ABSTRACT

AGGARWAL, RAVI. Integration of Functional Oxide Thin Film Heterostructures with Silicon (100) Substrates. (Under the direction of Professor Jagdish Narayan and Professor Roger Narayan).

The novel functionalities of metal oxides provide the opportunity for the development of next generation optoelectronic, spintronic and a host of other multifunctional devices. A critical issue in the development of practical devices based on metal oxides is the integration of high quality epitaxial oxide thin films with the existing silicon technology which is based on silicon (100) substrates. However, silicon is not suitable for epitaxial growth of oxides owing to its tendency to readily form an amorphous oxide layer at the film-substrate interface. The oxide films deposited directly on silicon exhibit poor crystallinity and are not suitable for device applications. To overcome this challenge, appropriate substrate templates must be developed for growth of oxide thin films on silicon substrates.

The present work is focused on developing integration methodology of functional oxides with Si (100) substrates using an yttria-stabilized zirconia (YSZ) template layer. If the deposition conditions are controlled properly, YSZ can be grown epitaxially on silicon substrates even if the native oxide is not etched prior to deposition. This is believed to occur by reaction between zirconium and native silicon dioxide. These Si (100) substrates with epitaxial YSZ template layer can be used to grow functional oxide thin films.

The above approach has been used to integrate zinc oxide (ZnO) thin films with Si (100) substrates. The wide band gap (~3.4 eV), large exciton binding energy (60 meV) and room temperature ferromagnetism make ZnO a potential candidate for a host of next generation
optoelectronic and spintronic devices. A thorough study on growth and properties of ZnO films on YSZ buffered Si (100) substrates was performed. The ZnO and YSZ films were deposited by pulsed laser deposition (PLD) technique. Detailed characterization of the deposited films was done using x-ray diffraction, transmission electron microscopy (TEM), electrical measurements and photoluminescence spectroscopy. Using YSZ buffer layer, we have been able to epitaxially integrate both non-polar (c-plane) and semi-polar (r-plane) ZnO films with Si (100) substrates. It was observed that, depending on the oxygen pressure during the deposition, ZnO can grow in two different crystallographic orientations (c-plane or r-plane) on YSZ buffered silicon. Experiments carried out to elucidate the role of oxygen pressure indicated that the crystallographic orientation of ZnO depends on the nature of atomic termination of YSZ layer. It has been proposed that crystallographic orientation of ZnO is controlled by chemical free energy associated with the ZnO/YSZ interface.

In order to form p-n junction with n-type ZnO, another multifunctional oxide $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) was epitaxially integrated with Si (100) substrates. LSMO is a p-type materials and exhibits interesting properties such as semiconductor to metal transition (SMT), room temperature ferromagnetism and colossal magneto resistance (CMR). Junctions based on CMR materials are of special interest, because their electrical and magnetic properties can be modulated by external electric and magnetic fields. It has been demonstrated that epitaxial nonpolar a-plane ZnO films can be grown on LSMO integrated with Si (100) substrates.
Integration of Functional Oxide Thin Film Heterostructures with Silicon (100) Substrates

by
Ravi Aggarwal

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

I dedicate this thesis to my family for their love, support and patience.
BIOGRAPHY

Ravi Aggarwal was born to Mr. Vedprakash Aggarwal and Mrs. Bimla Aggarwal in Gujarwas, a small village in Haryana state, in northern India. After completing his high schooling in the village school, he moved to Delhi for higher studies. He earned a Bachelor of Science (Honours) degree in Chemistry from Ramjas College, University of Delhi. His quest for science and engineering led him to prestigious Indian Institute of Science (IISc), Bangalore. At Indian Institute of Science, he pursued a four-year graduate program in Metallurgy. After earning his Master of Engineering degree in Metallurgy from IISc in 1998, he worked as an Assistant Manager in Technology and Quality group of a leading steel plant in India. After having a successful stint in industry, he took up a faculty position in 2002 at the department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi. He joined PhD program in Materials science and Engineering at North Carolina State University in Fall 2006. He is married to Anika and has a daughter, Arshi.
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Discussions and collaboration with my colleagues have considerably enriched my learning experience during my graduate study at NCSU. I take this opportunity to thank my colleagues Chunming Jin, Sudhakar Nori, Punam Pant, Wei Wei, Titas Dutta, Pranav Gupta, Tsung Han Yang, Alok Gupta and Siddhartha Mal. Their support throughout my doctoral research has been invaluable. I would also like to thank the administrative staff at the MSE department, particularly Edna Deas, for their prompt help in any official work. Without mentioning any specific names, I would like to thank from the bottom of my heart all my friends, on and off-campus, who have made my stay at Raleigh highly memorable.

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1. Introduction

Metal oxides display the most diverse range of functionality among all inorganic materials. The nature of metal-oxygen bond changes from being highly ionic to highly covalent as the electronegativity of metal atom increases. In most cases, the metal-oxygen bond exhibits a mixture of ionic and covalent character. The interplay between localized and itinerant character of electrons leads to wide range of electronic properties observed in oxides. Depending on the electronegativity of the cation, closed shell oxides can be wide band gap insulators (e.g. Al$_2$O$_3$) or may exhibit semiconducting behavior (e.g. ZnO). Oxides with partially filled conduction band containing mixed valence cations can give rise to highly conducting (e.g. SrRuO$_3$) or even high temperature superconductors (e.g. YBa$_2$Cu$_3$O$_7$). Many oxides display interesting metal–insulator transitions that are dependent on temperature (e.g. VO$_2$), pressure (e.g. NiO), or magnetic field (e.g. La$_{0.67}$Sr$_{0.33}$MnO$_3$). Other examples of functional oxides include ferroelectrics such as BaTiO$_3$, multiferroics such as BiFeO$_3$ and ferromagnetic oxides such as CrO$_2$.$^{1-3}$

Interest in fundamental properties and potential applications, has lead to significant research efforts in growing epitaxial oxide films. Though polycrystalline oxide films may be suitable for some applications, the superior properties of highly crystalline epitaxial films are more attractive both for applications and fundamental studies of material and surface properties. It is expected that development of high quality oxide films will potentially lead to development of heterostructures with new functionalities.
The functionalities of metal oxides make them potential materials for a host of next generation optoelectronic, spintronic and other multifunctional devices. A critical issue in the development of practical devices based on metal oxides is the integration of high quality epitaxial oxide thin films with the existing silicon technology which is based on silicon (100) substrates. When exposed to oxygen, silicon readily forms an amorphous oxide layer at the surface. The formation of amorphous oxide layer hampers epitaxial growth of oxides on silicon substrates. Hence, the most oxide films deposited directly on silicon exhibit poor crystallinity and are not suitable for device applications. To overcome this challenge, appropriate substrate templates must be developed for epitaxial growth of oxides on silicon substrates.

The focus of the present research work is on the epitaxial integration of functional oxides with Si (100) substrates. This has been achieved using a tetragonal yttria-stabilized zirconia (YSZ) template layer on Si (100) substrates. The YSZ/Si interface is thermodynamically stable and if the deposition conditions are controlled properly, YSZ can be grown epitaxially on silicon substrates. The YSZ buffered Si (100) substrates can be used to grow oxide thin films. We have used this approach to integrate zinc oxide (ZnO) and lanthanum strontium manganite (La$_{0.67}$Sr$_{0.33}$MnO$_3$)(LSMO) thin films with Si (100) substrates using pulsed laser deposition (PLD) technique. The wide band gap (~3.4 eV), high exciton binding energy (60 meV) and room temperature ferromagnetism make ZnO a potential candidate for a host of next generation optoelectronic and spintronic devices.$^{4-6}$ LSMO exhibits interesting properties such as semiconductor to metal transition (SMT), room temperature
ferromagnetism and colossal magneto resistance (CMR) and p-type conductivity.\textsuperscript{7,9} These properties make LSMO a potential materials for host of multifunctional devices. We have epitaxially integrated LSMO/ZnO heterojunctions with silicon substrates. Junctions based on CMR materials are of special interest, because their electrical and magnetic properties can be modulated by external electric and magnetic fields.\textsuperscript{10}

Rest of the thesis is organized in following chapters.

\textit{Chapter 2:} In this chapter, background knowledge pertinent to present study is presented.

\textit{Chapter 3:} A brief description of experimental techniques used for present work is given.

\textit{Chapter 4:} Experimental results on growth of YSZ buffer layer on silicon (100) substrates are presented.

\textit{Chapter 5:} Results on growth of c-plane oriented epitaxial ZnO films on silicon (100) substrates are discussed.

\textit{Chapter 6:} Detailed structural, electrical and optical characterization results for c-plane ZnO films grown on silicon substrates are presented in this chapter.

\textit{Chapter 7:} Results on growth and characterization of semipolar r-plane ZnO films integrated with silicon substrates are discussed.

\textit{Chapter 8:} Here the growth and characterization of ZnO/LSMO junctions integrated with silicon substrates are discussed.

\textit{Chapter 9:} A brief summary of the present work is given. Scope for future work is discussed.
References


2. Background Knowledge

2.1 Thin Film Epitaxy

The term ‘epitaxy' was first introduced by Royer\textsuperscript{1} to describe the phenomenon of the oriented growth of crystals of one material on the crystal surface of another material. The term has since been generalized to thin crystalline films grown with one or more well-defined orientations on a single-crystal substrate. In the strict sense epitaxy refers to the formation of single crystalline film on a substrate such that the film has a fixed orientation relationship with the substrate. Single crystalline epitaxy is not possible when the substrate and the film have different crystal symmetries in the growth plane. In such instances of thin film epitaxy, film may have more than one orientation relationship with the substrate.

Epitaxy can be further classified as homoepitaxy or heteroepitaxy. Homoepitaxy refers to the case where the film and substrate are the same material. Growth of epitaxial Si on Si wafers in the fabrication of bipolar and some MOS transistors by vapor phase epitaxy is the most significant example of homoepitaxy.\textsuperscript{2} The second type of epitaxy is known as heteroepitaxy and refers to films and substrates composed of different materials, e.g., GaN deposited on Al\textsubscript{2}O\textsubscript{3} substrates. Optoelectronic devices such as light-emitting diodes and lasers are based on compound semiconductor heteroepitaxial film structures. Since the film and the substrate materials are different in heteroepitaxy, the properties of heteroepitaxial films are influenced by crystallographic properties of the substrate and the film, the difference in film and substrate chemistry, and the difference in film and substrate thermal expansion coefficients.
The most relevant crystallographic properties to epitaxy are crystal symmetry and in-plane lattice constants which decide the lattice misfit. The lattice misfit between substrate and film is key parameter which controls growth, morphology and properties of the film. The lattice misfit is defined as:

\[ f = \frac{a_{\text{film}} - a_{\text{substrate}}}{a_{\text{substrate}}} \]  

2.1

2.2 Lattice Matching Epitaxy

In lattice matching epitaxy there is one-to-one matching of lattice parameters across the film-substrate interface. This matching of lattice parameters occurs by means of strain in the film (and up to some extent in the substrate) as the film grows pseudomorphically. The pseudomorphic growth of the film continues until a ‘critical thickness’ where the strain energy becomes large enough to trigger nucleation of dislocations. A schematic illustration of lattice matching epitaxy is given in Figure 2.1a. The critical thickness for dislocation nucleation is directly related to the misfit. In low misfit systems the critical thickness for dislocation nucleation may be quite large and dislocation nucleation and strain relaxation may not be possible. Also, these dislocations are nucleated at the film surface and must glide to the interface to relieve the strain. The obstacles to the glide of dislocations may result in a high threading dislocation density in the film, which is detrimental for devices.

2.3 Domain Matching Epitaxy

Conventional lattice matching epitaxy during thin film growth is possible as long as the lattice misfit between the film and the substrate is less than 7–8%. Above this misfit, it was
Figure 2.1 Schematic illustration of (a) lattice matching epitaxy (LME) and (b) domain matching epitaxy (DME), in which four lattice planes of film match with five lattice planes of substrate.

surmised that the film will grow textured or largely polycrystalline. The epitaxial growth in high misfit systems can be explained by domain matching epitaxy (DME), proposed by Narayan et al. In the domain matching epitaxy, we consider the matching of lattice planes, which could be different in different directions of the film–substrate interface. This is in contrast to LME in which there is one-to-one matching of lattice constants across the film–substrate interface. An important feature of the domain matching epitaxy concept is that most of the strain is relieved quickly within a couple of monolayers, so that the misfit strain and dislocations can be engineered and confined near the interface (Figure 2.1b). This makes it
possible for the rest of the film to be grown free of defects and lattice strains. In DME misfit is accommodated by matching of integral multiples of lattice planes, and there is one extra half plane (dislocation) corresponding to each domain. If the misfit falls in between the perfect matching ratios of planes, then the size of the domain can vary in a systematic way to accommodate the additional misfit.

