from the target. Whereas in a magnetron sputtering system³⁷ use of lower sputtering gas pressures enhances in the transfer of lead through the plasma to the film and thus requiring lesser lead enrichment of the target. Good quality films were deposited at temperatures ranging from 500 to 600°C.³⁷ In some cases they were deposited at much lower temperatures (250°C) followed by annealing in oxygen at 750°C.⁵ Sputtering of a compound PZT target led to the generation of O⁻ ions which caused uncontrolled bombard of the growing film surface resulting in a nonuniform surface composition and thickness across the film surface. This problem has been shown to be solved by many techniques including off-axis sputtering.

Ion beam sputter deposition (ISBD) processes have also been successfully used by a few researchers to deposit highly oriented, dense and smooth PZT films with controlled microstructure and properties.³⁸ Controlled bombardment of the film surface by low energy (~75 eV) oxygen ions leads to improved recrystallization of the films resulting in the formation of perovskite phase at temperatures as low as 500°C without forming the pyrochlore phase. It also results in the preferred

(001)-orientation in the PZT film. Typical values of remanent polarization were 25-30 μ C/cm². However, in ISBD-PZT capacitors on hybrid Pt/RuO₂ electrodes fatigue was not completely eliminated.³⁹ This could be because of damage on film/electrode interface due to scattered ions from the target. This is supported by the fact that similar films deposited by other processes such as laser ablation, MOCVD do not fatigue where ion-induced effects are absent.

Pulsed laser deposition (PLD) has been extensively used to deposit heterostructures of PZT and oxide electrodes of complex stoichiometry (YBCO or LSCO) which are relatively easy to deposit using PLD.^{40,41} 10% Pb-rich targets were required to counter the loss of lead due to its high volatility at high deposition temperatures generally used. Films were deposited at temperatures in the range of 550-670°C and at high background oxygen pressures (300-900 mtorr). Polycrystalline LSCO/PZT/Pt heterostructures were deposited on Pt/Ti/Si substrates. The films were highly (111) oriented with only perovskite phase. These films possess remanent polarization of about 5-10 μ C/cm² and showed longer polarization retention characteristics.⁴² Highly oriented PZT-based capacitors have been developed having comparatively large remanent polarization (30-40 μ C/cm²). This difference in the value of remanent polarization arises due to the fact that oriented films have mainly 180° domains which have lower strain after switching as compared to polycrystalline films. Also in the (001) oriented films the polarization vector is completely aligned in the direction of applied electric field which is not the case for the polycrystalline films. In another study, Grabowski et al.43 showed that PZT films were lead deficient if ambient oxygen pressure was less than 50 mtorr and deposition temperature was more than 600°C. Films deposited on $SrTiO_3$ (100) substrate showed better quality of crystalline perfection than on MgO (100).

High quality PZT films have also been deposited using chemical vapour deposition processes⁴⁴ and have shown good ferroelectric properties. Use of metalorganic precursors can decrease the processing temperature appreciably. PZT films of various Zr/Ti ratio, deposited on SrRuO₃ conducting electrodes, showed very good ferroelectric properties; high remanent polarization ($32-55 \,\mu\text{C/cm}^2$) and excellent fatigue resistance.⁵⁸ However an unusual observation was that PZT thin films near the morphotropic phase boundary show a minimum in the P_R which is opposite to the observations in the bulk PZT, mentioned previously.

6.7.1.3 Polarization Fatigue in PZT Films

Despite higher remanent polarization and low coercive fields, the major problem with PZT was severe fatigue on Pt electrodes. Films deposited on Pt/Ti/SiO₂/Si substrates suffer from fatigue i.e. drastic loss in remanent polarization after bipolar switching for more than 10^8 cycles (as shown in Fig. 6.10). Various models have been proposed to explain the ferroelectric fatigue mechanism and have been reviewed in detail.^{9,45,46} These models can be broadly listed as:

(i)formation of a surface layer^{47,48,49,50,51};

(ii)pinning of domain walls by segregation of defects in the wall region⁵²;

(iii)clamping of polarization reversal by volume defects⁵³;

(iv)suppression of nucleation of oppositely oriented domains at the surface^{54,55}; and

(v)damage of film/electrode interface.⁵⁶



FIGURE 6.10 Fatigue of PZT films on Pt electrodes; from ref. [9].

Some of the above models consider oxygen vacancies in PZT to play a major role in the fatigue of ferroelectric films on Pt electrodes. These models propose the creation of an oxygen deficient region at the film/electrode interface leading to fatigue through many different mechanisms.^{47,48,49,52,57,59} Absence of fatigue in the PZT films deposited on conducting oxide electrodes has supported the idea of oxygen vacancies playing a role in the fatigue process. It has been proposed that oxide electrodes

act as sinks for oxygen vacancies and prevent their accumulation at the electrode/film interface.⁵² Conducting oxide electrodes such as YBCO¹⁵, RuO₂¹⁶, LSCO¹⁸ and others proved to be better electrode materials for PZT thin films, as they did not suffer from fatigue as shown in Fig. 6.11. However PZT films on oxide substrates suffer from poor leakage characteristics.¹⁴ Nevertheless it has been shown that the integration of LSCO or hybrid Pt-LSCO provides a better alternative than other conducting oxide electrodes to the polarization fatigue problem as they do not fatigue up to 10¹² switching cycles.⁵⁸ Also these capacitors showed better imprint and retention characteristics.



FIGURE 6.11 Elimination of Fatigue in PZT films deposited on the oxide LSCO electrodes and its comparison with the PZT film on Pt electrodes; from ref. [40].

Another model is based on the comprehensive study of fatigue mechanism in PZT films produced by sol-gel and MOCVD processes.^{54,55} This model suggests that fatigue is a result of suppression of nucleation of oppositely oriented domains at the film surface. It was shown that under fast switching conditions, polarization measured as a function of number of cycles shows three distinct regimes. In region I, the decrease of polarization is nearly independent of the frequency and amplitude of the electric field. Fatigue in this region is explained by the local blocking of the nucleation sites of
oppositely oriented domains by space charge produced by strong switching electric field. Region II is marked by self rejuvenation of polarization due to an increase of switching polarization. This happens due to a large enough increase in the electrical conductivity of the sample so that the field can remove partly or completely the space charges which block the nucleation sites. In region III, polarization reduction takes place upon further cycling due to film degradation.

While there are no easy ways to check these models electrically, significant progress has been made by means of optical methods such as electron-paramagnetic-resonance (EPR) spectroscopy.^{59,60} These measurements have shown that pinning of domains by charge trapping at internal domain boundaries can be a primary fatigue mechanism. It has been suggested that polarization fatigue is a dynamic competition between domain wall pinning due to electron charge trapping and field assisted unpinning of the domain walls.⁵²

6.7.2 SrBi₂Ta₂O₉ (SBT) and SBT Thin Films



6.7.2.1 Introduction

FIGURE 6.12 Solid curves shows the hysteresis loop of a SBT film on Pt/Si before and after switching for 10^{12} cycles. Dashed curve is a plot of leakage current versus voltage in a 240nm thick BaBi₂Ta₂O₉ film at 293 K. At intended operating voltage of 5V leakage current is 1.0 nA/cm²; from ref. [30].

SBT emerged as an attractive alternative to PZT because it was shown that SBT films deposited on Pt electrodes did not suffer from fatigue, as shown in Fig 6.12.³⁰ Additionally SBT films showed longer polarization retention and possess ability to maintain good electrical properties even when the SBT

film is less than 100 nm thick. SBT belongs to the category of Bi-layered perovskite oxides, a family of Aurivillous phases with the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ where A is an alkaline earth element (e.g. Sr, Ca, Ba), B is a tetravalent or pentavalent element (e.g. Ta, Nb, Ti) and n denotes the number of perovskite units sandwiched between bismuth oxide layers and varies from 2 to 5 (for SBT, n is 2 as can be seen from the general formula).⁶¹



FIGURE 6.13 Crystal Structure of SBT. It can be seen that TaO_6 octahedra are sandwiched between Bi_2O_2 layers; from ref. [30].

It is well known that SBT is ferroelectric at room temperature and its room temperature structure is orthorhombic. Its space group is A2₁am and the primitive unit cell of SBT contains 28 atoms with two formula units. The crystal structure of SBT is schematically shown in Fig. 6.13. The lattice constants of this unit cell are a = 5.531 Å, b = 5.534 Å and c = 24.98 Å⁶² and it can be observed from these lattice constants that the structure of SBT is highly anisotropic. This high degree of structural anisotropy in SBT also results in high degree of anisotropy in ferroelectric properties, most important of them being remanent polarization. It has been reported that the remanent polarization is negligible

along the c-axis and is maximum along the a-axis.⁶³ In SBT, ferroelectricity arises from the structural distortion created due to the transition from paraelectric phase which is tetragonal, to the room temperature ferroelectric phase. This transition takes place at 608 K (i.e. Curie temperature). Distortion takes place in two ways: first is the atomic displacements along the orthorhombic a-axis from the corresponding positions in the parent tetragonal structure and second is the rotation of TaO_6 octahedra around the c- and a-axes. The first factor is responsible for the spontaneous polarization along a-axis. In contrast, displacements along the b- and c-axes are cancelled due to the presence of glide and mirror planes, respectively, and thus they do not contribute to the total polarization.

The absence of fatigue in SBT has been probed by many research groups. It has been concluded that the high mobility of oxygen vacancies leads to improved fatigue resistance.^{64,65} Shareef *et al.*⁶⁶ showed that weak domain wall pinning could be the reason for the absence of electrical fatigue in the SBT films. Weak domain wall pinning in SBT can be viewed as a self recovery mechanism during bipolar switching which helps in the rejuvenating of remanent polarization. The weak domain wall pinning has been attributed to two factors: smaller magnitude of the remanent polarization in SBT which results in the weaker charge trapping and/or lower charge density at the domain boundaries compared to PZT. Another factor is relatively low oxygen vacancy concentration in the perovskite sub-lattice in the SBT unit cell.

Another important aspect of SBT is the improvement in the ferroelectric properties of SBT by altering its composition. It has been shown that Bi-excess and Sr-deficient SBT films posses higher remanent polarization and lower coercive field as compared to the stoichiometric films.^{67,68} This is due to larger distortion in the TaO₆ octahedra because of substitution of larger Sr²⁺ ions by the smaller Bi³⁺ ions.⁶³ Authors also reported the theoretical remanent polarization of stoichiometric polycrystalline SBT to be about 18 μ C/cm². Remanent polarization of SBT can also be increased up to 20 μ C/cm² by substitution of Ta with Nb.^{69,70} This increase in the remanent polarization has been attributed to the enhanced structural distortion due to stronger covalent interaction of bonds in the octahedral unit after substitution of Ta with Nb. However this substitution also leads to a substantial increase in the coercive field which makes the Nb doped SBT less attractive. For a solid solution of SBT-SBN, SrBi₂Ta_{1-x}Nb_xO₉, coercive field increases up to three times at x=1 compared to the value at x=0.

6.7.2.2 SBT Thin Films

SBT thin films have been studied in detail by many authors since 1995 when fatigue free SBT films on Pt electrodes were discovered. Thin films have been deposited by different techniques such as sputtering, laser ablation, MOCVD, sol-gel and MOD or spin coating. SBT thin films are deposited at higher temperatures than PZT. These temperatures vary from 700 to 900°C depending upon the nature of the processing technique. Many authors have reviewed the growth of SBT in detail which can be found elsewhere.⁷¹ Volatility of bismuth during the processing is also an issue although it is not as acute a problem as lead in PZT. The following sections briefly discuss the past work carried out on growth of polycrystalline and epitaxial SBT films using different processes.

6.7.2.2.1 <u>Polycrystalline SBT Films</u>

Most of the early work in the field of SBT thin films was devoted towards the deposition of polycrystalline SBT films on various substrates. Among physical vapour deposition process, sputtering and laser ablation have extensively been used. Many authors have reported the deposition of SBT films by RF magnetron sputtering. There are more reports on sputter deposition of polycrystalline SBT films than the epitaxial films. Reported values of remanent polarization are widely scattered, from 4 to 10 μ C/cm², lower values being more reliable and consistent with the values for the films deposited using different processes. Cho et al.⁷² reported the deposition of polycrystalline SBT films on Pt/Ti/SiO₂/Si substrates by using a Bi-excess SBT target at room temperature followed by annealing in a pure oxygen atmosphere. It was found that the structure of the films was a function of argon gas pressure during the film deposition. Best quality perovskite SBT films were formed at 150 mtorr sputtering pressure (Ar/O₂: 1/1) and a post anneal at 800°C for 2 h in an oxygen atmosphere. This was attributed to the improved crystallization of the films under these conditions. The films showed a remanent polarization of the order of 4-5 μ C/cm². An impurity phase formed at lower sputtering pressures and low annealing temperatures and periods. Same authors reported⁷³ the sputter deposition of partially c-axis oriented $Sr_{0.9}Bi_xTa_2O_9$ films on Pt/Si substrates. It was shown that the films deposited at higher sputtering pressure (~300 mtorr) showed higher degree of c-axis orientation. Degree of c-axis orientation was further enhanced by incorporating a higher level of Bi (x = 2.6) in the film. Ferroelectric measurements showed a low value of remanent polarization, $\sim 5 \,\mu C/cm^2$. Work on the laser ablation of SBT started with the development of polycrystalline SBT films. Films were deposited on Pt/Ti/SiO₂/Si substrates. In one case⁷⁴ films were

partially doped with Nb and deposited at 700°C in 200 mtorr oxygen ambient. The value of remanent polarization reported was about 10 μ C/cm². However, as mentioned earlier, Nb doping of SBT increases the value of P_R but it also leads to an appreciable increase in the E_c which is not desirable. In another case⁷⁵, films were deposited at 450°C in 900 mtorr oxygen atmosphere and then annealed at 750°C in an atm. oxygen. The films were polycrystalline and showed remanent polarization of the order of 3-4 μ C/cm². Somewhat later, Desu *et al.*⁷⁶ showed the c-axis oriented growth of SBT on Pt/MgO substrates. However c-axis oriented films showed very little polarization as compared to the polycrystalline films because of the c-axis not being a ferroelectric direction in SBT. Rastogi *et al.*⁷⁷ reported the control of crystallite orientation using an O₂-plasma discharge. They showed that in the absence of plasma the films tended to be preferentially c-axis oriented and showed little polarization. However, upon application of plasma voltage of 300V, films showed preferential (115) orientation and a higher remanent polarization (~6.5 μ C/cm²).

Among chemical processes, metal organic decomposition (MOD) or solution decomposition has been the most extensively used method for deposition of polycrystalline SBT films because of its simplicity over other chemical processes such as MOCVD. Amanuma et al.⁷⁸ reported the deposition of SBT films on Pt/Ti/SiO₂/Si substrates. Well crystallized films with intense (115) reflection were obtained at a firing temperature of 700°C as compared to the films at other firing temperatures. The films showed a P_R of about 5 μ C/cm². The amount of c-axis oriented SBT increased upon increasing the firing temperature. Rodriguez et al.⁷⁹ reported the formation of a Bi-deficient pyrochlore phase in films fired at 775°C. The estimated stoichiometry of this phase was $Sr_{0.2}(Sr_{0.5}Bi_{0.7})Ta_2O_{6.75}$. This phase was detrimental to the formation of ferroelectric SBT phase because it created a large deviation in the cation stoichiometry. Composition dependence of the ferroelectric properties was investigated by some authors.^{80,81} Hu *et al.*⁸² reported increased remanent polarization (~9.5 μ C/cm²) in the polycrystalline SBT films deposited on Pt/Ti/SiO₂/Si substrates which were annealed by modified annealing process. This annealing method combined rapid annealing with layer by layer annealing of the SBT films after each MOD coating step. In another study⁸³, SBT films grown on Pt/ZrO₂/SiO₂/Si and Pt/TiO₂/SiO₂/Si showed higher remanent polarization (~ $8-10 \,\mu$ C/cm²) as compared to SBT films on Pt/Ti/SiO₂/Si ($P_R \sim 5 \mu C/cm^2$) at 5 V. This was attributed to the decreased roughness of the bottom electrode upon using the oxide layers. Polycrystalline SBT films have been grown on Pt/Ti/SiO₂/Si substrates by CVD processes. Seong et al.⁸⁴ reported the deposition of SBT films at 550°C by plasmaenhanced MOCVD process. The films showed the co-existence of (115) oriented SBT along with caxis oriented SBT. The remanent polarization was ~7 μ C/cm² at an applied voltage of 5 V (no film thickness quoted). Sol-gel has been used by some researchers as a route to fabricate SBT films.⁸⁵ Films were dried at 150°C after deposition on platinized Si substrates and then calcined at 350°C in air. SBT films heat treated at 700°C showed a preferred (115)-orientation and exhibited a remanent polarization of ~4 μ C/cm² at an applied voltage of 5 V. It should be noted that the film thickness was not quoted in all cases so in some places voltage has been mentioned in place of field.

In summary polycrystalline SBT films have been deposited using both physical vapour and chemical deposition processes. Physical vapour deposition processes employ temperatures up to 800°C Whereas films deposited by chemical processes use temperatures up to 750°C. The value of remanent polarization was found to be in the range \sim 5-9 µC/cm².

6.7.2.2.2 Epitaxial SBT Films

It would be worthwhile to mention at the start of this section that much of the work of others reported here has been carried out in parallel with the present work on epitaxial SBT films, and it will be referred to in the following chapters about the results on SBT films. Among all the thin film deposition processes, pulsed laser ablation has been the most extensively used process for depositing epitaxial SBT films.

Initial reports on epitaxial SBT films were towards c-axis oriented films. Many authors have reported the deposition of highly c-axis-oriented SBT films on various substrates such as SrTiO₃ (100), LaAlO₃ (100), MgO (100) and (001) LaAlO₃-Sr₂AlTaO₆.^{86,87,88,89,90} However these films do not exhibit any ferroelectricity. Absence of ferroelectricity in c-axis oriented films diverted the focus of research towards deposition of non-c-axis-oriented SBT films. The idea is that these films would possess a finite remanent polarization perpendicular to the film plane because the c-axis of SBT is inclined to the substrate normal. Of course, an ideal epitaxial film would be the one having c-axis in the plane and a-axis being parallel to the substrate normal. Many attempts have been made by many research groups towards the deposited on single crystal SrTiO₃ (110) and Si (100) substrates by some groups^{91,92,93} and these films have been shown to exhibit remanent polarization values up to ~11 μ C/cm² (at an applied field of 500 kV/cm). Also (103)-oriented SBT films have been deposited on single crystal SrTiO₃ (111) and Si (100) substrates^{94,95} and these films showed P_R values upto ~6

 μ C/cm². Moon *et al.*⁹⁰ reported the sputter deposition of epitaxial a-/b-axis-oriented SBT films on single crystal MgO (110) substrates. However this is quite surprising because of the high degree of lattice mismatch between the film and substrate (~7% along SBT [100] or [010]). This report cannot be relied upon completely as no pole figures were presented and the TEM and infrared observations do not appear to be very conclusive. In another study, Lettieri *et al.*⁸⁹ showed the deposition of (110)-oriented SBT films on LaSrAlO₄ (110) substrates along with a component of c-axis oriented SBT.

6.8 Present Work

SBT thin films were chosen as the subject of this study because of their technological importance in non-volatile ferroelectric random access memory (FRAM) applications. The present work deals with pulsed laser deposition of epitaxial SBT thin films on various single crystal substrates. Low remanent polarization in the polycrystalline films and SBT's highly anisotropic structure and its influence on the ferroelectric properties make it essential to study epitaxial SBT films of various orientations in a comprehensive manner. Attempts were made to deposit SBT on single crystal SrTiO₃ (100) and (110), TiO₂ (110) and LaSrAlO₄ (110) substrates. Films were characterized by XRD, AFM, SEM and TEM. Electrical measurements were made using Sawyer-Tower circuit.

Choice of pulsed laser deposition as the deposition technique for growing SBT films comes from its ability to deposit stoichiometric films from a compound target of SBT. Also, this process does not involve the bombardment effects of film or plasma species which are observed in high energy deposition processes e.g. plasma sputtering which can have negative bombardment effects on the surface of a growing film, leading to modifications in the film structure and morphology. The targets used for depositing the films were slightly Bi-excess with compositions SrBi_{2.6}Ta₂O₉ and SrBi_{2.3}Ta₂O₉. This composition was chosen because slightly Bi-excess films have been shown to exhibit better ferroelectric properties than the stoichiometric films.⁸¹

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Chapter 7 Epitaxial SrBi₂Ta₂O₉ Films of c-axis Orientation

This chapter presents and discusses the results obtained on $SrBi_2Ta_2O_9$ films grown on $SrTiO_3$ (100) substrates. Detailed X-ray diffraction and atomic force microscopy studies were performed to study the structural and morphological aspects. Scanning electron microscopy and energy dispersive spectrum analysis were carried out to investigate the compositions of the films, in particular Bi/Ta ratio. Ferroelectric measurements were carried out to assess the ferroelectric behaviour of the films.

8.1 Introduction

It was discussed in Chapter 6 that polycrystalline SBT thin films on Pt possess low values of remanent polarization. In addition, SBT has a highly anisotropic structure and hence highly anisotropic ferroelectric properties. Combination of these factors requires SBT films to be deposited in a highly epitaxial manner with good chemical and structural quality.

Single crystal SrTiO₃ (100) was chosen as a substrate in the beginning because it is a widely used substrate for many applications e.g. High T_c applications and is readily available. It has a cubic structure with lattice parameter a = 3.905 Å. (100) surface of SrTiO₃ can be schematically represented as shown in Fig. 7.1. Also, it provides a good lattice match for the SBT film. The lattice mismatch between the (001) plane of SBT and the (100) plane of SrTiO₃ is approximately 0.3% along the [001] or [010] direction of the film and [$\overline{1}10$] directions of SrTiO₃. The proposed epitaxy between SBT films and SrTiO₃ substrate can also be represented schematically as shown in Fig. 7.2. It can be

observed from this figure that the (001) plane of the SBT is rotated by 45° with respect to the (001) plane of SrTiO₃ for perfect alignment.



FIGURE 7.1 Atomic Structure of (100) surface of SrTiO₃

An AFM image of the substrate surface after cleaning is shown in Fig. 7.3. This image shows terraces on the surface which are about 1.5-2 Å high, corresponding to half unit cell height of $SrTiO_3$. These became more pronounced after annealing at 800°C in 27 Pa flowing oxygen prior to the deposition of SBT film. This happens due to removal of carbonaceous substances which could be present after cleaning the substrates with organic solvents e.g. acetone and propanol.

Oxide substrates are morphologically stable as compared to metals e.g. Pt which is a conventional bottom electrode for depositing ferroelectric thin films. Doping of $SrTiO_3$ by Nb in very small amounts leads to the creation of charge carriers in it and makes it conducting¹, which solves the problem of it being highly insulating.



FIGURE 7.2 Schematic of proposed epitaxy between SBT films and SrTiO₃ (100) substrate (F-film, and S-substrate).