The matching of m planes of film with n planes of substrate will lead to a residual strain of:

\[ \varepsilon_r = \frac{md_f}{nd_s} - 1 \tag{2.2} \]

Where m and n are simple integers and d_f and d_s are the interplanar spacing of film and substrate respectively. In case of perfect matching, residual strain is zero and md_f = nd_s.

If \( \varepsilon_r \) is finite, then two domains may alternate with a certain frequency to provide for a perfect matching according to:

\[ (m + \alpha)d_f = (n + \alpha)d_s \tag{2.3} \]

where \( \alpha \) is the frequency factor, for example, if \( \alpha = 0.5 \), then m/n and (m+1)/(n+1) domains alternate with an equal frequency. Assuming \( d_f > d_s \), we have n > m. The difference between n and m could be 1 or some function of m.

\[ n - m = 1 \text{ or } f(m) \tag{2.4} \]

Since the concept of DME was first proposed, it has been shown to be important for growing thin heterostructures with large lattice misfit. Some typical examples for the DME growth are TiN/Si (100) heterostructures, III-nitride epitaxy on Si(111), and ZnO and III-nitrides on sapphire (0001).
2.4 Zinc Oxide

Zinc oxide is a wide and direct band gap semiconductor with a band gap of ~3.37 eV at room temperature.\(^4\) Since the mid 1990’s there has been a great interest in ZnO thin films and nanostructures. A large body of this research is focused on developing ZnO as an alternative material for blue and ultraviolet opto-electronic devices,\(^5,6\) which are currently based on gallium nitride (GaN). One of the biggest advantages of ZnO over GaN is its high excitonic binding energy, 60 meV compared to 30 meV for GaN. The high excitonic energy makes ZnO a potential candidate for exciton recombination-based lasing devices, which can operate at room temperature or higher.\(^7,8\) Room temperature lasing has been realized using zinc oxide thin films.\(^9-11\) Doping with Ga or Al makes zinc oxide highly conductive.\(^12,13\) This has stimulated research to develop ZnO as a transparent conducting oxide (TCO), as a cheaper alternative to indium tin oxide (ITO). Zinc oxide has large piezoelectric coefficients, which makes it useful material for transducers and actuators.\(^14,15\) Room temperature ferromagnetism in transition metal (e.g., Fe, Mn, Co, and Ni) doped ZnO, makes it a potential candidate for next generation spintronic devices.\(^16-19\) The electrical conductivity of ZnO thin films is very sensitive to the adsorbed species. This high surface sensitivity makes zinc oxide a promising material for gas sensors.\(^20,21\) Strong non-linear resistance of polycrystalline ZnO is the basis of commercially available ZnO varistors. Zinc oxide exhibits strong luminescence in green-white range of the spectrum.\(^22,23\) The other properties of ZnO which make it preferable over other wide-band-gap materials are its high energy radiation stability and amenability to wet chemical etching.\(^24\) Several experiments confirmed that ZnO is very resistive to high-energy
radiation making it a very suitable candidate for space applications.\textsuperscript{25-27} ZnO is easily etched in all acids and alkalis, and this provides an opportunity for fabrication of small-size devices.

### 2.4.1 Crystal Structure of ZnO

Zinc oxide crystallizes in the hexagonal wurtzite-type structure. This structure belongs to the space group P6\textsubscript{3}mc. This structure is composed of two interpenetrating hexagonal-close-packed (hcp) sublattices of Zn and O atoms (Figure 2.1). These two sublattices are displaced from each other by 0.375 c along the c-axis. This displacement of Zn and O sublattices makes this structure non-centrosymmetric and imparts a polarity to ZnO along the c-axis. In this structure each zinc ion is surrounded tetrahedrally by four oxygen ions and vice versa. Though the tetrahedral coordination is indicative of sp\textsuperscript{3} covalent bonding, ZnO has substantial ionic character. The ionicity of ZnO is at the border between covalent and ionic semiconductors.

![Figure 2.2 Wurtzite crystal structure of ZnO. Zinc and oxygen atoms are shown in white and yellow colors, respectively. (Wikipedia)](image)

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The lattice constants of ZnO hexagonal unit cell are $a=3.2499$ Å and $c=5.2066$ Å. The ratio $c/a$ of the elementary translation vectors, with values around 1.602, deviates slightly from the ideal value of $c/a= 1.633(\sqrt{8/3})$ for hexagonal close packed structure. Though wurtzite structure is the most favorable structure of ZnO, under certain conditions ZnO may exist in cubic rock salt or zinc blende-type structures. The zinc-blende ZnO structure is metastable and can be stabilized only by heteroepitaxial growth on cubic substrates, such as ZnS. The rock salt structure of ZnO is stable at high pressures. The four most common face terminations of wurtzite ZnO are the polar Zn terminated (0002) and O terminated (000\overline{2}) faces (c-plane), and the non-polar (1\overline{1}0\overline{0}) (c-plane) and (10\overline{1}0) (m-plane) faces which both contain an equal number of Zn and O atoms. One of the most important semi-polar planes in ZnO is (10\overline{1}2) (r-plane). The important crystallographic planes in ZnO are shown in Figure 2.3.

![Figure 2.3 Important crystallographic planes in ZnO.](image)

### 2.4.2 Band Structure and Electronic Properties of ZnO

ZnO is a direct-gap semiconductor with the global maxima of the valence band (VB) and the minima of the conduction band (CB) at the same point in the Brillouin zone, namely at $k=0$. 
The lowest unoccupied orbital (LUMO), or the bottom of the conduction band is formed from the 4s levels of Zn\(^{2+}\). The top of the valence band, or highest occupied molecular orbital (HOMO), is formed from the 2p levels of O\(^{2-}\). The band gap is \(~3.37\) eV at room temperature. The band structure of ZnO in the vicinity of the fundamental band gap is shown in Figure 2.4. The effective electron mass is quite isotropic, with a value around \(m_e = 0.28m_o\). The hole masses are similar for the A, B and C valence bands, with typical values of \(m_{h\parallel A,B} = 0.59m_o\), \(m_{h\parallel C} = 0.31m_o\), and \(m_{h\perp C} = 0.55m_o\).

![Figure 2.4 Band structure of ZnO in the vicinity of the fundamental band gap.](image)

2.4.3 Native Defects and Doping in ZnO

The native defects in semiconductors often control doping, minority carrier lifetime, and luminescence efficiency. They also assist the diffusion mechanisms involved in growth, processing, and device degradation. Doping forms the basis of much of semiconductor...
technology and can be drastically affected by native point defects. Such defects may cause self-compensation: for instance, in an attempt to dope the material p-type, certain native defects which act as donors may spontaneously form and compensate the deliberately introduced acceptors. Hence understanding the behavior of native point defects is essential for successful application of any semiconductor. Possible native point defects in ZnO are: oxygen and zinc vacancies (V\(_\text{O}\) and V\(_\text{Zn}\)), interstitials (O\(_i\) and Zn\(_i\)), and antisites (O\(_{\text{Zn}}\) and Zn\(_{\text{O}}\)). These defects can exist in neutral as well as in single or double ionized states and can give rise to various mid-gap states in ZnO. The estimated defect levels in ZnO are shown in Figure 2.5. Zinc interstitials and oxygen vacancies are believed to be the predominant defects in ZnO.

![Energy level diagram of native defects in ZnO](image)

**Figure 2.5** Energy level diagram of native defects in ZnO.

As-deposited intrinsic ZnO films always exhibit n-type conductivity. The donor concentration in intrinsic ZnO films is strongly dependant on the processing conditions and varies in the range 10\(^{17}\)-10\(^{19}\) cm\(^{-3}\). This intrinsic n-type conductivity in ZnO is generally
attributed to native point defects. Oxygen vacancies and zinc interstitials have been often mentioned as sources of n-type conductivity in ZnO. First-principles calculations suggest that the unintentionally incorporated hydrogen can also result in intrinsic n-type conductivity of ZnO.\textsuperscript{32}

Intentional n-type doping is relatively well established through the substitution of group III elements (Al, Ga, In) on the Zn sites and donor concentrations beyond $10^{20}$ cm$^{-3}$ have been achieved.\textsuperscript{33} However, all efforts to obtain reliable p-type doping in ZnO have so far been mainly unsuccessful.\textsuperscript{34} Like many other wide band gap semiconductors, such as GaN, it is very difficult to obtain p-type doping in ZnO. This can be attributed to many different reasons. The same intrinsic defects responsible for n-type conductivity tend to aggravate the efforts for p-type doping by compensating the potential acceptors. Low solubility of the dopants in the host material is also another possibility. Deep impurity levels can also be a source of doping problem, causing significant resistance to the formation of shallow acceptor level. Known acceptors in ZnO include group-I elements such as Li, Na, and K. Other candidate acceptors for ZnO include Cu, Ag, Zn vacancies, and group-V elements such as N, P, and As. However, many of these form deep acceptors and do not contribute significantly to p-type conduction. Presently it is believed that the most promising dopants for p-type ZnO are the group-V elements, particularly nitrogen.\textsuperscript{35}

Most practical optoelectronic devices, such as LEDs and lasers rely on quantum wells for carrier/optical confinement. Band gap engineering of the semiconducting material is a key
requirement for devices based on quantum wells. The band gap of ZnO can be engineered with relative ease by alloying with CdO or MgO, and is an effective means of increasing or decreasing the energy band gap respectively.\(^{29}\) The band gap of CdO is 2.2 eV and can be alloyed with ZnO to decrease the band gap. MgO, on the other hand, has a band gap of 7.8 eV and can be used for increasing the band gap of ZnO. Though ZnO has a wurtzite crystal structure, CdO and MgO both crystallize in rock-salt structure. This presents a problem for ZnO based alloys with high content of CdO or MgO, in which case phase separation is expected to occur. However, for moderate contents of CdO and MgO, CdZnO and MgZnO alloys retain the wurtzite crystal structure of ZnO and still providing a wide range of band gaps (2.3-4.0 eV).\(^{31}\)

2.4.4 ZnO Thin Film Growth

Most of the current technological applications of ZnO, such as varistors, and piezoelectric devices are based on polycrystalline films deposited on glass substrates. The techniques used to grow polycrystalline films of ZnO include chemical spray pyrolysis, screen painting, sol–gel synthesis and oxidation of Zn films. However, for electronic and optoelectronic applications, high-quality single-crystal epitaxial films with minimal concentrations of native defects and controlled doping are required. High quality epitaxial ZnO films have been grown by techniques such as pulsed laser deposition (PLD), chemical vapor deposition (CVD), metal-organic CVD (MOCVD) and molecular-beam epitaxy (MBE), and sputtering. Sapphire substrates are commonly widely used for heteroepitaxial growth of ZnO films. The growth orientation of ZnO on (0001) sapphire is polar c-plane (0002), while it grows in non-
polar a-plane (11$ar{2}$0) orientation on (10$ar{1}$2) sapphire. Other substrates which have been used for growth of ZnO films include GaN, AlN, SiC, GaAs, Si and ScAlMgO$_4$. Homoeptaxial growth of ZnO has been also attempted. Lattice parameters of prospective substrates for growth of ZnO films are tabulated in Table 2.1.

**Table 2.1 Details of prospective substrates for ZnO growth**

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Lattice parameters $\alpha$ (Å)</th>
<th>Lattice mismatch (%)</th>
<th>Thermal-expansion coefficient, $\alpha$ (K$^{-1}$)</th>
<th>$\alpha_\perp$ (10$^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Hexagonal</td>
<td>3.252</td>
<td>--</td>
<td>2.9</td>
<td>4.75</td>
</tr>
<tr>
<td>GaN</td>
<td>Hexagonal</td>
<td>3.189</td>
<td>18</td>
<td>5.7</td>
<td>4.15</td>
</tr>
<tr>
<td>AlN</td>
<td>Hexagonal</td>
<td>3.112</td>
<td>45</td>
<td>5.3</td>
<td>4.2</td>
</tr>
<tr>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
<td>Hexagonal</td>
<td>4.757</td>
<td>50 (8.4% after 30$^\circ$ in-plane rotation)</td>
<td>7.3</td>
<td>8.0</td>
</tr>
<tr>
<td>6H-SiC</td>
<td>Hexagonal</td>
<td>3.080</td>
<td>35</td>
<td>4.4</td>
<td>4.88</td>
</tr>
<tr>
<td>Si</td>
<td>Cubic</td>
<td>5.430</td>
<td>40.1</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>ScAlMgO$_4$</td>
<td>Hexagonal</td>
<td>3.246</td>
<td>009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>Cubic</td>
<td>5.652</td>
<td>42.4</td>
<td>6.8</td>
<td></td>
</tr>
</tbody>
</table>

### 2.5 Substrate and Buffer Layer Materials

#### 2.5.1 Silicon

Silicon is a group VI element semiconductor. Most of the commercial electronic devices are currently based on silicon. Owing to large scale industrial use, silicon substrates are widely and cheaply available. Hence integration of new functional materials with silicon substrate
offers unique technological advantage. Silicon has a diamond-cubic crystal structure (Figure 2.6) with lattice constant of 5.431 Å. The thermal expansion coefficient of Silicon is \(~2.6 \times 10^{-6} \text{ K}^{-1}\). The band gap of silicon is \(~1.12 \text{ eV}\) at room temperature. Silicon substrates are available in large sizes (up to 400 mm diameter). Both n-type and p-type silicon substrates with different doping concentration are available. One of the biggest challenges in integrating oxide materials with silicon is the tendency of silicon to readily form an amorphous silicon dioxide oxide (SiO2) layer.

![Diamond cubic crystal structure of Silicon.](image)

**Figure 2.6** Diamond cubic crystal structure of Silicon.

### 2.5.2 Yttria Stabilized Zirconia (YSZ)

Yttria-stabilized zirconia (YSZ) is an attractive buffer layer for the subsequent growth of numerous oxide materials on non-oxide substrates. YSZ has a high dielectric constant (\(~25\)) and large bandgap (7.8 eV). YSZ has excellent chemical stability on silicon. The free energy
of formation of ZrO$_2$ ($\Delta G_{800 \text{ K}} = -941.6 \text{ kJ kmol}^{-1}$) is smaller than that of SiO$_2$ ($\Delta G_{800 \text{ K}} = -734.2 \text{ kJ kmol}^{-1}$). The thermal expansion coefficient of YSZ is $\sim 11.4 \times 10^{-6} \text{ K}^{-1}$. Crystal structure of YSZ is dependent on the yttria content. Pure zirconia (ZrO$_2$) is monoclinic. When doped with 3-5 mol % yttria, the tetragonal phase of zirconia is stabilized at room temperature. Yttria content of 8 mol % or higher makes cubic phase of zirconia stable at room temperature. Lattice parameters of tetragonal YSZ (space group P4$_2$/nmc) are $a = 3.6067$ Å, $c = 5.1758$ Å (for 3 mol % Y$_2$O$_3$ doped ZrO$_2$). Cubic YSZ crystallizes in a fluorite-type structure (space group $Fm\bar{3}m$) with a lattice parameter $\sim 5.1289$ Å (for 15 mol % Y$_2$O$_3$ doped ZrO$_2$). A unit cell of tetragonal YSZ is shown in Figure 2.7.

Figure 2.7 Crystal structure of tetragonal YSZ. Oxygen atoms are shown in red color while (Zr, Y) atoms are shown in green color.

2.5.3 Cerium Oxide (CeO$_2$)

Cerium oxide (ceria) is an attractive buffer layer for epitaxial growth of oxides. Cerium oxide has a cubic fluorite structure (space group Fm3m) shown in Figure 2.8. The Lattice
parameter of CeO2 (5.411 Å) is very close to that of silicon (5.431 Å). Cerium oxide has a moderate band gap of ~ 3.2 eV and relatively high dielectric constant. The thermal expansion coefficient of CeO2 is ~ 9.9 x 10^-6 K^-1. Good diffusion barrier properties make CeO2 an excellent choice for growth of complex oxides such as YBa2Cu3O7.

Figure 2.8 Crystal structure of cerium oxide (CeO2). Oxygen atoms are shown in red color while Ce atoms are shown in green color.

2.5.4 Lanthanum Strontium Manganite (LSMO)

Perovskite manganites with general formula A_{1-x}B_xMnO3 (where A is a lanthanum (La) and B an alkaline-earth (Ba, Ca, Sr) element) have attracted much attention due to the observation of a colossal magnetoresistance (CMR) effect. The CMR effect occurs in the 0.2 < x < 0.5 doping range. Among these materials, La_{0.67}Sr_{0.33}MnO3 (LSMO) has been studied intensively because of their high Curie temperature. LSMO crystallize into the perovskite structure shown in Figure 2.9. The cubic lattice parameter of LSMO is 3.87 Å. At high temperatures LSMO is paramagnetic and semiconducting. When the temperature is
decreased a transition from the paramagnetic to ferromagnetic metallic state occurs at the Curie temperature. In LSMO, Mn exists in two states: Mn$^{3+}$ and Mn$^{4+}$. An electron localized at a Mn$^{3+}$ ion can hop on the vacant place of a neighboring Mn$^{4+}$ ion (which corresponds to the movement of a hole in the opposite direction). The transfer of a charge carrier occurs simultaneously from Mn$^{3+}$ to O$^{2-}$ and from O$^{2-}$ to Mn$^{4+}$. Because Hund’s rule coupling is strong, the carriers can hop from one Mn ion to another only if the core spins of the two ions are parallel. This double-exchange mechanism is the basic mechanism of electrical transport and explains the observed simultaneous occurrence of metallic conductivity and ferromagnetism in the manganites.\^{39} Because the same electrons are responsible for electrical transport and ferromagnetic interaction, the paramagnetic-to-ferromagnetic transition in the doped manganites is accompanied by an insulator-to-metal transition around the ferromagnetic Curie temperature. An external magnetic field applied at temperatures around T$_{C}$ promotes alignment of the local spins and hence reduces the randomness of the electron hopping, which increases the electrical conductivity markedly, giving rise to the CMR effect.

Due to high spin polarization, the manganites show a great potential for applications in magnetic tunnel junctions (MTJs), which are promising candidates for nonvolatile magnetic random access memory. Also, p-n junctions based on the colossal magnetoresistance (CMR) oxides are of special interest, because their electrical and magnetic properties can be modulated by external electric and magnetic fields. It is possible to fabricate electronic devices with high electric and magnetic sensitivity, which can be used for various applications such as magnetic field detector and magnetic storage.\^{40-44}
Figure 2.9 Perovskite structure of LSMO.
References


3. Experimental Techniques

In this chapter, details of thin film deposition and characterization methods used in the present work are discussed. All the films in the present study were deposited using pulsed laser deposition. The structural characterization of the films was done by x-ray diffraction and transmission electron microscopy. Electrical properties of the films were characterized by Hall effect and four-point resistivity measurements. Photoluminescence spectroscopy was performed for optical characterization of zinc oxide films. Only brief description of the relevant experimental techniques is given in this chapter. Further details on these techniques are available in the references provided at the end of the chapter.

3.1 Substrate Preparation

In the present study, Si (100) substrates were used for thin film deposition. The substrates were 300-500 µm thick. During storage and handling it is usual for dust particle and organic impurities to stick to substrate surface. If not cleaned, the particles and organics may hamper nucleation and epitaxial growth of thin films on these substrates. Hence substrates were cleaned prior to thin film deposition. The substrates were first put into acetone bath and which was heated to ~130 °C for 3 minutes. Subsequently, substrates in acetone bath were ultrasonically agitated for 5 minutes to remove particulates. This was followed by ultrasonic cleaning of substrates in an ethanol bath to clean acetone. Finally, substrates were dried by blowing high purity nitrogen. After cleaning, substrates were immediately loaded into the pulsed laser deposition chamber. Substrates were glued to heating plate in the deposition chamber using a fast drying silver paste.
3.2 Pulsed Laser Deposition

All thin films in the present study were deposited using pulsed laser deposition (PLD). Pulsed laser deposition is a low pressure physical vapor deposition technique. The schematic diagram of the PLD system used in the present study is shown in Figure 3.1. A high energy laser is focused on the material to be deposited, referred to as target. The interaction of the target material with laser leads to localized vaporization and formation of highly energetic plasma.\textsuperscript{1, 2} This phenomenon is frequently referred to as laser ablation. The ablated material is ejected in a direction normal to the target surface in the form of a plume. The material in this plume is deposited on the substrate which is usually heated.

The peak power of most commercial lasers is inversely correlated with the duration of the laser pulse. Since ablation of most materials requires very high energy densities, typically nanosecond, and sometimes femtosecond, lasers are used for pulsed laser deposition.

\begin{center}
\textbf{Figure 3.1} A schematic diagram of the pulsed laser deposition chamber.
\end{center}
Excimer lasers are most commonly used for pulsed laser deposition due to the fact that these lasers can deliver high energy densities with high energy photons. The emission wavelength of excimer lasers depends on the composition of the gas that is used in the laser cavity. ArF (193 nm) and KrF (248 nm) excimer lasers are most commonly used for pulsed laser deposition.

The laser-solid interaction in pulsed laser deposition, which leads to ablation of target materials and formation of a highly energetic plume, can be divided into two parts: (i) interaction of the laser beam with the bulk target and (ii) interaction of the laser beam with the ablated material in the plume. The intense heating of the target surface by high powered nano-second lasers leads to instantaneous melting/evaporation of the surface layers. Coupling of the laser with the target material plays an important role in ablation efficiency. Laser ablation of materials exhibits threshold behavior and ablation takes place only when laser fluence (energy per unit area) exceeds a minimum value. This threshold is a function of laser properties (e.g., emission wavelength and pulse width) as well as material properties. The threshold for laser ablation depends strongly on the optical properties (e.g., the absorption coefficient, $\alpha$) and the thermal properties (e.g., the thermal diffusivity, $\kappa$) of the target material. The material ablated from the target further interacts with the laser beam and gets heated by the laser beam. It has been estimated that plasma temperatures in PLD may reach $10^4$ K. A schematic of laser-material interaction in PLD is shown in Figure 3.2. The stoichiometric transfer of material from target to the film is one of the biggest advantages of PLD. This makes PLD suitable for deposition of multi-elemental complex materials such as...
YBCO. In comparison to thermal evaporation processes, where kinetic energy of the species is \( \sim 100 \) meV, the kinetic energy of the pulse laser ablated species is very high and is in the range 10-100 eV. This promotes high surface mobility in the growing film and hence film growth can be achieved at lower temperatures compared to thermal evaporation methods.

\[ \text{Figure 3.2 Schematic diagram showing the different phases present during laser irradiation of a target: (A) unaffected target, (B) evaporated target material, (C) dense plasma absorbing laser radiation, (D) expanding plasma outer edge transparent to the laser beam.}^{10} \]

Each ablation pulse in PLD provides material sufficient for growth of a sub monolayer only. Hence film thickness can be controlled very effectively. One of the main problems in the pulse laser deposited films is the non-uniformity of the thickness which results because of the \( \cos^n \theta \) profile of the plume.\(^2\) This limits the application of PLD for large area thin film depositions. Another important issue is the generation and deposition of particulates during laser ablation. Laser wavelength, pulse duration, energy fluence, laser spot size, pulse frequency, target-substrate distance, substrate temperature and background gas and pressure
are important parameters in the pulsed laser deposition. In the present study a Lambda LPX 100 KrF excimer laser with a wavelength of 248 nm and a pulse width of 25 ns was used. A laser spot size of ~ 4 mm x 2 mm was used to achieve a forward directed plume. The pulse frequency used was in the range 5-10 Hz and energy density was in the range 3-5 J/cm². The target-substrate distance was maintained at 4.5 cm for all the depositions. Most of the depositions were carried out with substrate temperatures in the range of 500-850 °C. The PLD chamber was evacuated to ~5x 10⁻⁷ Torr before heating the substrate for thin film deposition. In many cases, oxygen was introduced into the PLD chamber during film deposition.