FIGURE 7.3 AFM image and a line scan of the cleaned surface of $SrTiO_3$ (100) substrate, image is 700 nm x 700 nm in size.

8.2 Film Deposition

Films were deposited in an oxygen atmosphere in a laser ablation chamber shown in Fig 4.3. The deposition temperature for the films was varied from 600 to 800°C. The laser fluence was varied for the values ranging between 1 to 3 J/cm². The background oxygen pressure was maintained at 27 Pa for all the runs and all the films were 200 nm thick unless otherwise stated. Laser repetition rates were varied from 1 to 10 Hz. The target used for depositing the films possessed a slight Bi-excess with composition SrBi_{2.6}Ta₂O₉.

8.3 X-ray Diffraction Results and Discussion

 θ -2 θ scans, rocking curve scans and pole figure analyses were carried out for identifying the phases and to investigate the structural perfection of SBT. These results are presented in context with the effect of various process variables, namely film deposition temperature, laser fluence, and laser repetition rate on their effect on the film structure.

8.3.1 Effect of Deposition Temperature on the Structure of Films

Films were deposited at various temperatures to study the effect of deposition temperature on the film structure and to determine the optimum growth temperature. Films were deposited at a laser fluence of approximately 2.5 J/cm² and a laser repetition rate of 4 Hz. Fig. 7.4 shows the θ -2 θ scans of SBT films deposited at temperatures ranging from 600 to 800°C. These scans exhibit the presence of very strong c-axis orientation, evident from very strong (00*l*) type SBT peaks along with a strong (100) reflection from the substrate at $\theta \approx 22.78^{\circ}$. It can also be seen from these scans that this strong c-axis orientation of the films did not alter when the deposited at 600°C which are marked by the presence of additional peaks close to (002), (004) and (008) peaks of SBT and at 2 $\theta = 41-42^{\circ}$. These unknown phases could not be characterized conclusively because of overlapping of peaks from many oxides of film species, the most probable impurity phases being Bi-Ta-O and several forms of Bi₂O₃. The presence of unidentified phases has been reported earlier in SBT films deposited on (001) LaAlO₃-Sr₂AlTaO₆ substrates² but not on (100) SrTiO₃. These results show that higher deposition temperatures are required to achieve a high degree of c-axis orientation and to avoid the crystallization of impurities.



FIGURE 7.4 θ -2 θ scans of SBT films deposited on (100) SrTiO₃ substrates at (a) 800 °C, (b) 700 °C, and (c) 600 °C (* - unknown impurity peaks, s-substrate).

8.3.2 Assessment of the Quality of the Films

8.3.2.1 Rocking Curve Analysis

Rocking curve analysis was carried out to investigate the epitaxial quality of the films. The lower the value of FWHM (full width half maximum) of this curve, the better is the quality of epitaxy. A rocking curve scan of (00<u>10</u>) reflection of a SBT film deposited at 800°C, 4 Hz laser repetition rate and a laser fluence of 2.5 J/cm², is shown in Fig. 7.5. It showed a FWHM value of ~0.06-0.07°, which is an indication of excellent quality of epitaxy and out of the plane alignment when compared with the substrate FWHM which is 0.05°. Figure 7.6 shows a plot of rocking curve FWHM values of (00<u>10</u>) reflection for the SBT films deposited at different temperatures. This plot shows that the SBT films deposited at 800°C showed minimum FWHM (~0.06°).



FIGURE 7.5 Rocking curves of $(00\underline{10})$ reflection of SBT film deposited at 800 °C on (100) SrTiO₃ substrates.



FIGURE 7.6 A plot showing the dependence of FWHM of (00<u>10</u>) peak of SBT films on the film deposition temperature.

8.3.2.2 Pole Figure Analysis

Another important parameter to assess the quality of films is the in-plane alignment of the film with the substrate. This was done by carrying out pole figure analysis of the films and then comparing it with the single crystal stereographic projection of the material. (115) pole figure analysis was carried out for this investigation and also to determine the in-plane orientation relationship between the film and the substrate. (115) reflection of SBT was chosen for this purpose for two reasons: (i) it does not coincide with any of the substrate peaks and (ii) it has higher intensity which helps in getting a pole figure with good intensity of poles.³

One such pole figure from a highly (00*l*) oriented SBT film deposited at 800°C and 4 Hz, laser repetition rate, shown in the Fig. 7.7, exhibits four very distinct and sharp spots between $\psi = 50-60^{\circ}$. This pole figure, when compared with the stereographic projection of single crystal SBT, shows highly single crystalline nature of the film and also illustrates very strong in-plane alignment of the film. The angular spread of these poles is less than 3-4° both along ψ and ϕ , which is representative of high quality of epitaxy. The in-plane orientation relationship was determined as $(001)_{\text{SBT}} \parallel (100)_{\text{SrTiO}_3}$ and $[100]_{\text{SBT}} \parallel [110]_{\text{SrTiO}_3}$. This epitaxial relationship between SBT films and SrTiO₃ substrate also fits the schematic model proposed in Fig. 7.2. Very good quality of (001) epitaxy of SBT films on (100) SrTiO₃ is not surprising due to very low lattice mismatch between the (001) plane of SBT and



FIGURE 7.7 (115) pole figure of the SBT film deposited on (100) SrTiO₃ at 800 °C, 4 Hz laser repetition rate and a laser fluence of 2.5 J/cm² (Drawn on Wulff net, each ring corresponds to ψ =10 °).

8.3.3 Effect of Laser Fluence

The laser fluence was varied in order to study its effect on the films' phase and structure. Fig. 7.8 shows the θ -2 θ scans of SBT films deposited at varying laser fluence at 800°C deposition temperature. It can be seen from these figures that the films deposited at 2.5 J/cm² were strongly c-axis oriented without any impurities. However reducing the laser fluence from 2.5 to 1.8 J/cm² led to the appearance of unidentified peaks. These can be seen as shoulders on the (002), (004) (008) and (00<u>10</u>) peaks (although the peak close to (008) could be confused with (115) SBT). Additional impurity peaks were observed at $2\theta = 10^{\circ}$ and $41-42^{\circ}$. These impurities were similar to the ones observed in the films deposited at 600°C except the one at $2\theta = 10^{\circ}$. Again it was not possible to identify these phases conclusively due to overlapping of peaks with many oxides of film species.

Changing the laser fluence will have an influence on the ablation characteristics of the film species, especially Bi because of its relatively high volatility as compared to other elements. This could be a possible reason for the appearance of impurity phases in the film when laser fluence is varied. It was not possible to detect these changes by EDS, possibly due to their smaller magnitude.



FIGURE 7.8 θ -2 θ scans of SBT films deposited at 800 °C on (100) SrTiO₃ substrates at varying laser fluences: (a) 2.5 J/cm² (b) 2.1 J/cm², and (c) 1.8 J/cm² (* - unknown impurity peaks).

8.3.4 Effect of Laser Repetition Rate

Variation in laser repetition rate can significantly affect the kinetics of the film growth influencing the structure of the films. SBT Films were deposited at varying laser repetition rates from 1 to 10 Hz to observe these effects if present. These films were deposited at 800°C using laser fluence of 2.5 J/cm². All the films were strongly c-axis oriented as confirmed by θ -2 θ scans. Structural quality of these films was analysed by rocking curve analysis. The rocking curve FWHM of (00<u>10</u>) reflection for these films was plotted as a function of laser repetition rate and is shown in Fig. 7.9. It can be seen from this figure that although there is not any appreciable change in FWHM of the films upon changing the laser repetition rate, a local minimum is observed at 4 Hz. These results show that the deposition rate does not influence the film quality severely as compared to other process parameters such as temperature and laser fluence. This also shows that kinetics of film growth does not affect the structure of the film as long as deposition temperature and laser fluence are kept at optimum values.



FIGURE 7.9 A plot showing the dependence of rocking curve FWHM of (00<u>10</u>) reflection of SBT films on the laser repetition rate.

8.4 SEM and EDS Results

SEM was performed to investigate the microstructure of the films. Sample were coated with gold to avoid charging due to their insulating nature. Microstructures of two films were compared: one was highly (001) oriented film which was deposited at 800°C and 4 Hz laser repetition rate and the other was a polycrystalline film with presence of many undesired phases which was deposited at 600°C, 10 Hz laser repetition rate and 15 Pa O_2 . SEM micrograph of the impure SBT film (Fig. 7.10 (a)) shows that the film's surface is quite 'grainy' and it does not have a compact microstructure. Presence of contrast between features could be an indication of presence of more than one phase (indicated by 1 and 2). Another SEM micrograph, as shown in Fig. 7.10 (b) of the highly (001) oriented film shows that the film surface is very smooth and basically nothing could be resolved under the limitation of SEM resolution (observed contrast is the artefact). This shows the effect of film quality under varying film deposition conditions on the microstructure of the film.

EDS was performed on the SBT films to analyze the effect of various process variables on the compositional uniformity of these films. In particular Bi:Ta ratio was investigated as Bi content of the film is an important parameter which affects the ferroelectric properties of SBT tremendously. Sr content could not be measured accurately because of the strong signal of Sr from the substrate. Table 7.1 shows the effect of various process variables on the Bi:Ta ratio of the films. It can be seen that this ratio decreases as the deposition temperature increases. This could possibly be explained by lowering of sticking coefficient of Bi from the film as the deposition temperature is increased. From XRD scans, it was observed that the films deposited at 800°C showed minimum FWHM value in the rocking curve analysis and no impurities. From this it can be speculated that at this temperature evaporation of Bi is optimum in such a way it does not promote the formation of impurities such as Bi_2O_3 and also maximizes the formation of c-axis oriented SBT.

In one deposition run at 800°C and 4 Hz laser repetition rate, the background oxygen pressure was reduced to 20 Pa. This resulted in lesser Bi in the film as compared to the film deposited at 27 Pa. This may again be due to enhanced oxygenation of the films and hence higher Bi incorporation or improved binding of Bi in the film at higher deposition pressures.

Processing Temperature (°C)	Laser Fluence (J/cm ²)	Background Oxygen Pressure (Pa)	Bi/Ta Ratio
600	2.5	27	1.25 ± 0.05
700	2.5	27	1.16 ± 0.05
800	2.5	27	1.07 ± 0.05
800	2.5	20	0.95-1.0

TABLE 7.1 Effect of processing variables on Bi: Ta ratio of SBT films





FIGURE 7.10 SEM images of $SrBi_2Ta_2O_9$ films deposited on $SrTiO_3$ (100) substrates (a) at 600 °C and 10 Hz and (b) at 800 °C and 4 Hz; 1 & 2 indicate presence of more than one phase in (a).

8.5 Morphological Studies

8.5.1 Film Morphology

Films deposited at different temperatures were investigated using AFM to study their morphologies. AFM micrographs of the films deposited at 600, 700 and 800°C are shown in Fig. 7.11 (a), (b) and (c). These films were deposited at a laser fluence of 2.5 J/cm^2 and a laser repetition rate of 4 Hz. The root mean square (RMS) roughness of these films varied between 10 and 15 Å for an area of $5x5 \mu m$, which is a fraction of the unit cell height of SBT in the c-direction (24.98 Å). There was no noticeable change in the surface roughness and morphology of the films when the deposition temperature was lowered to 700°C. An observation of images in Fig. 7.11 (a) and (b) shows the presence of multiterraced islands on the surface of the film. Film deposited at 600°C showed the presence of islands but the terraces were not clearly seen which could be due to the presence of impurities in this film shown by the XRD and SEM investigations. These observations may suggest that the growth of these films can be either by the 'Stranski-Krastanov' growth mechanism or 'Volmer-Weber' or island type growth mechanism (refer to Chapter 2). These islands were uniformly distributed over the complete surface of the film, with diameters varying between 350 and 500 nm. This island diameter remained constant for the films deposited at all deposition temperatures, suggesting that the kinetics of the film growth or lateral diffusion of film species on the substrate surface is not strongly influenced by this variation in the deposition temperature. Morphology of these films was also compared with the morphology of a completely impure and polycrystalline film which was deposited at 600°C, 10 Hz laser repetition rate and 15 Pa O_2 which seen in Fig. 7.11 (d). This film was very rough with a RMS roughness of about 5 nm and did not show formation of islands. These observations also reveal that improved epitaxy leads to an improved morphology of the films.