### 3.3 X-Ray Diffraction

X-ray diffraction is a very convenient, nondestructive tool for lattice parameter measurement, phase identification and determination of crystallographic orientation and texture. In x-ray diffraction a material is probed with x-rays having wavelength close to the lattice spacing. The conditions for diffraction are given by Bragg’s law:

\[ \lambda = 2d \sin \theta \]  

In the present work θ–2θ scans were performed using Rigaku D-MAX/A diffractometer with Cu Kα radiation. This instrument is a two-circle diffractometer in which the sample can be rotated along one of the axis (θ-axis) and also the detector can be rotated independently (2θ-axis). A schematic diagram for this diffractometer is shown in Figure 3.3. This diffractometer is based on Bragg-Brentano parafocusing diffraction geometry. In this geometry, the detector
is at 2θ and the sample surface is at θ angle to the incident beam. The incident beam, normal to sample surface and detector are in the same plane. Since the diffracted beam always lies in the plane containing the incident beam and plane normal, and due to the restricted rotation of the sample only along θ-axis, this diffractometer can be used to access diffraction information only from the planes which are parallel to surface of the sample.

\[ \text{Figure 3.3 A schematic diagram of Rigaku D-MAX/A diffractometer used for } \theta-2\theta \text{ scans.} \]

\textit{DS: Divergence slit, ASS: Anti scatter slit, RS: Receiving slit, MRS: Monochromator receiving slit}

Though two-circle diffractometer gives information about the growth orientation, it does not give any information on in-plane orientation of thin film. Knowing in-plane orientation is important to establish epitaxy. The in-plane orientation of thin films can be accessed by four-circle diffractometer. In addition to rotation along θ-axis and 2θ-axis, in four-circle diffractometer the sample can be tilted with respect to the incident beam (ψ-axis) and also
rotated 360 degrees around the surface normal (φ-axis). A schematic diagram of four-circle diffractometer is shown in Figure 3.4.

*Figure 3.4* A schematic diagram of the Philips X’Pert diffractometer used for φ-scans.
IBO: Incident beam optics, DBO: Diffracted beam optics

The in-plane epitaxial details can be established by φ-scans. To perform a φ-scan an appropriate crystallographic plane (hkl), which is inclined to the growth plane (sample surface) is identified. The θ and 2θ angles are set to corresponding to Bragg angle for the identified plane. The sample tilt, ψ is set equal to the crystallographic angle between the growth plane (sample surface) and the (hkl) plane identified for the φ-scan. The diffraction intensity is then recorded as a function of sample rotation along φ-axis. If the film is epitaxial, the φ-scan exhibits sharp peaks at certain φ-angles. On the other hand if the in-plane orientation of the film is random, there is no appreciable variation in the diffraction intensity in the φ-scan. Another way to assess and represent texture in materials is through pole figures. Pole figures are constructed by combining the data of φ-scans recorded at
different sample tilts (in the range $\psi = 0$ to $\psi = 90$ degrees). In the present study the Philips expert system was used to perform $\phi$-scans and pole figure measurements. Stereographic projections are very useful in analyzing $\phi$-scan data. Stereographic projections can be used to calculate the $\psi$ and $\phi$ angles, and also to know the relative position and number of peaks expected in the $\phi$-scan for single crystalline materials.

3.4 Transmission Electron Microscopy

Transmission electron microscope (TEM) utilizes electrons to image materials. Owing to very small de Broglie wavelength of electrons (e.g., $\lambda = 0.0251$ Å for electrons accelerated through 200 keV), resolutions of the order of 1 Å can be achieved, which makes possible imaging with atomic resolution. Transmission electron microscopes can be operated in two basic modes: imaging and diffraction. In the present study TEM characterization was done to get atomic scale details of interfaces, misfit dislocations, crystalline defects, grain boundaries and other microstructural features in the deposited films. Selected area electron diffraction (SAED) patterns were also acquired to establish the epitaxial details. Unlike $\theta-2\theta$ x-ray diffraction scans, SAED patterns can give information about in-plane crystallographic orientation of textured thin films. In-plane orientation of the deposited thin films was established by indexing SAED patterns.

In TEM images the contrast arises because of the scattering of the incident electron beam as it passes through the sample. The electron wave can change both its amplitude and its phase
as it traverses the specimen and both types of change can give rise to image contrast. Thus a fundamental distinction we make in the TEM is between amplitude contrast and phase contrast. In many situations both types of contrast may contribute to the image. However, often TEM operating conditions are selected in a way that one type of contrast dominates. Two types of amplitude contrast are possible: mass-thickness contrast and diffraction contrast. Mass-thickness contrast occurs due to the incoherent elastic scattering of electrons. This type of contrast is important when imaging non-crystalline samples. Diffraction contrast occurs due to the coherent elastic scattering at Bragg angles. The later is the basis of forming bright field (BF) and dark field (DF) images. The BF images are formed by selecting the direct beam while DF images are formed by selecting only one of the diffracted beams.

High resolution TEM (HRTEM) imaging is based on phase contrast and relies on the difference in phase among the electron waves scattered through a thin sample. In contrast to BF or DF imaging, in which a single electron beam is used to form the image, phase-contrast image requires the selection of more than one beam. In HRTEM the objective astigmatism has to be minimized to achieve atomic resolution. Other main requirement for a HRTEM is highly coherent and monochromatic electron beam. The interpretation of contrast in HRTEM images is not easy as it is sensitive to many factors: the appearance of the image varies with small changes in the thickness, orientation, or scattering factor of the specimen, and variations in the focus or astigmatism of the objective lens.
In the present study, a JEOL 2000 FX TEM was used for bright/dark field imaging and electron diffraction. This microscope is equipped with a LaB₆ filament and was operated at 200 kV. The high resolution TEM characterization was done using a JEOL 2010 F microscope operated at 200 kV. This microscope is equipped with a field emission gun which provides highly coherent electron beam. This microscope can also be operated in STEM, STEM-Z contrast and EELS spectroscopy modes. Most of the TEM samples were cross section samples. A few plan view samples were also investigated. The electron transparent TEM samples were prepared by mechanical grinding, dimpling and ion milling.

3.5 Hall Effect Measurement

Hall measurement is a very simple and quick method to determine the carrier density, the carrier type and mobility. This measurement is based on the Lorentz force acting on the moving electrons in the presence of a magnetic field. Lorentz force results in Hall voltage in a direction perpendicular to both the applied electric and the magnetic fields. In order to determine both the mobility ($\mu$) and the sheet density ($n_S$), a combination of a resistivity measurement and a Hall measurement is done. We have used van der Pauw technique to do these measurements. The thin film samples were cut in the shape of a ~1 cm x 1cm squares. Electrical contacts were made on the four corners using indium pads and gold wires. First the resistances $R_A$ and $R_B$ were measured as shown schematically in Figures 3.5 (a) and (b). Subsequently a magnetic field was applied perpendicular to the substrate surface and Hall voltage $V_H$ was measured (Figure 3.5c).
Figure 3.5 A schematic diagram showing Hall measurements in van der Pauw configuration.

From these measurements sheet resistance ($R_S$), carrier density ($n_S$) and mobility ($\mu$) were calculated using the following set of equations:

\[
\exp\left(-\frac{\pi R_A}{R_S}\right) + \exp\left(-\frac{\pi R_B}{R_S}\right) = 1 \tag{3.2}
\]

\[
n_S = \frac{iB}{q|V_H|} \tag{3.3}
\]

\[
\mu = \frac{|V_H|}{R_S iB} = \frac{1}{q n_S R_S} \tag{3.4}
\]

While carrying out Hall measurements, it should be ensured that contacts to the sample are ohmic and small in size. The lateral dimensions of the sample should be large compared to film thickness and contact size. The sample should be uniform and the thickness should be known accurately to estimate the carrier concentration. Also, the sample should be enclosed in dark space to minimize photoconductive and photovoltaic effects.
3.6 Four-Point Resistivity Measurement

The resistivity measurements in this study were done using a four-point probe method. A schematic of this method is shown in Figure 3.6. In this setup four collinear probes are used. Current flows through two outer electrodes. The voltage difference is measured between inner electrodes through which no current flows. In the four-point probe configuration, contact resistance and resistance of leads are eliminated.

Once the V/I ratio has been measured by four-point probe method, the sheet resistivity for thin films (ρ) can be calculated by using the equation \( \rho = \frac{\pi V}{\ln(2) I} \):

\[\rho = \frac{\pi V}{\ln(2) I}\]  

3.5

![Figure 3.6 Schematic showing four point resistivity measurement setup.](image)

In the present study the contacts to the film were made through gold wires attached to the film by indium pads. The electrical measurements were performed using an Agilent HP8545 semiconductor parameter analyzer. The measurements were done in the temperature range of 15-380 K. The sample was cooled using a closed cycle helium cryostat.
3.7 Photoluminescence Spectroscopy

Photoluminescence refers to light emission when a sample is excited with an external source of light. When irradiated with light of suitable wavelength, electrons in the sample are excited to higher energy levels. The radiative transition of the excited electron from the higher energy levels to lower energy levels gives rise to luminescence. Two types of spectra are usually recorded in photoluminescence measurements—photoluminescence spectrum (PL) and photoluminescence excitation (PLE) spectrum. To record the PL spectrum, the sample is illuminated with a specific wavelength of light and the variation of luminescence intensity is measured as function of luminescence wavelength. In PLE spectrum, the intensity of specific luminescence wavelength is recorded as a function of wavelength of the illuminating light. The PL spectrum contains information about radiative energy levels in the sample. The PLE spectrum gives the information about the energy transformation among the energy levels in the sample.9,10

![Figure 3.7 A Schematic of the optical arrangement of Hitachi F2500 fluorescence spectrophotometer.](image)
The PL measurements in the present study were carried out at room temperature using a Hitachi F2500 fluorescence spectrophotometer. A schematic diagram of this spectrophotometer is shown in Figure 3.7. A Xe lamp is used as the excitation source in this spectrometer. A diffraction grating on the incident beam side is used to select the desired wavelength for the excitation beam. The excitation wavelength can be varied from 220 nm to 800 nm. The light emitted by the sample goes to a photomultiplier through another diffraction grating where it is recorded by a computer.
References


5 XRD user manual, Department of Materials Science and Engineering, North Carolina State University.


8 NIST Electronics and Electrical Engineering Laboratory wbsite


4. Growth and Structural Characterization of Epitaxial Yttria Stabilized Zirconia Films on Si (100) Substrates

In this chapter, results on growth of yttria stabilized zirconia (YSZ) thin films on silicon substrates are presented. YSZ films were grown on Si (100) substrates by pulsed laser deposition. The deposited films were characterized by x-ray diffraction and transmission electron microscopy. The experimental results show that by controlling processing conditions, epitaxial tetragonal YSZ thin films can be grown on Si (100) substrates.

4.1 Introduction

Yttria stabilized zirconia has been widely investigated for applications in solid oxide fuel cells, gas sensors, ionic membranes, and gate dielectrics.\textsuperscript{1,2,3,4} Ionic conductivity in stabilized Zirconia arises from mobile oxygen vacancies that are created by acceptor type of doping.\textsuperscript{5} YSZ has excellent stability in both oxidizing and reducing atmospheres, making it useful for various processes and applications.\textsuperscript{6,7} YSZ thin films have attracted a lot of attention for their use as buffer layers in the growth of oxides.\textsuperscript{8,9} YSZ, when used as a gate electric, can reduce the leakage currents by about five orders of magnitude than that in the case of SiO\textsubscript{2} for equivalent oxide thickness.\textsuperscript{10} Cubic YSZ buffer layers have been used for the growth of high quality superconducting YBaCuO films on silicon and sapphire substrates.\textsuperscript{11,12} Although, there are many reports in the literature which discuss the growth of cubic YSZ thin films, not much work has been done on the growth of tetragonal YSZ buffer layers. In the present work, we demonstrate that under appropriate deposition conditions, tetragonal YSZ can be grown epitaxially on silicon substrates even in the presence of thin
native oxide. It is believed to occur by reaction between zirconium rich plume and silicon dioxide.\textsuperscript{13} We have established optimum conditions for the growth of epitaxial tetragonal YSZ on Si (100) substrates. The results on structural characterization of YSZ films are also presented. Si (100) substrates with YSZ template layer can be used to grow functional oxide thin films. As discussed in subsequent chapters, we have used the tetragonal YSZ buffer layers to integrate two different functional oxides, ZnO and La\textsubscript{0.33}S\textsubscript{0.67}MnO\textsubscript{3}, with Si (100) substrates.

### 4.2 Experimental Details

Excimer pulsed laser deposition was used to grow tetragonal YSZ films on Si (100) substrates. Prior to deposition, Si (100) substrates were ultrasonically cleaned in acetone and methanol. In this study, a KrF laser with a wavelength of 248 nm and a pulse width of 25 ns was used. Pulse rate of 5 Hz and an energy density of \( \sim 3 \text{ J/cm}^2 \) were used for all the depositions. The target-substrate distance was maintained \( \sim 4.5 \text{ cm} \) during the depositions. A high-purity 5 mol % \( \text{Y}_2\text{O}_3 \)-doped\textsuperscript{–}\( \text{ZrO}_2 \) target was used. The chamber was evacuated to \( \sim 5 \times 10^{-7} \text{ Torr} \) before the substrate was heated for deposition. The deposition was done at two different substrate temperatures, 750 °C and 800 °C. To remove thin native oxide on the silicon substrate, YSZ was initially (100, 200, 300 or 1000 pulses) deposited in vacuum. Oxygen was subsequently introduced into the chamber (\( P_{\text{O}_2} = 5 \times 10^{-4} \text{ Torr} \)). The total number of YSZ pulses was 3000. X-ray diffraction characterization was done using Rigaku x-ray with Cu K\( \alpha \) radiation. Cross-sectional samples of these films were characterized by a JEOL 2010F high resolution transmission electron microscope.
4.3 Results and Discussion

The X-ray diffraction (XRD) pattern of the YSZ/Si(100) heterostructures prepared at two different temperatures (750 °C and 800 °C) is shown in Figure 4.1. It can be seen that at the lower growth temperature of 750 °C, only a very small hump is observed in XRD pattern around 34.6 degrees. This indicated poor crystallinity of YSZ films deposited at 750 °C. On the other hand, a sharp peak corresponding to (002) orientation of YSZ (34.65 degrees) is observed for the YSZ film grown at 800 °C. The XRD pattern also shows that yttria-stabilized zirconia grows only in the (002) orientation.

Figure 4.1 XRD patterns of YSZ/Si (100) heterostructures for two different deposition temperatures of YSZ.
To remove the native oxide layer on silicon, YSZ should be initially deposited in a highly oxygen-deficient environment (low background pressure conditions). Once YSZ is nucleated epitaxially on silicon, oxygen rich conditions are required to achieve good crystalline quality of YSZ. Hence, the number of pulses deposited in low background pressure (before oxygen is introduced in the chamber) should be optimized to obtain high quality YSZ films. Hence in the present study, we studied the effect of number of YSZ pulses deposited in vacuum on the crystalline quality of YSZ on Si (100) substrates. The XRD results for these samples are shown in Figure 4.2.

**Figure 4.2** XRD patterns for sample with varying number of pulses of YSZ deposited in vacuum. After deposition of indicated number of pulses in vacuum, rest of YSZ deposition (total 3000 pulses) was done in an oxygen atmosphere ($P_{O_2} = 5 \times 10^{-4}$ Torr).
This XRD data shows that for the YSZ films in which only 100 or 200 pulses were deposited in vacuum, YSZ peaks are very weak, indicating poor crystallinity of these films. Strong YSZ (002) peaks for samples in which 300 or 1000 pulses of YSZ were deposited in vacuum indicate good crystalline quality of these films. These results can be explained by postulating that at least ~300 pulses are required to remove the native oxide on silicon and to facilitate the nucleation of epitaxial YSZ.

Transmission electron microscopy investigation was performed to establish epitaxial details of the YSZ films. High resolution transmission electron micrographs of the YSZ/Si interface from two different areas are shown in Figure 4.3. In some regions (Figure 4.3a) the YSZ/Si interface is very clean and atomically sharp. However, in some regions (Figure 4.3b) there is a thin (~1 nm) amorphous layer at the interface, where atomic arrangement is disturbed. The selected area electron diffraction pattern from the silicon and YSZ layers is shown in the Figure 4.4. Indexing of this pattern shows that the diffraction spots are from the [110] zone axis of silicon and the [100] zone axis of tetragonal YSZ. Hence, it can be concluded that the yttria-stabilized zirconia layer is single crystalline and grow epitaxially on silicon with the orientation relationship:

\[
\text{YSZ } [110] \parallel \text{Si } [100] \text{ and YSZ } (001) \parallel \text{Si}(001)
\]

The epitaxial nature of YSZ films indicates that the amorphous layer present in some regions at the YSZ/Si interface (Figure 4.3b) forms during later stages of growth (once oxygen is introduced in the chamber for YSZ growth) due to oxygen diffusion after nucleation of epitaxial YSZ.
Figure 4.3 High resolution TEM images from two different region of YSZ/Si interface for the sample in which YSZ growth temperature was 800 °C and initial 1000 pulses were deposited in vacuum.
It is worth mentioning here that YSZ grew epitaxially even though the native oxide on the Si (100) substrate was not removed prior to deposition. This can be explained on the basis of following reaction: $\text{Zr} + 2\text{SiO}_2 \rightarrow \text{ZrO}_2 + 2\text{SiO}$. The SiO that forms is quite volatile and evaporates at the deposition temperature used in the present study (800 °C). During the initial stage of the deposition, oxide present on the silicon substrate is removed by the above reaction, thus facilitating the epitaxial growth of yttria-stabilized zirconia on silicon.

![Figure 4.4](image)

**Figure 4.4** Selected area electron diffraction pattern from a cross-section TEM sample of YSZ/Si (100) heterostructure. For this sample, YSZ growth temperature was 800 °C and initial 1000 pulses were deposited in vacuum.

The arrangement of YSZ on Si (100) according to the orientation relationship established by electron diffraction studies is shown in Figure 4.5. It can be seen from this figure that lattice
misfit between YSZ and silicon is \(~6.2\%\) and the edge of YSZ unit cell is aligned with the diagonal of the Si unit cell.

\[
\begin{align*}
\text{Misfit} &= 6.2\% \\
5.43\text{ Å} & \quad 3.80\text{ Å}
\end{align*}
\]

**Figure 4.5** Schematic showing arrangement of two unit cells of tetragonal YSZ (smaller squares) on one unit cell of silicon (larger square)

### 4.4 Summary

We have shown that tetragonal YSZ films can be epitaxially grown on silicon (100) substrates. It was established that good crystalline quality of YSZ films on Si (100) substrates can be achieved if at least initial 300 pulses of YSZ are deposited in oxygen deficient conditions in the chamber. Also, the deposition temperature must be at least 800 °C to achieve good crystalline quality of YSZ films. The orientation relationship of the epitaxial YSZ films was established to be: YSZ[110] \(\parallel\) Si[100] and YSZ(001) \(\parallel\) Si(001). Transmission electron microscopy showed a thin amorphous layer at some regions on the Si/YSZ interface. This has been attributed to the formation of amorphous SiO\(_2\) during the later stages of growth because of oxygen diffusion to the Si/YSZ interface.
References


5. Growth of Biepitaxial ZnO Thin Films on Si (100) Substrates Using Yttria Stabilized Zirconia Buffer Layer

An approach for integrating epitaxial zinc oxide thin films with Si (100) substrates is presented here. We demonstrate that using an epitaxial yttria-stabilized zirconia buffer, epitaxial ZnO films can be grown on Si (100) substrates. Pulsed laser deposition technique was used to deposit YSZ and ZnO films on Si (100) substrates. Detailed X-ray diffraction characterization, including phi scans, indicated that the ZnO films grew epitaxially with fixed orientation relationship on YSZ buffered Si (100) substrates. Under different growth conditions used in the present study, growth orientation of ZnO was (0002). Phi scans showed that crystallographic orientation of ZnO with respect to YSZ buffer layer was a function of deposition temperature. Integration of epitaxial zinc oxide thin films with Si (100) substrates is an important step towards developing practical applications of zinc oxide in a variety of optoelectronic devices.

5.1 Introduction

The direct and wide band gap (~3.3 eV at 300K) of zinc oxide (ZnO) has motivated significant research efforts due to its potential use in blue and ultraviolet optoelectronic devices. The large exciton binding energy of 60 meV for zinc oxide, compared to 21 meV for gallium nitride, makes it a potential candidate for exciton recombination-based lasing devices, which can operate at room temperature or higher. The high conductivity of doped zinc oxide is being also explored for use in transparent conducting oxide applications. Growth of high quality thin films of zinc oxide on conventional microelectronic substrates is
a critical step towards realizing the aforementioned applications. Sapphire is a widely used substrate to grow epitaxial zinc oxide films; however, for practical applications it is desirable to integrate zinc oxide with existing silicon technology. It is difficult to grow zinc oxide directly on silicon, as it easily forms an amorphous SiO₂ layer, which hampers epitaxial growth of zinc oxide. To overcome this problem, different buffer layers such as titanium nitride⁵, gallium nitride⁶, and yttria-stabilized zirconia (YSZ)⁷ have been used to integrate zinc oxide with silicon (111) substrates. On the other hand, efforts to grow epitaxial ZnO films directly on Si (100) substrates⁸ or using a buffer layer⁹ have been largely unsuccessful and have resulted in multiple orientations. It needs to be emphasized here that Si (100) has four-fold symmetry and there are no planes in zinc oxide with similar symmetry. Consequently, if zinc oxide grows epitaxially on Si (100), it will have at least two different in-plane orientations.

Here, we report that tetragonal YSZ (lattice parameters: a = 3.60 Å, c = 5.18 Å) buffer layer can be used to grow biepitaxial hexagonal zinc oxide (lattice parameters: a = 3.25 Å, c = 5.21 Å) thin films on Si (100) substrates (lattice parameter: a = 5.43 Å). Our results show that zinc oxide grows on YSZ with the c-axis of zinc oxide perpendicular to the plane of the film. In the film plane, orientation of ZnO was found to be dependent on growth temperature.

5.2 Experimental Details

Pulsed laser deposition was used to grow tetragonal YSZ and zinc oxide films on Si (100) substrates in order to prepare ZnO/YSZ/Si (100) heterostructures. One YSZ/Si (100)
heterostructure was prepared for structural characterization. Prior to deposition, the Si (100) substrates were ultrasonically cleaned in acetone and methanol. In this study, a Lambda LPX 100 laser was operated using a wavelength of 248 nm, a pulse width of 25 ns, a pulse rate of 5 Hz, and an energy density of 3 J/cm². The target-substrate distance was maintained ~4.5 cm during the depositions. High-purity 5 mol % Y₂O₃ doped- ZrO₂ and ZnO targets were ablated using an automated target control system. A base vacuum of ~ 5 x 10⁻⁷ Torr was utilized during these studies. The substrate temperature was maintained at 800 °C for deposition of YSZ layer. ZnO film was deposited at three different temperatures: 600 °C, 700 °C and 800 °C. To remove the oxide on the silicon substrate, YSZ was deposited initially (1000 pulses) in vacuum. Oxygen was subsequently introduced into the chamber (P₀₂ = 5 x 10⁻⁴ Torr) and 3000 pulses of YSZ were deposited. Substrate temperature was subsequently adjusted to ZnO deposition temperature and 4500 pulses of ZnO were then deposited. X-ray diffraction studies were done using Philips X’Pert PRO x-ray diffractometer with Cu Kα radiation.

5.3 Results and Discussion

The X-ray diffraction (XRD) pattern of the YSZ/Si (100) film (Figure 5.1a) shows that yttria-stabilized zirconia grows only in the (002) orientation. The x-ray diffraction patterns for ZnO/YSZ/ Si (100) heterostructures grown at different temperatures are shown in Figures 5.1b, 5.1c and 5.1d. These patterns show that zinc oxide grows only in (0002) orientation on YSZ buffer layer at all the deposition temperatures used in the present study. In these XRD patterns, YSZ peaks cannot be distinguished as they overlap with ZnO (0002) peaks. A narrow and strong ZnO (0002) peak indicates good crystalline quality of zinc oxide thin
films. The full width at half maximum of the ZnO (0002) peak estimated from this plot is 0.16 degrees, which indicates minimal misalignment of zinc oxide along the c-axis as well as good crystallinity.

**Figure 5.1** X-ray diffraction data ($\theta$-2$\theta$ scan) for (a) YSZ/Si (100) and ZnO/YSZ/Si (100) heterostructures in which ZnO was deposited at (b) 600 °C (c) 700 °C and (d) 800 °C.

The $\theta$-2$\theta$ scan x-ray diffraction data does not provide any information on in-plane crystallographic orientation of textured thin films. The in-plane orientation of YSZ and ZnO layers in ZnO/YSZ/Si (100) heterostructures was established by x-ray diffraction $\phi$ -scans. The $\phi$ -scan data for c-plane ZnO/YSZ/Si (100) heterostructures, in which ZnO layer was grown at 800 °C, is shown in Figure 5.2. For silicon substrate, $\phi$ -scan was done for (202)
planes ($2\theta = 47.34^\circ$ and $\psi = 45^\circ$). The $\phi$-scan for YSZ layer was done at $2\theta = 30.25^\circ$ and $\psi = 54.2^\circ$, which corresponds to (101) peak of tetragonal YSZ. The 4-fold symmetry seen in the $\phi$-scan of YSZ confirms that it is epitaxial and tetragonal. Also, it can be seen that YSZ (101) peaks are at 45 degrees from Si (202) peaks. Hence, the epitaxial relationship of YSZ with silicon substrates can be written as: $[110]_{YSZ} \parallel [100]_{Si}$ and $(001)_{YSZ} \parallel (001)_{Si}$. This observation is consistent with the results presented in the previous chapter.