(a)







FIGURE 7.11 AFM micrographs of the SBT films on (100) SrTiO₃ deposited at (a) 800 °C and (b) 700 °C and (c) 600 °C at 4Hz, 2.5 J/cm², and 27 Pa O₂ (d) film deposited at 600 °C, 10 Hz, and 15 Pa O₂ (film thickness = 200 nm).

8.5.2 Mechanism of Film Growth

To study the growth of epitaxial SBT films in a more detailed fashion, a film of about 10 nm thickness was deposited which is equivalent to approximately 4 unit cells of SBT (for a c-axis oriented film). The AFM micrograph of this film is shown in Fig. 7.12 (a), exhibiting flat terraces of width 70-80 nm and height of the order of 3-4 Å. This suggests 2-D step-wise growth of the film, with step height approximately corresponding to the unit-cell height of the $SrTiO_3$ as shown in Fig. 7.3. A slightly thicker film (40 nm, equivalent to16 unit cells of SBT) (see Fig. 7.12 (b)) again shows 2-D step-wise growth, with similar terraces and step heights. In addition one can observe the nucleation of island type features at a few sites on these terraces (marked by arrows). Such nucleation may happen at high energy sites such as defects or dislocations, according to classical thin film nucleation and growth theory.⁴ This transition in the growth mode (from a 2-D step growth to 3-D island growth) could be due to strain relaxation in the films after a particular thickness, which in our case appears to be about 40 nm, approximating to a 15-16 unit-cell thick film. As the film growth starts, the increase in thickness leads to an increase in the overall strain in the film. This strain can be withstood by the film up to a certain critical thickness. There is a competition between relaxation of energy by the formation of dislocations or defects at the film-substrate interface and accumulation of strain energy in the film. After the critical thickness, relaxation of strain energy leads to the formation of defects and relaxation at the film surface at a few places. Since these defect sites are of higher energy, they become preferred nucleation centres for the incoming atoms. Thus this is the onset of change in the growth mode of the film from complete 2-D to 3-D as schematically shown by Fig 7.13. The smallest terrace height in the island growth is between 5 and 8 Å (about a quarter of the unit cell height) as shown in Fig. 7.12 (c). This value of terrace height is about half of the height of terminating layers (Bi-O or Sr-O) in SBT which could mean that the film surface has both Sr-O and Bi-O terminations.





FIGURE 7.12 AFM micrographs of the SBT films on (100) $SrTiO_3$ deposited at 800 °C with different thicknesses: (a) 10 nm (b) 40 nm (arrows indicating sites of island nucleation) and (c) line scan across the surface of a 200 nm thick film.



FIGURE 7.13 Schematic representation of growth mechanism of the SBT films.

8.5.3 Effect of Laser Repetition Rate on the Film Morphology

We also studied the effect of changing the laser repetition rate on the film morphology and roughness in order to determine the maximum deposition rate for producing very smooth and epitaxial SBT films. The films were deposited at 800°C at a laser fluence of 2.5 J/cm² and a background oxygen pressure of 27 Pa. The morphology of the films remained similar for all repetition rates, exhibiting island growth. The dependence of RMS roughness on the repetition rate is summarised in Table 7.2. The RMS roughness of the films deposited at repetition rates of 1 and 4 Hz is approximately 10-15 Å, whilst it is about 20 Å for the films deposited at 7 Hz and rises to 30-40 Å at 10Hz. These data suggest that up to a certain deposition rate of 0.12 nm/s, corresponding to the repetition rate of 4 Hz, the rate of surface of diffusion of film species is sufficient to form smooth films before they become buried by the incoming deposition flux.

Laser Repetition Rate (Hz)	RMS Roughness (Å)	
10	30-40	
7	15-20	
4	10-15	
1	10-15	

TABLE 7.2 RMS roughness measurements of SBT films deposited on (100) $SrTiO_3$ at 800 °C at different laser repetition rates

8.6 Ferroelectric Measurements

Ferroelectric measurements were made on the (001) oriented SBT films deposited onto Nb-doped (100) SrTiO₃, which acted as a conducting bottom electrode, using a Sawyer-Tower Circuit. The schematic of the sample during measurements is shown in Fig. 7.14. Fig. 7.15 shows a hysteresis loop (a plot between polarization (μ C/cm²) and electric field (kV/cm)) of a c-axis oriented SBT film. There is effectively no ferroelectric loop observed and the film showed no ferroelectric activity. This is due to the fact that remanent polarization is negligible along the c-axis of SBT (refer to Chapter 6).



FIGURE 7.14 Schematic of the circuit configuration for hysteresis measurement.



FIGURE 7.15 P-E hysteresis loops of SBT film deposited on (100) $SrTiO_3$ at 800 °C.

8.7 Summary

Highly epitaxial and smooth c-axis oriented SBT films can be deposited on $SrTiO_3$ (100) substrates. Best quality films were grown at a deposition temperature of 800°C using laser fluence of 2.5 J/cm² with laser repetition rate of 4 Hz in a oxygen atmosphere at a background pressure of 27 Pa. The films showed a rocking curve FWHM value of 0.06°. Deviation from these processing conditions led to the formation of many impurities which can not be conclusively identified. The films showed an island morphology. It was also found that there was a growth mechanism transition from 2-D step flow growth to 3-D Stranski-Krastanov at a thickness of about 40 nm. The films did not show any ferroelectric activity.

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Chapter 8 Epitaxial SrBi₂Ta₂O₉ Films of Non-c-axis Orientation

SBT films were deposited on single crystal $SrTiO_3$ (110) substrates in order to deposit highly epitaxial and smooth non-c-axis oriented films. Films were deposited under various processing conditions and were characterized using X-ray diffraction and atomic force microscopy.

8.1 Introduction

It was shown in Chapter 7 that c-axis oriented SBT films do not show any ferroelectric activity. Since polycrystalline SBT films do not show high values of remanent polarization, it is highly desirable to deposit epitaxial SBT films with non-c-axis orientation. For this purpose single crystal SrTiO₃ substrates with (110) orientation were chosen.

SrTiO₃ (110) substrate has a rectangular mesh in its (110) plane as shown in Fig. 8.1. Since this mesh does not accommodate c-axis oriented SBT, it can be useful for depositing SBT films with non-c-axis orientation. Comparison with (103) or (110) oriented epitaxial YBCO thin films on this substrate^{1,2} shows that it can be possible to deposit non-c-axis oriented SBT films on this substrate in a similar fashion. This is because SBT has a similar anisotropic structure to YBCO with a = 3.817Å, b = 3.883Å and c = 11.683Å.



FIGURE 8.1 Schematic representation of (110) plane of SrTiO₃.

8.2 Film deposition

Films were deposited by laser ablation at temperatures varying from 600 to 800°C. The laser fluence was varied for the values ranging between 1 to 3 J/cm². The background oxygen pressure was maintained at 27 Pa for all the runs and all the films were 200 nm thick unless otherwise stated. The target used for depositing the films possessed a slight Bi-excess with composition $SrBi_{2.6}Ta_2O_9$.

8.3 X-ray Diffraction Results and Discussion

X-ray diffraction was performed on the film to identify the phases and assess the structural quality of the films. Films were deposited under varying temperature and varying laser fluence to optimise these parameters.

8.3.1 Effect of Deposition Temperature

The θ -2 θ scans of the films deposited on (110) SrTiO₃ at temperatures between 600 and 800°C are shown in Fig. 8.2. These films were deposited at a laser fluence of 2.5 J/cm², a laser repetition rate of 4 Hz and a background oxygen pressure of 27 Pa. It can be seen that these films exhibit the presence of a very strong (115) SBT peak, with the weaker (117), (033) or (01<u>13</u>) and (22<u>12</u>) peaks along with strong (110) and (220) substrate peaks. No change in the film orientation is seen with varying deposition temperature. However no impurity peaks were observed at low temperatures e.g. 600°C which were seen in the films deposited on SrTiO₃ (100) substrates. Also, all films had mixed orientations which was not expected.



FIGURE 8.2 θ -2 θ scans of SBT films on (110) SrTiO₃ substrates, deposited at a laser fluence of 2.5 J/cm² and temperatures (a) 800 °C, (b) 700 °C, and (c) 600 °C (splitting of K α_1 and K α_2 can be seen in the (2 2 0) peak of SrTiO₃); s-substrate.

8.3.2 Effect of Laser Fluence

Having found that the change in film deposition temperature does not have any influence on the structure of the films, further investigations were made towards changing other process parameters towards depositing epitaxial SBT films with single preferred non-c-axis orientation. Laser fluence was varied in order to do this. Fig. 8.3 shows the diffraction patterns of the SBT films deposited at 800°C at varying laser fluences. In this case, the film deposited at low fluence of 1.8 J/cm² showed
only the $(22\underline{12})$ SBT film peak along with strong (110) and (220) substrate peaks, whilst the films deposited at higher fluences exhibited mixed orientations of SBT. These observations show that at a laser fluence of 1.8 J/cm², the SBT film is completely (116) oriented (in the (116) oriented film, we see only the (22<u>12</u>) peak, the (116) reflection is not seen because of systematic absences). Growth of (116) oriented SBT films on (110) SrTiO₃ substrates was also reported in some of the contemporary work^{3,4} but there is no report of the (115), (117) and other orientations of SBT on this substrate. These films also did not show the presence of any impurity phases.



FIGURE 8.3 θ -2 θ scans of SBT films deposited at 800 °C on (110) SrTiO₃ substrates at varying laser fluences: (a) 2.5 J/cm² (b) 2.3 J/cm², (c) 2 J/cm², and (d) 1.8 J/cm² (splitting of K α_1 and K α_2 can be seen in the (2 2 0) peak of SrTiO₃); s-substrate.

8.3.3 Quality of Epitaxy

8.3.3.1 Rocking Curve Analysis

Fig. 8.4 shows the rocking curve of $(22\underline{12})$ reflection of a (116) oriented SBT films deposited at 800°C at a laser fluence of 1.8 J/cm². The FWHM of this peak is 0.171°. This value, when compared



with the FWHM of the rocking curve of the substrate (0.06°) suggests good quality of the (116) epitaxy of the SBT films.

FIGURE 8.4 Rocking curves of the $(22\underline{12})$ reflection (fluence: 1.8 J/cm²) of SBT film deposited at 800 °C on (110) SrTiO₃ substrate.

8.3.3.2 Pole Figure Analysis

The (115) pole figure of the purely (116) oriented film (see Fig. 8.5) clearly shows six sharp, distinct spots at about $\psi = 5^{\circ}$ and 65° corresponding to (115), (115) and (115) poles. A comparison of this pole figure with the (116) stereographic projection of single crystal SBT shows that there are two sets of such spots, which are mirror images of each other. Ideally, in a single crystal there is one extra spot at $\psi = 81.28^{\circ}$ for (115) pole but it could not be seen in our films because of limitations of the texture goniometer due to defocusing effects after $\psi = 70^{\circ}$. These observations show that there are 180° twins in the films. However, films were highly epitaxial, as evident by the sharpness of spots, and possessed excellent in-plane alignment with the substrate plane. Angular spread of the poles was 4-5°, which is indicative of good quality epitaxy.