![Figure 5.2](image)

**Figure 5.2** $\phi$-scan data for ZnO/YSZ/ Si (100) heterostructures for the sample in which ZnO layer was grown at 800 °C.

The $\phi$-scan for ZnO layers was done at $2\theta = 36.3^\circ$ and $\psi = 18.15^\circ$, which correspond to the (10 11) peak of zinc oxide. The $\phi$-scan of ZnO film deposited at 800 °C shows twelve peaks.
which are 30 degrees apart (Figure 5.2). Well defined peaks in $\phi$-scan indicate that the ZnO grows epitaxially on YSZ. The ZnO growth direction, and hence the rotation axis in $\phi$-scan, was [0001] for all the ZnO films deposited in the present study. ZnO exhibits 6-fold symmetry around [0001] axis, and consequently assuming only one in-plane orientation, six peaks are expected in the $\phi$-scans for ZnO film. Twelve peaks in the $\phi$-scans for ZnO films indicate existence of two in-plane orientations in these films. In this $\phi$-scan YSZ (101) and ZnO (10$\bar{1}$1) peaks are at same $\phi$-angle. This indicates that in these films, in the growth plane, [11$\bar{2}$0] direction of ZnO is parallel to [100] or [010] directions of YSZ. Hence the complete epitaxial relationship for ZnO films grown at 800 °C can be written as:

$$[10\bar{1}0]_{\text{ZnO}} \parallel [100]_{\text{YSZ}} \text{ or } [2\bar{1}0]_{\text{ZnO}} \parallel [100]_{\text{YSZ}}$$

$$\text{and } (0002)_{\text{ZnO}} \parallel (001)_{\text{YSZ}}$$

**Figure 5.3** Schematic showing two possible orientations of hexagonal zinc oxide unit cell on tetragonal YSZ unit cell for films ZnO grown at 800 °C. Misfit values were calculated by considering the closest matching planes.
According to above epitaxial relationship, there are two in-plane orientations of ZnO films. This ‘biepitaxial’ relationship is expected because YSZ (001) has four-fold symmetry while ZnO (0002) has six-fold symmetry. These two orientations are schematically shown in the Figure 5.3. It should also be noted that these two orientations are equally likely.

Epitaxial growth of ZnO (0002) on YSZ (001) cannot be explained using the conventional lattice matching epitaxy model because of the different lattice symmetries and large misfit involved. It can be seen from Figure 5.3 that misfit between zinc oxide and YSZ is 9.7% in one direction and 21.8% in another direction. On the other hand, epitaxy with such large misfits can be explained in the framework of domain matching epitaxy (DME), in which matching of planes instead of matching of lattices is considered.\(^{11}\) Along the \([2\overline{1}0]\) direction of zinc oxide, 9.7% misfit can be completely accommodated by two types of domains. In one domain, ten ZnO (\(\overline{2}110\)) planes match nine YSZ (100) planes. In the other domain, eleven ZnO (\(\overline{2}110\)) planes match ten YSZ (100) planes. The misfit will be completely relaxed if these domains alternate with a relative frequency of 5:2. Similarly, along the \([10\overline{1}0]\) direction of zinc oxide, the 21.8% misfit can be completely accommodated by two alternating domains, in one of which four ZnO (01 \(\overline{1}0\)) planes match three YSZ (010) planes. In the other domain, five ZnO (01 \(\overline{1}0\)) planes match four YSZ (010) planes. The misfit will be completely relaxed if these domains alternate with a relative frequency of 5:7.
To investigate the effect of ZnO growth temperature on in-plane orientation of ZnO, we performed $\phi$-scans on the other two samples in which ZnO films were grown at 600 °C and 700 °C. The $\phi$-scans for all three different ZnO growth temperatures are compared in Figure 5.4. From this figure it can be seen that for ZnO films grown at 600 °C, there are twelve peaks, as observed for ZnO films grown at 800 °C.

![Figure 5.4 Comparison of $\phi$-scan data for ZnO/YSZ/ Si (100) heterostructures for different ZnO growth temperatures.](image)

For ZnO films grown at 800 °C, YSZ (101) and ZnO (1011) peaks are at the same $\phi$-angle. However, for the ZnO films grown at 600 °C, ZnO (1011) peaks are rotated 15 degrees from the YSZ (101) peak. This indicates that in these films the [10$ar{1}$0] direction of ZnO is parallel
to [110] or [1\{10\}] directions of YSZ. These two orientations are schematically shown in the Figure 5.5. These observations indicate that different in-plane crystallographic orientations of ZnO are stable at 600 °C and 800 °C. The in-plane orientation of ZnO films grown at 600 °C is rotated by 15 degrees from that of ZnO films grown at 800 °C. In-plane rotation of orientation of ZnO with respect to underlying substrate, with changing temperature, has been also reported for ZnO films deposited on c-sapphire substrates.\textsuperscript{14-16} This has been attributed to existence of more than one local minima in the film-substrate interface energy.\textsuperscript{16} For ZnO films deposited at 700 °C, in addition to twelve strong peaks, twelve weak peaks can be seen. These weak peaks are 15 degrees apart in $\phi$ angle from the strong peaks. This observation can be explained by postulating that 700 °C lies in the transition temperature range in which ZnO rotates from one orientation (Figure 5.3) to another (Figure 5.5).

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{alignment.pdf}
\caption{Schematic showing two possible orientations of hexagonal zinc oxide unit cell on tetragonal YSZ unit cell for films ZnO grown at 600 °C. Misfit values were calculated by considering the closest matching planes.}
\end{figure}
5.4 Summary

It has been shown that zinc oxide thin films can be epitaxially integrated with Si (100) substrates using a tetragonal yttria-stabilized zirconia buffer layer. Growth of the zinc oxide thin film on the YSZ buffer layer was found to be biepitaxial with minimal misalignment along the c-axis of zinc oxide; the full width at half maximum of the (0002) \( \text{ZnO} \) peak was \( \sim 0.16 \) degrees. X-ray diffraction \( \phi \)-scans showed that for the growth temperature of 800 °C, zinc oxide grows epitaxially on YSZ in two different orientations: [10\( \overline{1} \)0]\( \text{ZnO} \) || [100]\( \text{YSZ} \) or [2\( \overline{1} \)\( \overline{1} \)0]\( \text{ZnO} \) || [100]\( \text{YSZ} \) and (0002)\( \text{ZnO} \) || (001)\( \text{YSZ} \), in which one orientation rotated by thirty degrees from the other. Two in-plane orientations of ZnO have been explained on the basis of four-fold symmetry of the (001) planes of YSZ and six-fold symmetry of the (0002) planes of zinc oxide. It was also observed that different in-plane crystallographic orientations of ZnO are stable at 600 °C and 800 °C. The epitaxial growth of zinc oxide has been explained on the basis of domain matching epitaxy.
References


6. Structural, Electrical and Optical Characterization of Biepitaxial Zinc Oxide Films Grown on Si (100) Substrates

In this chapter, results on structural, optical, and electrical characterization of the ZnO films deposited on YSZ buffered Si (100) substrates are presented. Transmission electron microscopy investigations confirmed that the ZnO films deposited on YSZ buffered Si (100) were biepitaxial; two different in-plane orientations of ZnO were observed. These in-plane orientations were rotated thirty degrees with respect to each other. Electrical properties of ZnO films were characterized by Hall measurement and temperature dependent resistivity measurements. Photoluminescence spectra of the biepitaxial ZnO film showed strong excitonic emission and very weak defect-related green band emission.

6.1 Introduction

In the previous chapter, growth of epitaxial ZnO films on yttria-stabilized zirconia (YSZ) buffered Si (100) substrates was reported. It was established that ZnO grows with a fixed orientation relationship on YSZ buffered Si (100), with [0001]_{ZnO} \parallel [0001]_{YSZ} along the growth direction and two different orientations in the film plane.¹ As the two in-plane orientations of ZnO are rotated by 30 degrees, the grain boundaries in these films can be either low-angle boundaries or 30 degree boundaries. In order to distinguish them from the single crystalline epitaxial films, we have referred the ZnO films with two in-plane orientations as biepitaxial. In the present study, detailed structural, electrical and optical characterization was performed on biepitaxial ZnO films grown on YSZ buffered Si (100) substrates. This study is an important step towards integration of high quality ZnO films with
Si (100) substrates. This work also provides an improved understanding of thin film growth in systems with large lattice mismatch and different in-plane symmetries.

6.2 Experimental Details

The ZnO/YSZ/Si (100) heterostructure was grown in a high vacuum chamber using pulsed laser deposition. A KrF excimer laser with 248 nm wavelength and 25 ns pulse duration was used to ablate the target materials. A pulse repetition rate of 5 Hz was used in this study. A high-purity commercial 5 mol % Y₂O₃ - ZrO₂ target was used to grow the YSZ buffer layer. The target used for growth of the ZnO film was prepared in-house using a standard solid-state sintering process. Silicon (100) wafers were cleaned with acetone and methanol in ultrasonic bath. The native oxide layer was not etched prior to deposition. The YSZ and ZnO films were grown using a laser fluence of ~ 3 J/cm² and a substrate temperature of 800 °C. The chamber was pumped to a vacuum of ~ 5 x 10⁻⁷ Torr before substrate was heated for film deposition. The YSZ buffer layer was initially (1000 laser pulses) deposited at background pressure (oxygen deficient condition) in order to remove the thin native oxide layer on the silicon substrate. The YSZ buffer layer was subsequently grown in an oxygen environment with oxygen partial pressure of 5 x 10⁻⁴ Torr. The total number of laser pulses used for the growth of YSZ buffer layers was 4000. This was followed by deposition of 4500 pulses of ZnO at an oxygen partial pressure of 5 x 10⁻⁴ Torr.

Structural characterization of the ZnO/YSZ/Si (100) heterostructure was carried out using x-ray diffraction (XRD) and transmission electron microscopy (TEM). θ-2θ scans were
performed using a Rigaku x-ray diffractometer with copper Kα radiation. A JEOL 2000FX transmission electron microscope and a JEOL 2010F high resolution transmission electron microscope were used for TEM characterization. Electrical characterization was performed using an HP8545 semiconductor parameter analyzer. Resistivity was measured as a function of temperature by four-probe method. Room temperature mobility was measured using the Hall effect measurement. Photoluminescence (PL) spectroscopy was performed at room temperature using a Hitachi F-2500 fluorescence spectrophotometer.

6.3 Results and Discussion

6.3.1 Structural Characterization

Figure 6.1 shows the θ-2θ XRD pattern of the ZnO/YSZ/Si (100) heterostructure. As discussed in the previous chapter (Section 5.3), reflections from the zinc oxide (0002) planes and the YSZ (002) planes overlap and cannot be distinguished. Hence, this diffraction pattern indicates that YSZ and ZnO grow in (002) and (0002) orientations, respectively. The narrow (0002) diffraction peak indicates good crystalline quality of the ZnO film.

A transmission electron micrograph of the ZnO/YSZ/Si (100) heterostructure is shown in Figure 6.2a. From this figure, it can be seen that yttria-stabilized zirconia buffer layer and zinc oxide thin film are ~300 nm and ~200 nm thick, respectively. The STEM Z-contrast image (Figure 6.2b) shows that interfaces in the prepared heterostructure are sharp. Figure 6.2 (c) shows the selected area diffraction pattern obtained from a cross-sectional sample of
Figure 6.1 θ-2θ x-ray diffraction data for ZnO film grown on YSZ buffered Si(100) substrate.

the ZnO/YSZ/Si (100) heterostructure. The selected area diffraction pattern was obtained from all of three layers in the ZnO/YSZ/Si (100) heterostructure. As indexed in the Figure 6.2c, the diffraction spots of the silicon (100) substrate and the YSZ buffer layer correspond to [011] and [100] zones, respectively. This indicates that the in-plane epitaxial relationship of YSZ and silicon is [110]_{YSZ} || [100]_{Si}. Hence, the complete epitaxial relationship between the silicon (100) substrate and the YSZ buffer layer can be written as: [110]_{YSZ} || [100]_{Si} and [001]_{YSZ} || [001]_{Si}. This epitaxial relationship is schematically illustrated in Figure 6.3 (a). Silicon has a diamond cubic structure with a lattice parameter of 5.43 Å. Yttria-stabilized zirconia, with 5 mol % yttria content, has a tetragonal structure with lattice parameters of a = b = 3.60 Å and c= 5.18 Å. The lattice misfit for cube-on-cube growth of (100) planes of
Figure 6.2 A transmission electron microscopy results of ZnO/YSZ/ Si (100) heterostructure (a) Bright field TEM image (b) STEM –Z contrast image (c) Selected area diffraction pattern obtained from all three layers of a cross-section sample (d) Selected area diffraction pattern of the ZnO layer, obtained from a plan-view sample.
yttria-stabilized zirconia on a silicon (100) substrate is ~ 33.7 %. The large misfit value implies that cube-on-cube growth is not energetically favorable for YSZ. Figure 6.3 (a) shows that the YSZ buffer layer grows on the silicon (100) surface in an edge-on-diagonal relationship. This 45° in-plane rotation of YSZ with respect to silicon, in which [110]_{YSZ} is aligned with [100]_{Si}, leads to a misfit of 6.25%.

The diffraction spots attributed to the ZnO film (Figure 6.2c) correspond to two different zones: [10\overline{1}0] and [2\overline{1}0]. This indicates that the ZnO film grew epitaxially with two different in-plane orientations, which are rotated by 30° with respect to each other. This result was confirmed by a selected area electron diffraction pattern from a plan view sample. The diffraction pattern shown in Figure 6.2d contains two sets of diffraction spots from the [0001] zone. The two sets of diffraction spots are rotated by 30° with respect to each other; this result confirms two in-plane orientations of ZnO. The epitaxial relationship of the ZnO film on the YSZ buffer layer is schematically shown in Figure 6.3b. This figure demonstrates that ZnO can grow in two different orientations that are rotated by 90° because YSZ exhibits four-fold symmetry. Since ZnO exhibits six-fold symmetry, the angle between these two orientations of ZnO is 30°. These two orientations of ZnO on YSZ are crystallographically and energetically equivalent. Hence, the nucleation of any of these orientations is equally likely during growth of the ZnO film. Consequently, the ZnO film consists of two types of grains, which are crystallographically rotated by an angle of 30°. The in-plane epitaxial
The relationship between ZnO and YSZ can be written as $[10\overline{1}0]_{ZnO} \parallel [100]_{YSZ}$ for one type of ZnO grains and $[2\overline{1}0]_{ZnO} \parallel [100]_{YSZ}$ for another type of ZnO grains.

The ZnO film is biepitaxial since it exhibits two different in-plane orientations. These biepitaxial films contain $30^\circ$ boundaries that differ from single-crystalline epitaxial films, which contain only low angle grain boundaries. Biepitaxial growth is the result of different symmetries of the ZnO film and the YSZ buffer layer along the growth direction. The $(0001)$ plane of zinc oxide exhibits six-fold symmetry, while the $(001)$ plane of tetragonal YSZ exhibits four-fold symmetry. The ZnO film grows on $(001)$ surface of YSZ with preferred in-plane orientation, in which one of the six edges of the hexagonal unit cell of ZnO is parallel to one of the four edges of the square unit cell of YSZ.

The lattice parameters of hexagonal zinc oxide are $a = 3.25\, \text{Å}$ and $c = 5.21\, \text{Å}$. Since the in-plane symmetries of the ZnO film and the YSZ buffer layer are not similar, poor lattice matching is observed along different in-plane directions. Along the $(001)_{YSZ}$ direction, the $(2\overline{1}0)_{ZnO}$ planes are parallel to the $(100)_{YSZ}$ planes with misfit of $\sim 9.7\%$. In the $(010)_{YSZ}$ direction, the $(01\overline{1}0)_{ZnO}$ planes are parallel to the $(010)_{YSZ}$ planes with misfit of $\sim 21.8\%$. These large misfit values indicate that epitaxial growth of the ZnO film on the YSZ buffer layer falls into the domain matching epitaxy (DME) regime. Misfit of $21.8\%$ along the $(010)_{YSZ}$ direction can be accommodated by two types of domains having a relative frequency of $5/7$. Across the ZnO/YSZ interface, four ZnO $(01\overline{1}0)$ planes match three YSZ
Figure 6.3 Schematic illustrations of epitaxial relationships for (a) YSZ/Si (100) and (b) ZnO/YSZ.
(010) planes in first domain and five ZnO (0110) planes match four YSZ (010) planes in the second domain. Along the [100]$_{YSZ}$ direction, misfit of 9.7% can be accommodated when ten ZnO (1110) planes match nine YSZ (100) planes in one domain and eleven ZnO (1110) planes match ten YSZ (100) planes in another domain. Misfit will be completely relaxed if these domains occur with a relative frequency of 5/2.

A high resolution transmission electron microscopy image of the interface between the YSZ buffer layer and the ZnO film is shown in Figure 6.4a. The inset contains a fast Fourier transform (FFT) pattern of the high resolution transmission electron microscopy image, which results from the [100] zone of the YSZ buffer layer and the [2110] zone of the zinc oxide film. The interface is sharp without any evident reaction between the layers in the ZnO/YSZ/Si (100) heterostructure. To observe matching of planes at the ZnO/YSZ interface, the diffraction spots from the (0110)$_{ZnO}$ planes and (010)$_{YSZ}$ planes were masked in the fast Fourier transform (Figure 6.4a) in order to form an inverse fast Fourier transform (IFFT) image (Figure 6.4b). Four (0110)$_{ZnO}$ planes matching three (010)$_{YSZ}$ planes between (0110)$_{ZnO}$ planes and (010)$_{YSZ}$ planes can be observed in this image. This result confirms domain matching epitaxial growth of the zinc oxide film in the ZnO/YSZ/Si (100) heterostructure.

Figure 6.5 is the dark-field transmission electron microscopy image that was obtained by selecting diffraction spots only from the [2110] zone of the ZnO film. This image shows
Figure 6.4 (a) High resolution transmission electron microscopy image obtained from the YSZ buffer layer and the ZnO film. The corresponding fast Fourier transform pattern is shown in the inset. (b) Inverse fast Fourier transform image obtained by selecting the $(01\overline{1}0)_{ZnO}$ and the $(010)_{YSZ}$ diffraction spots from the fast Fourier transform in part (a), which indicates that three YSZ planes match four ZnO planes across the ZnO/YSZ interface.
Figure 6.5 A dark field transmission electron microscopy image of the ZnO/YSZ/Si(100) heterostructure. Illuminated grains in the ZnO layer are attributed to the \([2 \bar{1} 1 \bar{0}]\) zone and darker grains are attributed to the \([10 \bar{1} 0]\) zone.

The two different orientations of the grains in the ZnO film; the illuminated regions correspond to grains from the \([2 \bar{1} 1 \bar{0}]\) zone, while the darker regions correspond to grains from the \([10 \bar{1} 0]\) zone. This image indicates that the YSZ buffer layer and ZnO film are \(~300\) nm thick and \(~200\) nm thick, respectively. These thickness values correspond to a deposition rate of 0.75 Å/pulse for the YSZ buffer layer and a deposition rate of 0.45 Å/pulse for the ZnO film. The in-plane size of the grains is \(~50\) nm. This image also indicates that growth of ZnO grains is columnar.
Figure 6.6 (a) High resolution transmission electron microscopy image obtained from the boundary region of two differently oriented grains. (b) Fast Fourier transform (FFT) pattern of the high resolution image. (c) Inverse fast Fourier transform of the image, which was formed by selecting the $(01\bar{1}0)$ spots and the $(2\bar{1}\bar{1}0)$ spots in (b).
A high resolution transmission electron micrograph showing the boundary of two differently oriented grains of a ZnO film, which was obtained from a cross-section transmission electron microscopy sample, is shown in Figure 6.6a. The two grains are distinguished by the dissimilar plane spacing. The fast Fourier transform of this image (Figure 6.6b) indicates that the image results from [10\(\overline{1}0\)] and [2\(\overline{2}1\)0] zones of ZnO. Figure 6.6c is the inverse fast Fourier transform image that was formed by selecting only (01\(\overline{1}0\)) and (2\(\overline{2}1\)0) spots in Figure 6.6b. This IFFT image shows that (01\(\overline{1}0\)) and (2\(\overline{2}1\)0) planes are parallel for the two grains with a sharp transition. From both the high resolution transmission electron micrograph and the inverse fast Fourier transform image, it can be seen that the grain boundary is very coherent with minimal disorder.

6.3.2 Electrical Characterization

The room temperature resistivity of the zinc oxide film was measured to be 0.14 \(\Omega\) cm. The mobility and n-type carrier concentration values obtained using the Hall effect method were 46 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and 9.5 \(\times\) 10\(^{17}\) cm\(^{-1}\), respectively. Though mobility values as high as 155 cm\(^2\) V\(^{-1}\) s\(^{-1}\) have previously been obtained for epitaxial ZnO films grown on c-plane sapphire substrates using multi-step deposition processes, mobility values below 100 cm\(^2\) V\(^{-1}\) s\(^{-1}\) are typically observed for epitaxial ZnO films.\(^3\),\(^4\) The grain boundaries in epitaxial ZnO films grown on c-sapphire substrates are low angle boundaries. On the other hand, c-textured ZnO films grown on amorphous fused silica substrates contain a random mixture of low angle grain boundaries and high angle grain boundaries. As previously mentioned, the biepitaxial
ZnO film consists of two types of grains, which are crystallographically rotated by an angle of 30°. Approximately 50% of the grain boundaries in the films are expected to be low angle boundaries and 50% of the grain boundaries in the films are expected to be 30° boundaries. Considering the symmetry of ZnO around the c-axis, the 30° boundary is the largest angle boundary possible for c-axis oriented ZnO films. As a result, biepitaxial ZnO films may be useful for examining the effects of high angle boundaries on electric transport properties. Without any optimization of parameters for deposition or post-deposition annealing, the mobility value for the biepitaxial ZnO film (~ 46 cm² V⁻¹ s⁻¹) is better than that reported for the epitaxial ZnO film processed using a single-step deposition process (30 cm² V⁻¹ s⁻¹). These results indicate that 30° boundaries do not significantly reduce mobility of ZnO films. This effect may be attributed to minimal atomic disorder observed at 30° boundaries.

Figure 6.7 Conductivity as a function of temperature for ZnO film grown on the YSZ buffered Si (100) substrate.
The variation of conductivity with temperature was examined between 13 K and 300 K (Figure 6.7). This figure indicates that the relationship between conductivity and temperature is dissimilar at lower temperatures and at higher temperatures. The relationship between temperature and conductivity can be modeled using the equation:

\[
\sigma = \sigma_0 \cdot T^m \cdot \exp \left( - \frac{Q_a}{kT} \right)
\]

6.1

In this equation, \( \sigma \) is the conductivity, \( \sigma_0 \) is a constant, \( T \) is the temperature, \( m \) is a coefficient that correlates the variation of mobility with temperature, and \( Q_a \) is the activation energy that is related to relevant donor energy levels. According to this equation, if the temperature dependence of mobility is not significant, then an approximate value of activation energy can be calculated from the slope of the \( \ln(\sigma) \) vs \( 1/T \) plot. As shown in Figure 6.7, the activation energy calculated for temperatures above 70 K is \( \sim 12 \) meV. This value is comparable to the reported values for thermal activation of n-type conduction in ZnO.\textsuperscript{5, 6} The low activation energy of \( \sim 0.4\text{eV} \) at temperatures less than 50 K observed in the present study has been reported earlier and is generally attributed to impurity band or defect band effects.\textsuperscript{6, 7}

### 6.3.3 Photoluminescence Studies

Photoluminescence spectra were obtained for the biepitaxial ZnO film at several excitation wavelengths between \( \lambda=220 \text{ nm} \) and \( \lambda=340 \text{ nm} \) (Figure 6.8). The photoluminescence spectra feature a strong ultraviolet emission band centered at \( \lambda=377 \text{ nm} \) (3.29 eV) and a weak emission band centered at \( \lambda=538 \text{ nm} \) (2.30 eV). Near band edge emission (\( \sim \lambda=377 \text{ nm} \)) in the zinc oxide film was attributed to exciton-related emission. The full width at half maximum (FWHM) of the photoluminescence peak is \( \sim 12 \text{ nm} \) (104 meV). ZnO films
typically exhibit green band emission near $\lambda = 540$ nm, which is attributed to point defects in the material. As shown in the Figure 6.8 inset, green band emission in the biepitaxial ZnO film was weak; the full width at half maximum of green band emission was $\sim 100$ nm.