The presence of twinning can be explained by Fig. 8.6, which is a schematic representation of the ways in which the (116) plane of SBT aligns itself on this substrate. This figure shows that there are

two ways in which the (116) film plane can align itself with the (110) plane of the SrTiO₃ substrate. The c-axis of SBT can point in two directions, at 90° to each other, and these two possible configurations should then be mirror images of each other. This explains why we get two sets of (115) poles in the (115) pole figure. From pole figure analysis, we also analysed the in-plane orientation relationship between film and substrate which was determined as $(116)_{SBT} \parallel (110)_{SrTiO_3}$ and $[1\bar{1}0]_{SBT} \parallel [1\bar{1}0]_{SrTiO_3}$.



FIGURE 8.5 (115) pole Fig. of the (116) oriented SBT film deposited on (110) SrTiO₃ substrate at 800 °C; 1 and 2 represent the twins (drawn on Wulff net, each ring corresponds to ψ =10 °).



FIGURE 8.6 Schematic representation of alignment of (116) plane of SBT with (110) plane of $SrTiO_3$ showing two growth directions which are mirror images of each other.

8.3.4 Discussion on XRD Results

The results for (116) oriented films are in agreement with those obtained by Nagahama *et al.*.⁴ However, in the case of films with mixed orientations, the presence of strong (115) and weaker (117), (033) or (01<u>13</u>) and (22<u>12</u>) reflections indicates the presence of three different orientations in the SBT film. We speculate that a variation in the Bi content of the film upon changing the laser fluence is responsible for this change in the film orientation which was also thought to be a reason for the microstructural changes for the films deposited on SrTiO₃ (100) (refer to Chapter 7). It is known that a variation in the Bi content of SBT leads to considerable distortion in the structure⁵. This distortion may affect the in-plane lattice dimensions, and hence alter the nature of the epitaxy. However it was not possible to notice such small variations (atomic fraction~0.1) in the Bi content of the film using EDS showed larger scatter (> \sim 0.1-0.2).

8.4 Morphological Studies

8.4.1 Effect of Laser Fluence on the Morphology

Fig. 8.7 shows AFM images of SBT films deposited at 800°C at different laser fluences, giving SBT films with either mixed or (116) preferred orientation. These images exhibit a very different morphology, which is corrugated in nature, as compared to the island type morphology of c-axis oriented SBT films seen on (100) SrTiO₃ substrates (see Chapter 7). The RMS roughness of the (116) oriented film is about 10-15 Å whilst it is 20-25 Å for the film with mixed orientation (over an area of $5x5 \ \mu m$), illustrating that the surface roughness increases with the appearance of mixed orientation in the film (induced by variation in the laser fluence). However both mixed and (116)-oriented growth of SBT films lead to a corrugated film morphology, which is also evident from the line scans across the films.

8.4.2 Scheme of Epitaxy

To investigate the growth manner of these films, we combined the observations from the pole figures (which indicate the crystallographic directions on the substrate surface and the orientation relationship between the film and the substrate) with the direction of the elongated grains in the AFM images. We found that the elongated grains in these images run along the $[0\ 0\ 1]$ direction in the (110) plane of the substrate. The corrugated morphology is along the $[1\ 10]$ direction (perpendicular to the direction of the elongated grains) in the (110) plane. We propose (116) epitaxy of SBT on (110) SrTiO₃ in the manner shown in Fig. 8.8. It is possible that the polished SrTiO₃ (110) surface has (100) planes at 45° to it because of (100) planes being charge neutral and energetically most stable. So, when SBT is grown on SrTiO₃ (110), it grows preferentially along the c-axis on the SrTiO₃ (100) planes with the c-axis of SBT at 45° to the substrate normal. This kind of growth can lead to the (116) planes of the films being parallel to the (110) plane of the substrate, though with accompanying strain: the angle between (001) and (116) planes of SBT parallel to (110) plane of SBT parallel to (110) plane of SBT at 45° which would involve straining of the film.



1100 210



FIGURE 8.7 AFM micrographs of the 200 nm thick SBT films on (110) SrTiO₃ deposited at 800 $^{\circ}$; (a) (116) oriented film and (b) film with mixed orientation; F-film and S-substrate.



FIGURE 8.8 Schematic of the (116) epitaxy of SBT films on (110) SrTiO₃.

8.5 Summary

Highly (116) oriented and smooth SBT films were deposited on $SrTiO_3$ (110) substrates at 800°C. Increasing laser fluence above 1.8 J/cm² leads to formation of films with mixed orientations, (115), (117), (033) or (01<u>13</u>) and (116). (116) oriented films were highly epitaxial as shown by low FWHM of the rocking curve and exhibited excellent in-plane alignment within the substrate plane as shown by pole figures. There was however presence of 180° twinning in the films. This was due to the two ways in which the film can align itself on the substrate. The RMS roughness of the films was about 10-15 Å. The films showed a corrugated morphology which was a result of the manner in which (116) oriented film aligns itself on the SrTiO₃ (110) substrate.

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Chapter 9 SrBi₂Ta₂O₉ Films of a-/b-axis Orientation

This chapter presents the results of SBT films deposited on TiO_2 (110) and LaSrAlO₄ substrates. Emphasis was paid towards depositing completely a-axis oriented SBT films. Deposition of Sr_2RuO_4 films was also carried out which can be used as a bottom electrode on these substrates. Films were deposited under different processing conditions. X-ray diffraction, atomic force microscopy and transmission electron microscopy were used to carry out the structural and morphological studies.

9.1 Introduction

Following the successful deposition of non-c-axis oriented SBT films on $SrTiO_3$ (110) substrates (see Chapter 8), efforts were extended to deposit epitaxial completely a-axis oriented films on compatible single crystal substrates. Since the polar axis of SBT lies within its a-b plane, for FRAM applications, it would be ideal to deposit highly epitaxial a-axis oriented films because they should, ideally, possess maximum remanent polarization. This chapter is about the deposition of a-axis oriented films on two substrates, TiO_2 (110) and LaSrAlO₄ (110) which is discussed in sections 9.2 and 9.3. Section 9.4 discusses the efforts towards the deposition of Sr_2RuO_4 films and fabrication of SBT/Sr_2RuO_4 heterostructure on LaSrAlO₄ (110) substrates.

9.2 Films on TiO₂ (110)

(110)-cut TiO₂ (or Rutile) was chosen as a possible substrate for depositing a-/b-axis SBT films because the (110) plane of TiO₂ has a structural similarity with the a-/b-plane of SBT (both are rectangular). Fig. 9.1 shows a schematic representation of the (110) surface of TiO₂. Also Rutile is a readily available material and relatively cheap. It has a body centred tetragonal structure with lattice

constants a = 4.594 Å and c = 2.958 Å.¹ Target composition for depositing these films was SrBi_{2.3}Ta₂O₉. To the best of my knowledge, this is the first work on the deposition of SBT films on TiO₂ (110) substrates.



FIGURE 9.1 Schematic Representation of TiO₂ (110) surface.

Fig. 9.2 shows the schematic representation of proposed scheme of epitaxy of a-/b-axis oriented SBT on TiO₂ (110) plane. The lattice mismatch between the (110) plane of TiO₂ and (100)/(010) plane of SBT is ~4% along the [001] direction of SBT and [110] direction of TiO₂ and 6.7% along the [100]/[010] direction of SBT and [001] direction of TiO₂.

9.2.1 Effect of Cleaning and Annealing on the Substrate Surface Before Film Deposition

As received substrates were not clean as shown by AFM investigation of their surface. Fig. 9.3 (a) shows that the substrate surface carried many dirt particles and the surface appeared to be quite rough. Cleaning of the surface with acetone and propanol showed a remarkable improvement in the substrate surface as shown in Fig. 9.3 (b) as evident by the reduced grey scale on the right side of the image. Cleaned substrates were annealed at temperatures as high as 900°C in vacuum followed by heating in an oxygen atmosphere, prior to deposition of the SBT films. Annealing of substrates led to substantial improvement in their surfaces. An AFM image of these substrates after annealing is shown in Fig. 9.3 (c) and this shows the step like features on the substrate surface and a smoother surface. This could be due to removal of carbonaceous substances after heating in oxygen.



FIGURE 9.2 Schematic of possible epitaxy between (100)/(010) oriented SBT films and TiO₂ (110).





FIGURE 9.3 AFM images of surface of TiO_2 (110) substrate (a) in as received state, (b) in cleaned state, and (c) in annealed state. Dimensions of all images are in microns.

9.2.2 Film Deposition

Films were deposited at temperatures from 800 to 900°C. The background oxygen pressure was kept at 27 Pa for all the runs unless mentioned otherwise. The laser repetition rate was varied from 1 to 6 Hz. The laser fluence was 2.5 J/cm² for all the runs. Films were 200 nm thick unless mentioned otherwise.

9.2.3 XRD Results and Discussion

9.2.3.1 Effect of Deposition Temperature

Fig. 9.4 shows the θ -2 θ scan of SBT films deposited on TiO₂ (110) substrates at different temperatures. Laser repetition rate was kept at 4 Hz for all films. All the films show the presence of the (200) or (020) SBT peak along with the presence of many other unidentified impurities and some c-axis-oriented SBT. It was not possible to precisely assign this peak to either (200) or (020) because of their very similar d-spacing and hence 2 θ value. The impurities could not be specified because of overlapping of peaks from many Bi-O, Ta-O, Sr-O and Bi-Ta-O compounds. However films deposited at about 870°C showed the maximum degree of a-/b-axis oriented SBT. Films deposited at other temperatures exhibited reduced amount of a-/b-axis oriented SBT and increased amount of impurity formation. The maximum intensity ratio of (200)/(020) SBT peak to the strongest impurity peak, $I_{(200)SBT}/I_{impurity}$, was 0.5 for the films deposited at 870°C and decreased for the films deposited at 870°C. This shows that the maximum crystallization of SBT was also maximum in the films deposited at 870°C. This shows that the maximum crystallization of SBT was also maximum in the films deposited at 870°C.

9.2.3.2 Effect of Laser Repetition Rate

Fig. 9.5 shows the effect of laser repetition rate on the film structure. The films were deposited at 870°C and at a laser fluence of approximately 2.5 J/cm². The films were deposited at laser repetition rates of 1, 4, and 6 Hz. These films also showed the formation of many unidentified impurities, and c-axis SBT along with some a-/b-axis oriented SBT. However films at 4 Hz showed maximum degree of formation of SBT, both a-/b-axis oriented and c-axis oriented along with lesser impurity formation. This shows that repetition rate has an effect on the extent of SBT phase formation in the film. One of the possible reasons for this change could be variation in the kinetics of adsorption or evaporation of Bi (which is the most volatile of all film species) upon varying the laser repetition rate which governs the residence time of film species on the film surface before they are buried by incoming flux of film





FIGURE 9.4 θ -2 θ scans of SBT films deposited on TiO₂ (110) at different temperatures; (a) 840 °C, (b) 870 °C, and (c) 900 °C.



FIGURE 9.5 θ -2 θ scans of SBT films deposited on TiO₂ (110) at different laser repetition rates; (a) 4 Hz, (b) 6 Hz, and (c) 1Hz; s - substrate, *- impurities.

9.2.3.3 Effect of Annealing

When SBT films are deposited in an in-situ manner, then both film phase and impurities can nucleate at the substrate surface at the start of film growth. However, if the films are deposited at room temperature to condense the film species on the substrate without forming any crystalline phase and then they are annealed ex-situ; this could lead to the formation of either SBT phase or impurities in higher proportion depending upon which phase nucleates first. So if nucleation and crystallization of a-axis oriented SBT phase precedes impurity phases, then it would be easier for SBT phase to grow in the bulk provided it grows at a faster rate to avoid or minimize any impurity formation. In the present study, SBT films were first deposited at room temperature at 27 Pa oxygen pressure. These films were then annealed at various temperatures in $\frac{1}{2}$ atm. oxygen. Fig. 9.6 shows θ -2 θ scans of two such films which were annealed at 870° and 900°C respectively. However, as can be seen from these scans, these films showed more deterioration in the structure of the films. The (200)/(020) peak of the films is very weak as compared to the films grown at higher temperature. Also there was no c-axis SBT present. These observations show that the crystallisation of SBT was very poor and conditions were conducive for the formation of impurities when films were grown in an ex-situ manner.

9.2.3.4 Epitaxy

The rather high lattice mismatch between the film and the substrate is possibly the reason for the relatively low degree of a-/b-axis orientation in the film and the formation of impurities. The use of compatible buffer layers having intermediate lattice constants may prove useful to successfully grow SBT films on TiO_2 with a higher degree of a-/b-axis orientation, and this remains a subject of further investigation.



FIGURE 9.6 θ -2 θ scans of SBT films deposited on TiO₂ (110) at room temperature and annealed at different temperatures (a) 870 °C and (b) 900 °C; * - impurities, s – substrate.

9.2.4 AFM Studies

AFM images revealed that the films were very rough (RMS roughness ~ 10nm) (see Fig. 9.7). Outgrowths of many impurities can be observed on the film surface. High roughness of the film surface could be a manifestation of the poor film quality (in general highly epitaxial films show smoother surface). Roughness of the films was approximately similar for all the films deposited in this study.



FIGURE 9.7 AFM image of a SBT film on TiO_2 (110) showing a very rough surface and outgrowth.

9.2.5 Summary

SBT films were deposited on TiO_2 (110) substrate in various processing conditions. It was observed that films possessed partial a-/b-axis oriented SBT along with c-axis oriented SBT and many impurities which could not be conclusively assigned to a particular phase. Maximum degree of a-/baxis orientation was observed in the films deposited at 870°C and 4 Hz laser repetition rate. Large lattice mismatch between the film and the substrate could be the reason for poor nature of epitaxy. The films were very rough and outgrowths of impurities can be observed on the film surface.

9.3 Films on LaSrAlO₄ (110)

This section presents the results of SBT deposited on LaSrAlO₄ (110) substrates. LaSrAlO₄ is a tetragonal oxide whose lattice parameters are a = 3.755 Å and c = 12.62 Å.² The (110) plane of this substrate provides a rectangular mesh which is similar to the SBT (100)/(010) face. Possible epitaxy of (100) or (010) plane of SBT on (110) plane of LaSrAlO₄ substrate can be schematically represented as shown in Fig. 9.8. The lattice mismatch between the (100)/(010) plane of SBT and the (110) plane of LaSrAlO₄ are about 1% between the $[1\bar{1}0]$ direction of the substrate and [010]/[100] direction of the film and 4% between [001] directions of the film and the substrate. These values are low in comparison to the values for TiO₂ (110).



FIGURE 9.8 Schematic representation of the epitaxy of a-/b-axis oriented SBT film (F) on the LaSrAlO₄ (110) substrate (F).

AFM images of this substrate are shown in Fig. 9.9. These images show the difference between the morphology of as received substrate and substrate cleaned with acetone and propanol. These images reveal that the surface is very smooth in the as received state and becomes rougher after cleaning, indicating some kind of surface degradation. Thus substrates were used in the as received state.





FIGURE 9.9 AFM images of LaSrAlO₄ (110) surface; (a) in as received state, (b) after cleaning, (c) after annealing of cleaned surface, and (d) after annealing in as received state.

9.3.1 XRD Results

SBT films were deposited at temperatures varying from 800 to 900°C. Other deposition conditions were: laser fluence of 2.5 J/cm², laser repetition rate of 4 Hz and the background oxygen pressure of 27 Pa. Fig. 9.10 shows that the films deposited at about 870°C were highly epitaxial and (100) or (010) oriented evident from sharp diffraction peaks from only the (200) or (020) planes of SBT along

with the (110) peaks from the substrate. It was not possible to determine precisely whether the film peak was (200) or (020) because of their very close d-spacing and hence almost similar angular spacing (lattice parameters of SBT are a = 5.531 Å, b = 5.534 Å, and c = 24.98 Å).² The window for the formation of epitaxial (100)/(010) oriented SBT films was very narrow, about 15-20°C. Films deposited at non-optimal growth temperatures, as seen from the X-ray scans, did not show formation of any a-/b-axis oriented SBT. These films showed the formation of impurity phases, including different forms of bismuth oxide, Bi-Ta-O, and c-axis oriented SBT. The presence of these impurities has recently been reported by others in (110)-oriented SBT films on LaSrAlO₄ (110) deposited by PLD.³ Strict control of deposition temperature was more crucial than any other process parameter for achieving highly a-/b-axis oriented films. Although there has been a report of partial a-/b-axis oriented SBT film⁴, to the best of my knowledge, this is the first report on the deposition of a completely a-/b-axis oriented SBT film.



FIGURE 9.10 θ -2 θ scans of SBT films deposited at different temperatures; * - *impurities, s* – *substrate.*

9.3.1.1 Evaluation of Quality of Epitaxy

9.3.1.1.1 Rocking Curve Analysis

SBT films with preferred a-/b-axis orientation were also analysed by the rocking curve method. The rocking curve for one such film is shown in fig. 9.11. Good quality out of plane alignment of the film and hence good quality of epitaxy is demonstrated by reasonably low full width half maximum (~ 0.67°) of the (200)/(020) rocking curve of the film as compared with the substrate's (110) FWHM of 0.06°.



FIGURE 9.11 Rocking curves of (110) peak of LaSrAlO₄ substrate and (200) peak of SBT film.

9.3.1.1.2 Pole Figure Analysis

A (220) pole figure scan of the film was performed to assess the quality of in-plane alignment, and is shown in Fig. 9.12. This pole figure shows the presence of only two poles at about $\psi = 45^{\circ}$ situated opposite to each other, in a similar to the position of (220) poles in a (100)/(010) stereographic projection of SBT single crystal. Excellent sharpness of the (220) poles (angular spread of about 5° along both ψ and ϕ directions) demonstrates very high quality in-plane alignment of the film, illustrating its highly oriented nature. (113) phi scan at $\psi = 50.1^{\circ}$ (shown in Fig. 9.13) showed four sharp peaks. The FWHM ($\Delta\phi$) was about 5° which confirmed the good quality of epitaxy of the film. Based on the these measurements, the orientation relationship between the film and the substrate was determined as (110)_s // (100)_F or (010)_F, [001]_s // [001]_F and [110]_s // [010]_F or [100]_F.



FIGURE 9.12 (220) Pole figure of a fully a-b-axis oriented film showing two sharp (220) peaks (Wulff plot).



FIGURE 9.13 (113) phi scan of (110)/(010)-oriented SBT film showing four peaks corresponding to highly (100)/(010) oriented films.

On the basis of above investigations, it can be deduced that the epitaxy proposed in Fig. 9.8 matches the observations. The most likely factor which promotes a-/b-axis oriented SBT growth is the structural similarity and low lattice mismatch between the (100)/(010) plane of SBT and the (110) plane of LaSrAlO₄ as compared to the mismatches on TiO₂ (110) substrate, explaining the occurrence of epitaxy.

9.3.2 Morphological Studies

Morphological studies using AFM (illustrated in Fig. 9.14) revealed that the films on LaSrAlO₄ (110) were very smooth with a RMS roughness of the order of 25-30 Å (for 100 nm thick films). We also grew thinner films in order to study the morphology evolution of a-/b-axis oriented films. Fig. 9.14 also shows the AFM images of 10 and 40 nm thick films. It can be seen that 10 nm films exhibited the presence of columns which are about 100-150 nm in diameter and are equally spaced. The RMS roughness of the films is about 10 nm. The columns size became bigger (some columns have diameter upto 200 nm) in a 40 nm thick film. This process of column growth led to smoothening of the film surface which was also revealed by a decrease in the RMS roughness of the film to about 5-6 nm. Images of 100 nm thick films showed that these columns grew further into each other and led to a smoother film with RMS roughness of 1-2 nm. From these results, it appears that after the nucleation processes has taken place, initial stage film growth is dominated by preferential growth of columns in

the growth direction than in the lateral direction. In the later stages when columns are closer to each other, surface diffusion across the film surface predominates the diffusion along the film growth direction. Reason of this behaviour could lie in different interface energies between the film species and the substrate and between the film and the film species. Higher film-substrate energy would lead to higher rate of islands growth along the film growth direction than in the lateral direction until the substrate surface becomes completely covered with the film. At this point, islands start growing into each other because of improved diffusion of film species in the lateral direction too. The result of these processes is a relatively smoother surface for a 100 nm thick film. Based on these observations the growth behaviour of these films can be explained schematically as shown in Fig. 9.16. Comparisons are also made between the morphology and roughness of a highly a-/b-axis oriented and another film with the presence of impurities. Fig. 9.15 shows that the film with the presence of impurities is considerably rougher, with an RMS roughness of about 10 nm for a 100 nm thick film. However the noticeable aspect of this image is the manner in which grains are aligned in the substrate plane.





FIGURE 9.14 AFM images of SBT films of various thicknesses deposited on LaSrAlO₄; (a) 10 nm, (b) 40 nm, and (c) 100 nm thick film. Films were deposited at a laser fluence of 2.5 J/cm^2 , a laser repetition rate of 4 Hz and a background oxygen pressure of 27 Pa.



FIGURE 9.15 AFM images of a 100 nm thick SBT film with little a-/b-axis oriented SBT and many impurities, $R_{RMS} = 10$ nm.



FIGURE 9.16 Schematic representation of growth behaviour of a-/b-axis oriented SBT films on LaSrAlO₄ (110) Substrate.

9.3.3 Transmission Electron Microscopy

Cross sectional transmission electron microscopy (TEM) of fully a-/b-axis oriented SBT films was also performed. Fig. 9.17 (a) shows a high resolution TEM image of one such a-/b-oriented film showing that the film was well aligned with the substrate. Although the interface between the film and the substrate is not very clear, sharp lattice fringes along the a-/b-axis of the film are seen to be spaced at 12.5 Å (1/2 of the c-lattice parameter of SBT). A selected area diffraction pattern (shown in Fig.

(a)



9.17 (b)) confirms the excellent alignment between the film and substrate showing that diffraction spots from the film are very well aligned with respect to the spots from the substrate.

Film surface



FIGURE 9.17 (a) A high resolution cross sectional TEM micrograph of a SBT film on LaSrAlO₄ (110). The a (or b) lattice fringes are spaced at 12.5 Å (c/2 of SBT) (b) A selected area diffraction pattern, illustrating a-/b-oriented SBT and its alignment with the substrate (Courtesy: Stephen Lloyd).

9.3.4 Summary

In summary, we have successfully deposited fully a-/b-axis oriented SrBi₂Ta₂O₉ films on single crystal LaSrAlO₄ (110) substrates by pulsed laser deposition. Films were completely a-/b-axis oriented as confirmed by X-ray diffraction and TEM and showed excellent in-plane alignment with the substrates. 100 nm think films were very smooth with RMS roughness of the order of 2-3 nm. Film's roughness decreased upon increasing the thickness. Precise control over deposition temperature was required to produce highly a-/b-axis oriented films. It was not possible to precisely determine whether the films are purely a- or b-axis oriented or mixed a-/b-oriented due to very similar lattice spacing.

9.4 Deposition of SrBi₂Ta₂O₉/Sr₂RuO₄/LaSrAIO₄ (110) Heterostructures

9.4.1 Sr₂RuO₄ on LaSrAlO₄ (110)

This section presents the results of Sr_2RuO_4 films deposited on LaSrAlO₄ (110) substrates. Sr_2RuO_4 is a tetragonal oxide whose lattice parameters are a = 3.8732 Å and c = 12.745 Å.⁵ Also it is a conducting oxide⁶: its thin film showing resistivity of the order of 270 µΩ-cm and can therefore be used as a bottom electrode for FRAM devices. Another interesting aspect is that its (110) plane provides a rectangular mesh which is geometrically similar to the (100)/(010) face of SBT and LaSrAlO₄ (110). Fig. 9.18 shows a schematic representation of overlaying of (110) mesh of LaSrAlO₄ and Sr₂RuO₄, and (100)/(010) mesh of SrBi₂Ta₂O₉. It can be seen that the mismatches are: 3.14% along [110] directions of Sr₂RuO₄ and LaSrAlO₄, ~1% along [100]/[010] and [110] directions of SrBi₂Ta₂O₉ and Sr₂RuO₄, 1.34% along [001] directions of Sr₂RuO₄ and LaSrAlO₄ respectively, ~2% along [001] directions of SrBi₂Ta₂O₉ and Sr₂RuO₄ in the presence of a Sr₂RuO₄ bottom electrode, which also acts as a buffer layer to gradually reduce the overall lattice mismatch between the film and the substrate.

The films were deposited at temperatures from 800 to 1000° C at varying background oxygen pressures. The laser fluence was 3.5 J/cm² and the laser repetition rate was kept at 4 Hz. All the films deposited in these experiments were 100 nm thick unless mentioned otherwise.

9.4.1.1 X-ray Diffraction Results

Films were deposited at various temperatures and background oxygen pressures. Fig. 9.19 shows the θ -2 θ scans of Sr₂RuO₄ films deposited at temperatures from 800 to 1000°C. It can be seen from these figures that the films (sample 3) deposited at high temperature (1000°C) and low oxygen pressures (~0.01-0.2 Pa) were well crystallized and showed a single film peak at $2\theta \sim 32.3^\circ$ which could be either (110) peak of Sr₂RuO₄ or the (121) peak of SrRuO₃ alongwith high intensity (110) peak from the substrate at $2\theta = 33.73^\circ$. It was not possible to exactly assign this peak to either of the two phases due to their similar d-spacing. Films (sample 1) deposited at lower temperature (850°C) and higher pressure (15 Pa) showed a weak peak at approximately d = 2.744 Å ($2\theta \sim 32.6^\circ$) and 5.16 Å ($2\theta = 17.16^\circ$) with additional unidentified peaks at d = 2.81 Å ($2\theta \sim 31.78^\circ$) which could be an impurity peak. The peak at d = 2.74 Å belongs to (121) Sr₂RuO₄ or (110) for pseudo-cubic SrRuO₃ as films deposited at low temperature and higher oxygen pressure are SrRuO₃ because of its tendency to form under such deposition conditions.⁷ In another film (sample 2) deposited at 900°C and lower pressure

Chapter 9



FIGURE 9.18 Schematic representation of the epitaxy of *a*-/*b*-axis oriented SBT/ (110) $Sr_2RuO_4/LaSrAlO_4$ (110).



FIGURE 9.19 XRD scans of 100 nm thick SRO films deposited from Sr_2RuO_4 on LaSrAlO₄ (110) substrates; (a) film deposited at 850 °C and 15Pa, (b) 900 °C and 0.18 Pa and (c) 1000 °C and 0.1 Pa; * - impurities, s – substrate.

Sample	Temperature	pO ₂	Remarks
1	850°C	15 Pa	Weak (110) SrRuO ₃ , a peak at d = 3.098 Å
2	900°C	0.18 Pa	Very weak peak at $d = 5.16 \text{ Å}$
3	1000°C	0.01- 0.18Pa	(110)-oriented pseudo-cubic $SrRuO_3$ and/or Sr_2RuO_4

TABLE 9.1 Summary of XRD results of Films deposited from Sr_2RuO_4 target on LaSrAlO₄ (110) substrate

9.4.1.2 Phi Scans and Rocking Curve Analysis

Phi (ϕ) scans were carried out on the sample 3 which was either completely (110)-oriented Sr₂RuO₄ or (121)-oriented SrRuO₃, to verify whether the film phase was Sr_2RuO_4 or $SrRuO_3$. However, the main problem with detection of Sr_2RuO_4 arose from the fact the most of its peaks with reasonable intensity almost coincide with the substrate peaks which makes it very difficult to assess the film quality. Positions for the Sr₂RuO₄ will be almost the same as for LaSrAlO₄ because of same crystal system and very similar lattice parameters. Fig. 9.20 shows a schematic representation of the positions of (213) poles for a (110)-oriented Sr_2RuO_4 and (123)/(213) poles for a (121)-oriented $SrRuO_3$ ideally single crystal film. A (213) ϕ scan for (110) oriented Sr₂RuO₄ (shown in Fig. 9.21) shows 4 sharp peaks at $\psi = 28.5^{\circ}$. Its comparison with fig. 9.20 shows that the film is highly epitaxial and very well aligned with the substrate provided the phase is Sr_2RuO_4 . However these peaks could also come from the (213) reflection of the substrate. Following this we carried out ϕ scans for (123)/(312) peak of SrRuO₃ at almost the same 2 θ value as (213) reflection of Sr₂RuO₄. However the value of ψ was selected at 54.7° because reflection is possible at this angle only if the phase is SrRuO₃ (since other positions of poles are quite similar for both phases). It can be seen from Fig. 9.22 there are two sharp peaks, characteristics of the SrRuO₃ film. This shows that some component of the film definitely is (110)-SrRuO₃ if not 100% of the film. Unambigous determination of precise phase composition could not be possible by XRD. A rocking curve of such film (shown in Figure 9.23) shows FWHM value of 0.55° which shows that the epitaxial quality of either phase or both is good.



FIGURE 9.20 Schematic representation of pole positions for (a) (213) pole of (110) oriented Sr_2RuO_4 and (b) (123)/(312) pole positions for (121) oriented $SrRuO_3$.



FIGURE 9.21 (213) Phi scan for a (110)-oriented Sr_2RuO_4 film on LaSrAlO₄ (110) at Psi = 28.5° showing two peaks.



FIGURE 9.22 (123)/(312) Phi scan for a (121)-oriented SrRuO₃ film on LaSrAlO₄ (110) at Psi = 54.6° showing two peaks.



FIGURE 9.23 Rocking curve of the only peak of either (110)-oriented Sr₂RuO₄ or (121)-oriented SrRuO₃ film on LaSrAlO₄ (110).
The absence of Sr_2RuO_4 phase and presence of $SrRuO_3$ in the films deposited at lower temperatures and higher oxygen pressure is not surprising. It has been shown in the literature⁷ that such films are $SrRuO_3$ in nature. These conditions are conducive to the formation of $SrRuO_3$ phase. Sr_2RuO_4 tends to form only at high temperatures, normally above 950°C and at very low oxygen partial pressures (as low as a few mPa). We could achieve the temperatures as high as required for the formation of Sr_2RuO_4 , although it led to the melting of heater many times. Thus, the presence of $SrRuO_3$ in the films suggests that the background oxygen pressure may have been too high for Sr_2RuO_4 phase to form during film growth. Very low pressures are difficult to measure accurately using the gauges in the deposition system used for growing these films.

9.4.1.3 Transport Behaviour of the Film with Preferred Orientation

R-T behaviour of the films could be another factor which can prove presence of $SrRuO_3$ in the film. It has been known that $SrRuO_3$ thin films show a Curie transition in electrical resistance at about 150 K.⁸ 4-point R-T measurement was carried out on a 100 nm thick unpatterned film down to 35 K and is shown in Fig. 9.24. This curve shows a kink in the resistance at about 160-170 K. This confirms that the film phase is $SrRuO_3$.



FIGURE 9.24 *R*-*T* characteristics of a film deposited from Sr_2RuO_4 target at 1000 °C and 0.1 Pa O₂.

9.4.2 SBT on SRO/LaSrAIO₄ (110)

9.4.2.1 XRD Results



FIGURE 9.25 XRD scans of SBT/SRO heterostructure deposited on LaSrAlO₄ (110); * - impurities.

It should be noted that in the case of oriented films deposited from Sr_2RuO_4 target, due to ambiguity in the phase identification, film phase would be mentioned as SRO (Sr-Ru-O). Following the deposition of Sr-Ru-O (SRO) films on LaSrAlO₄ (110) substrates, attempts were made to deposit SBT films on top of SRO film. This was done only on the SRO films which were (121)-oriented SrRuO₃. Figure 9.25 shows the XRD patterns of two such films. It can be seen from these scans that none of the SBT films was purely (100)/(010) oriented. All the films carried some amount of impurity, characterized by peaks at $2\theta \approx 31.6^\circ$, 31.08° , 30.39° , 29.61° , 23.76° and 22.02° . A most probable impurity phase is Bi₂O₃ along with other possibilities such as Bi-Ta-O and other forms of Bi-O. This could be due to two possible reasons: (i) absence of completely (110)-oriented Sr_2RuO_4 layer and presence of $SrRuO_3$ and (ii) change in the temperature of the substrate surface after the deposition of the bottom electrode. This second factor has been found to affect the deposition characteristics of YBCO films on LaAlO₃ (100) substrates.⁹ It has been found that as soon as YBCO deposition starts, there is a substantial amount of change in the emissivity of the film. Since $LaAlO_3$ is transparent, radiation losses are huge and there is a big difference between the temperature of the substrate and heater. However, increase in the emissivity i.e. reduction in the transparency after YBCO deposition leads to reduction in the radiation losses and subsequent increase in the temperature of the film at the same heater current. Thus in order to maintain the same film temperature, the heater current needs to be decreased. The same could be happening in our case since LaSrAlO₄ is transparent but SrRuO₃/Sr₂RuO₄ is not so the heater current to deposit the SBT film will need to be lowered as the temperature difference between the film and substrate will be lower in the case of SBT deposition on $SRO/LaSrAlO_4$ as compared to that on bare LaSrAlO₄. In the present study, it was attempted to optimise the heater current required to grow a-/b-axis SBT again. However efforts, as evident from the XRD scans, were not very successful.

9.4.2.2 Ferroelectric Measurements

Ferroelecric measurements on these films showed that they were shorted or conducting. The possible cause for this may be conducting impurities such as Bi_2O_3 can make a network around the ferroelectric SBT phase and short the film within the film plane, as well as making a conducting path between bottom and top electrode.

9.4.3 Summary

Films were deposited from a Sr_2RuO_4 target on LaSrAlO₄ (110) substrates. θ -2 θ scans showed that films which were deposited at 1000°C and 0.1 Pa background oxygen pressure contained (121)oriented SrRuO₃. The films which were deposited at lower temperatures and higher pressures showed formation of SrRuO₃ phase with some unidentified impurities. High temperatures (>1000°C) required for epitaxial growth of Sr₂RuO₄ were not achievable easily due to melting of the heater at most times. SBT films deposited on (121)-oriented SrRuO₃/LaSrAlO₄ (110) were not phase pure and carried impurities. Ferroelectric measurements showed shorting of the films which could be due to formation of a conducting network or path by the impurity phases.

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Chapter 10 Conclusions and Further Work

This thesis discusses the deposition and characterization of highly epitaxial thin films of technologically important oxides. Initial work was on the deposition and characterization of highly epitaxial WO₃ thin films on various single crystal oxide substrates by magnetron sputtering. This was followed by their heat treatment with sodium vapour and electrical characterization for observing any existence of superconductivity. WO₃ thin films were chosen as a subject for this study because of the recent discovery of low and high temperature (~3 K and ~90 K) superconductivity at surfaces and twin boundaries in the bulk form of this oxide in reduced and sodium doped states respectively. The second phase of the project dealt with the deposition and characterization of single crystal thin films of SrBi₂Ta₂O₉ (SBT), a ferroelectric oxide, by pulsed laser ablation on various single crystal oxide substrates. SBT is an important oxide for non-volatile random access memory applications. Epitaxial films are of particular interest because of inferior ferroelectric properties of polycrystalline films. In particular it was necessary to investigate SBT films with different orientations because of its highly anisotropic behaviour, which has tremendous influence on device performance.

10.1 Conclusions on WO₃ Thin Films

Epitaxial WO₃ films were deposited on (100) SrTiO₃ and R-plane sapphire substrates by DC reactive magnetron sputtering at temperatures varying between 500 and 850°C. The films deposited on SrTiO₃ were highly epitaxial with (001) orientation. The phase of the films was monoclinic γ -WO₃ as determined by Raman spectroscopy (the room temperature equilibrium phase). Films deposited at higher temperatures showed the presence of (100), (010) and (001) oriented components in the film. It was observed that the quality of (001) orientation improved as the deposition temperature decreased to temperatures as low as 500°C. The orientation relationship of the films deposited on (100) SrTiO₃

was $[110]_{WO_3} \parallel < 110 >_{SrTiO_3}$ or $[010]_{WO_3} \parallel < 010 >_{SrTiO_3}$ as determined from the pole-figures. Morphological investigations by AFM revealed the columnar growth behaviour of these films. Films became smoother upon increasing the thickness from 6 to 30 nm. To the best of my knowledge, this is the first report on deposition of epitaxial WO₃ films on SrTiO₃ (100) substrates.

Films on R-sapphire were also epitaxial, with [001] orientation along the growth direction. The phase of the films was again monoclinic γ -WO₃ as determined by Raman spectroscopy. The epitaxy on R-plane sapphire is of higher quality than on (100) SrTiO₃, as indicated by the angular spread of poles in the pole figures, despite better lattice match with (100) SrTiO₃. In this case also, the quality of (001) orientation improved as the deposition temperature decreased to temperatures as low as 500°C. However (002) peak broadening was observed which could arise as a result of increasing residual stresses at lower deposition temperatures. The films deposited on R-plane sapphire maintained the same in-plane alignment with the substrate for all temperatures. The orientation relationship of the films was determined as $[1\bar{1}0]_{WO_3} \parallel [0\bar{1}0]_{Sapphire}$ and $[110]_{WO_3} \parallel [21\bar{1}]_{Sapphire}$. Morphology of the films was columnar type, similar to the films on SrTiO₃. In this case also, the RMS roughness of the films decreased upon increasing the film thickness from 6 to 30 nm and films were smoother than those on SrTiO₃ (100).

The heat treated films were not found to be superconducting as found by low temperature transport measurements. Many combinations of heat treatment times were attempted to achieve different doping or reduction levels. Although microprobe analysis showed that all the heat treated films were Na doped and oxygen deficient, the reduction or Na doping did not appear to lead to the presence of superconductivity.

10.2 Conclusions on SrBi₂Ta₂O₉ Thin Films

Epitaxial SrBi₂Ta₂O₉ films of different crystalline orientations were deposited on single crystal substrates of SrTiO₃ (100) and (110), TiO₂ (110), and LaSrAlO₄ (110). Highly c-axis oriented SrBi₂Ta₂O₉ films were successfully deposited on single crystal SrTiO₃ substrates of (100) orientation. These films were highly epitaxial and very smooth (RMS roughness of the order of 10-15 Å, increasing with increasing deposition rate). Very low rocking curve FWHM values (as low as 0.06°) showed excellent quality of epitaxy. The in-plane orientation relationship was determined as $(001)_{SBT} \parallel (100)_{SrTiO_3}$ and $[100]_{SBT} \parallel [110]_{SrTiO_3}$. Morphological investigations by AFM revealed a

multi-terraced island kind of morphology. Further investigations showed that there was a transition from 2-D layer by layer step-wise growth to a 3-D island or Stranski-Krastanov growth mechanism at a film thickness of about 40 nm. This was observed to happen due to nucleation of islands at defects on terraces at this thickness. Ferroelectric measurements of these films on Nb-doped SrTiO₃ substrates showed negligible ferroelectric activity.

Very smooth non c-axis oriented films were grown on (110) SrTiO₃ substrates. These films were highly (116) oriented or showed mixed orientation, depending upon the laser fluence. Films with mixed orientations formed at fluences higher than 2 J/cm², whilst highly (116) oriented films formed at lower fluence. Rocking curve FWHM of (116) oriented films was of the order of 0.17° which is an indication of excellent quality of film epitaxy. The in-plane orientation relationship between film and substrate was determined as $(116)_{SBT} \parallel (110)_{SrTiO_3}$ and $[1\bar{1}0]_{SBT} \parallel [1\bar{1}0]_{SrTiO_3}$. These films showed a corrugated morphology. The RMS roughness of (116) oriented films was of the order of 10-15 Å whilst those with mixed orientations showed a RMS roughness of 20-25 Å.

Towards the development of SBT films with a-axis orientation, ideal for FRAM applications, SBT films were deposited on single crystal substrates of TiO₂ (110) and LaSrAlO₄ (110). Films on TiO₂ (110) showed partial a-/b-axis orientation together with c-axis-oriented SBT and other unidentified impurities. Morphology of the films was very rough showing outgrowths of many impurities. The use of structurally compatible buffer layers will aid deposition of SBT films with a higher degree of a-/b-axis orientation on TiO₂ (110). We were successful in depositing highly epitaxial and smooth a-/b-axis oriented SBT films on single crystal LaSrAlO₄ (110) substrates. Good quality of epitaxy and excellent in-plane alignment with the substrate was confirmed by X-ray pole figures and TEM. Based on these investigations, the orientation relationship between the film and the substrate was determined as $(110)_{\rm S}$ // $(100)_{\rm F}$ or $(010)_{\rm F}$, $[001]_{\rm S}$ // $[001]_{\rm F}$ and $[1\bar{1}0]_{\rm S}$ // $[010]_{\rm F}$ or $[100]_{\rm F}$. The key to the epitaxy was the structural similarity and relatively low lattice mismatch (as compared to TiO₂ (110)) between the (100)/(010) plane of SBT and (110) plane of the substrate. 100 nm think films were very smooth with RMS roughness of the order of 20-25 Å. To the best of my knowledge, this work is the first report on completely a-/b-axis oriented SBT films.

We also attempted to deposit Sr_2RuO_4 films on LaSrAlO₄ (110) as bottom electrodes. Attempts were not successful as the film phase was $SrRuO_3$ with (121) preferred orientation. A possible reason for this is inability to work at very low oxygen pressures and high temperatures required to grow Sr_2RuO_4 phase. SBT films deposited on (121) oriented $SrRuO_3$ showed the presence of many impurities. This was also reflected in the ferroelectric measurements of the films showing that the films were shorted, attributed to the presence of conducting impurities such as Bi_2O_3 .

10.3 Suggestions for Further work

Further work needs to be done on trial depositions of Sr_2RuO_4 films on LaSrAlO₄ (110) substrates which can act as a conducting bottom electrode and also as a buffer layer between the SBT film and the substrate. Growth of fully (110)-oriented Sr_2RuO_4 films will enable us to deposit completely a-/baxis oriented films on $Sr_2RuO_4/LaSrAlO_4$ (110) heterostructures. An assessment of the ferroelecric behaviour of these films can also give us a clue about whether these films are purely a- or b- axis oriented or possess mixed a-/b- orientation which is not possible to determine by any other techniques used for structural characterization. Deposition of these films can be extended to commercially useful Pt/Si substrates. If the growth of (110)-oriented Sr_2RuO_4 films can be achieved on Pt/Si, this would act as a basis for depositing a-/b-axis oriented SBT films which would be ideal for a FRAM device based on SBT.

In addition, more work will be required to study a range of compositions of Bi-layered Aurivillous phases, which would enhance our understanding of ferroelectricity in these compounds and its dependence upon composition. In particular Bi₄Ti₃O₁₂ and its higher order derivatives are attractive candidates for this study because of their large remanent polarization. Dopants such as La, Sm, Y can be substituted on to the Bi sites in the Bi₄Ti₃O₁₂ structure in varying amounts to prepare a range of compositions. This will show the effect of dopant concentration on the ferroelectric behaviour of these oxides. Compounds showing good ferroelectric properties can be deposited in thin film form on various substrates. These substrates include both single crystal substrates for depositing epitaxial films and conventional Pt/Si substrates for polycrystalline or textured films. Structural aspects of thin film growth can be studied using X-ray diffraction, atomic force microscopy, and transmission electron microscopy. Detailed structural studies will help us to gain an understanding of the deposition conditions and enable us to improve the quality of the films. Films showing satisfactory ferroelectric properties can be used for FRAM device fabrication to assess their viability for commercial applications.

Appendix A: Glazer octahedral tilt system

Fig. A1 shows the basic unit of corner linked octahedra in a perovskite structure. The ideal structure is cubic (e.g. in $SrTiO_3$ at room temperature), but distortions in the structure are common either due to displacement of the cations from their ideal positions and/or by the tilting of the octahedra. Octahedral tilting can have a large effect on lattice spacing, and $Glazer^1$ developed a system of classification of this tilting which is very useful.



FIGURE A1 The basic unit of corner linked octahedra in a perovskite structure. A perovskite has general formula ABX₃, and the octahedra shown have X atoms at their corners, B atoms in their centres, and A atoms between them; from ref. [1].

Glazer considers all tilts as combinations of component tilts about the three tetrad axes. For small angle tilts, the axes are taken as the pseudocubic axes prior to tilting. When one octahedron is tilted in a particular way, it causes tilting of the neighbouring octahedra. Glazer only considers tilts that are 'freely available' and independent.

If an octahedron tilts in a positive sense around one axis, the neighbouring octahedra in directions perpendicular to that axis will become tilted in the opposite sense about that axis. However, a choice arises in the tilt of neighbouring octahedra along that axis. They can either be tilted in the same sense (denoted +), tilted in the opposite sense (denoted -), or not tilted at all around that axis (denoted o).

Fig. A2 shows an octahedron tilted in a positive sense around all three axes, denoted +++, and the tilts which this causes in neighbouring octahedra. The neighbouring octahedra have a blank left in the description of their tilts for axes for which there is a choice possible.



FIGURE A2 Schematic view of two adjacent layers. A tilt in the positive sense around the pseudocubic axes is denoted by +++. The resultant tilts in first and second neighbouring octahedra are shown, where – denoted a tilt in the opposite direction; from ref. [1].

The magnitudes of the tilts are indicated by three letters corresponding to the [100], [010] and [001] directions. For three different tilts, the letters abc are used. Equality of tilts is denoted by repeating the appropriate letter, e.g. aac means equal tilts around [100] and [010], with a different tilt around [001]. Superscripts are then applied to each letter, to denote whether neighbouring octahedra along that axis have a tilt in the same sense (+), the opposite sense (-) or no tilt (o).

For example, an $a^{\circ}a^{\circ}c^{-}$ tilt system involves only one tilt, along the [001] axis, and alternating layers have tilts in the opposite sense. An $a^{+}b^{+}c^{+}$ tilt is body centred, and an $a^{-}b^{-}c^{-}$ tilt is face centred.

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