Figure 6.8. Photoluminescence spectra for ZnO film grown on YSZ buffered Si (100) substrate, which were obtained using several excitation wavelengths. The inset shows the green band emission in detail.

As excitation wavelength decreases, the penetration depth of the beam decreases. Hence, shorter excitation wavelength gives the information near surface regions. As seen in Figure 6.8, the shape and width of excitonic emission do not significantly change with excitation wavelength. Excitonic emission is quite prominent even for 220 nm excitation, indicating
fewer surface related defects in the film. It should be noted that the green band emission becomes weaker with decreasing excitation wavelength and is undetectable at the smallest excitation wavelength ($\lambda=220$ nm).

Photoluminescence spectra for two excitation wavelengths ($\lambda=300$ nm and $\lambda=220$ nm) obtained from the ZnO film grown on the YSZ buffer layer and from the ZnO film grown on the fused silica substrate are shown in Figure 6.9. The ZnO layers in both the samples were prepared using similar deposition parameters. This data indicates that both films exhibit similar photoluminescence spectra for $\lambda=300$ nm excitation (Figure 6.9a). It should be noted that the green band emission for the ZnO film grown on the YSZ buffer layer is suppressed when compared to the green band emission for the ZnO film grown on the fused silica substrate. As shown in Figure 6.9b, the photoluminescence spectra for $\lambda=220$ nm excitation are dissimilar for the ZnO film grown on the YSZ buffer layer and for the ZnO film grown on the fused silica substrate. The spectra from $\lambda=220$ nm excitation for the ZnO film grown on the YSZ buffer layer is similar to that from $\lambda=300$ nm excitation. On the other hand, the readily differentiated excitonic emissions and green band emissions are replaced by a broad emission band in the violet-blue region for the ZnO film grown on the fused silica substrate. The contribution from excitonic emission is weak for the ZnO film grown on the fused silica substrate. Figure 6.9c shows excitation spectra for green band emission monitored at $\lambda=540$ nm. A significant difference is observed for excitation wavelengths shorter than $\lambda=240$ nm in the spectra obtained from the ZnO film grown on the YSZ buffer layer and from the ZnO
Figure 6.9 Comparison of ZnO film grown on YSZ buffered Si (100) substrate and ZnO film grown on fused silica substrate. (a) Photoluminescence spectra obtained using $\lambda=300$ nm excitation. (b) Photoluminescence spectra obtained using $\lambda=220$ nm excitation. (c) Excitation spectra obtained using $\lambda=540$ nm emission.
film grown on the fused silica substrate. These results suggest that short wavelengths excite \( \lambda = 540 \) nm emission more effectively for the ZnO film grown on the fused silica substrate than for the ZnO film grown on the YSZ buffer layer. The experimental observations suggest that green band emission is not related to surface defects but instead to point defects in the bulk of the material. Violet-blue emission is associated with surface and interfacial traps.\(^8\) It is important to note that violet-blue emission is almost undetectable for the ZnO film grown on the YSZ buffer layer, indicating that the biepitaxial ZnO film contains low densities of surface and interfacial defects. This result is also consistent with the fact that grain boundaries in the biepitaxial ZnO film are coherent, with minimum disorder at grain boundaries. In addition, our results indicate that large angle boundaries do not necessarily increase defect density. Formation of defects may be more sensitive to processing and substrate parameters.

### 6.4 Summary

We have shown that yttria-stabilized zirconia buffer layers can be used to grow high quality zinc oxide films on silicon (100) substrates. X-ray diffraction and transmission electron microscopy results show that biepitaxial ZnO films grow on YSZ buffer layer, with a single out-of-plane orientation and two in-plane orientations. The two in-plane orientations of the ZnO film were rotated by thirty degrees, which result from different symmetries of ZnO and YSZ along the growth direction. Biepitaxial growth of ZnO films on YSZ buffer layers has been explained by domain matching epitaxy, in which integral multiples of planes match across the film-substrate interface. These films exhibited a high mobility value of \( \sim 46 \) cm\(^2\)
V⁻¹ s⁻¹. The high mobility values obtained from biepitaxial ZnO films in spite of the high density of 30° grain boundaries has been attributed to the coherent nature of these boundaries. Photoluminescence studies of biepitaxial ZnO films indicated that these films exhibit good optical quality. The photoluminescence spectra showed very strong excitonic emission with minimal green band emission. The ZnO films also demonstrated minimal emission associated with surface (interfacial) defects. Understanding of this system is an important step towards integration of high quality ZnO films with Si (100) substrates for a variety of optoelectronic devices, including ultraviolet blue laser diodes and flat panel displays.
References


7. Semipolar R-Plane ZnO Films on Si (100) Substrates: Thin Film Epitaxy and Optical Properties

Here we report heteroepitaxial growth of (10\,\bar{1}\,2) oriented semipolar (r-plane) ZnO films on Si (100) substrates. The films were grown by pulsed laser deposition and integration of ZnO with silicon was achieved using a tetragonal yttria stabilized zirconia (YSZ) buffer layer. It was observed that ZnO films grown at temperatures in the range of 700-750 °C with relatively high oxygen pressure (~70 mTorr) were (10\,\bar{1}\,2) oriented. ZnO films deposited with lower oxygen pressures were found to be purely (0002) orientated. Experiments carried out to elucidate the role of oxygen pressure indicated that the crystallographic orientation of ZnO depends on the nature of atomic termination of YSZ layer. It has been proposed that crystallographic orientation of ZnO is controlled by chemical free energy associated with ZnO-YSZ interface. Detailed x-ray diffraction and transmission electron microscopy studies showed existence of four types of in-plane domains in r-plane ZnO films. Optical characterization demonstrated that photoluminescence of r-plane ZnO films was superior to that of c-plane ZnO films grown under similar conditions.

7.1 Introduction

Zinc oxide is a wide band gap semiconductor with significant potential for use in ultraviolet optoelectronic devices such as light emitting diodes (LEDs) and lasing devices.\textsuperscript{1, 2} ZnO has hexagonal wurtzite structure and has a preference to grow along the [0001] direction (c-axis). Along the c-axis, zinc and oxygen layers alternate, imparting a polar character to (0001)-oriented wurtzite ZnO. The piezoelectric and the polarity-induced electrostatic fields in
(0001) oriented wurtzite materials lead to spatial separation of electrons and holes, thereby reducing the radiative recombination probability. This impairs the light emitting efficiency of devices built with (0001)-oriented wurtzite active layers.\textsuperscript{3} One approach to overcome this limitation is to grow ZnO in nonpolar orientations in which polarization is zero.\textsuperscript{4} This has led to considerable research on the growth and characterization of two nonpolar orientations of ZnO, a-plane (11\(\bar{2}\)0) and m-plane (10\(\bar{1}\)0).\textsuperscript{5,7} The polarization effects can also be minimized by growing wurtzite materials in semipolar orientations. In recent years, there has been significant interest in growing GaN and other wurtzite nitride materials in semipolar orientations for optoelectronic devices.\textsuperscript{8-10} In these semipolar orientations, the polarization effects are minimal and higher amounts of dopants (e.g., indium in GaN) can be incorporated compared to nonpolar orientations. Since ZnO has similar crystal structure and properties to GaN, the semipolar orientations of ZnO are also expected to exhibit optoelectronic properties that are desirable for device applications. However, there has been little work on semipolar orientations of ZnO. The main reason for this is the strong tendency of ZnO to grow in polar c-orientation on most substrates, while very specific substrates and deposition conditions are required to grow non-polar or semipolar orientations of ZnO. One of the most important semipolar orientations in ZnO is (10\(\bar{1}\)2), which is referred to as the r-plane. As established for GaN, polarization effects are expected to be very small for r-plane oriented ZnO.\textsuperscript{11} In this paper, we present a novel approach to grow semipolar r-plane ZnO films. We demonstrate that r-plane ZnO films can be integrated with the easily available and technologically important Si (100) substrate.
In an earlier work, we have shown that tetragonal YSZ can be grown epitaxially on Si (100) substrates using pulsed laser deposition. Further, we have demonstrated heteroepitaxial growth of polar c-plane ZnO films on YSZ buffered Si (100) substrates. In the present study, we show that the semipolar r-plane orientation of ZnO can be epitaxially grown on YSZ buffered Si (100) by controlling the deposition conditions. It has been shown that the growth orientation of ZnO on YSZ buffered silicon depends on the nature of atomic termination of YSZ layer, which is controlled by oxygen pressure. Detailed x-ray diffraction (XRD) and transmission electron microscopy (TEM) investigations were carried out to assess the structural details of the films. The photoluminescence spectra for r-plane ZnO films have been compared with those for c-ZnO films grown under similar conditions.

7.2 Experimental Details

YSZ buffer layer and ZnO films were grown on Si (100) substrates using KrF excimer pulsed laser deposition (\(\lambda = 248 \text{ nm}\)). Prior to deposition, silicon substrates were ultrasonically cleaned with acetone and methanol. High-purity YSZ (5 mol \% - Y\(_2\)O\(_3\) doped ZrO\(_2\)) and ZnO targets were used for the deposition. The energy density used in this study was \(\sim 3 \text{ J/cm}^2\). A target-substrate distance of 4.5 cm and a pulse rate of laser of 5 Hz were utilized. The growth temperature was maintained at 800 °C for deposition of YSZ layer. ZnO growth was done at 700 °C, 750 °C or 800 °C. To remove the oxide layer on silicon, 400 pulses of YSZ were deposited in vacuum. Oxygen was subsequently introduced in the chamber. 600 pulses of YSZ were then deposited at an oxygen partial pressure of 0.5 mTorr. After adjusting the substrate temperature to ZnO growth temperature, 6000 pulses of ZnO were deposited.
Growth of ZnO was performed at three different oxygen partial pressures in the range of 0.5 - 70 mTorr. X-ray diffraction studies were done using X’Pert PRO MRD HR x-ray diffractometer (Philips, Eindhoven, the Netherlands) with Cu Kα radiation. Cross-sectional samples of the ZnO/YSZ/Si (100) heterostructures were characterized using 2000FX and 2010F high resolution transmission electron microscopes (JEOL, Tokyo, Japan). Photoluminescence (PL) spectroscopy of the as-grown samples was done at room temperature using an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan).

7.3 Results and Discussion

In the first set of the experiments, growth of ZnO films on YSZ buffered Si (100) was investigated at three different oxygen partial pressures at a fixed ZnO growth temperature of 700 °C. The x-ray diffraction data for the reference YSZ/Si (100) sample and the ZnO/YSZ/Si (100) samples is shown in Figure 7.1. The XRD patterns for ZnO/YSZ/Si (100) samples in this figure show that ZnO grows solely in (0002) orientation at lower oxygen partial pressures (0.5 mTorr and 7 mTorr). In contrast, at an oxygen partial pressure of 70 mTorr, ZnO grows only in the (10 1 2) orientation; no other orientation of ZnO is present (Figure 7.1d). It should be noted that YSZ (002) and ZnO (0002) peaks are very close and it may seem difficult to index them unambiguously. However, this ambiguity can be removed by looking at the second order peaks, which have larger separation, and also by comparing the intensities of YSZ (002) and ZnO (0002) peaks. The ZnO (0002) peaks are around 100 times more intense than YSZ (002) peak, for which intensity is expected to remain
unchanged as YSZ deposition conditions were identical for all of the samples. The XRD pattern in Figure 7.1a shows that tetragonal YSZ grows only in the (002) orientation.

We have also examined the effect of temperature on growth behavior of ZnO on the YSZ buffer by fixing the oxygen partial pressure at 70 mTorr. The x-ray diffraction data for these samples is shown in Figure 7.2. It was observed that ZnO grows only in the (10\(\overline{1}2\)) orientation at 700 and 750 °C. However, (0002) orientation of ZnO was also present along with (10\(\overline{1}2\)) orientation for ZnO grown at 800 °C. Hence, it can be concluded that (10\(\overline{1}2\))

![Figure 7.1 X-ray diffraction \(\theta-2\theta\) scan data for (a) YSZ/Si (100) heterostructure and (b, c and d) ZnO/YSZ/Si (100) heterostructures grown at different oxygen partial pressures. The ZnO growth temperature was 700 °C for all the samples.](image)
orientation is favored over (0002) orientation at low temperatures and high oxygen partial pressures.

Figure 7.2 X-ray diffraction θ-2θ scan data for ZnO/YSZ/Si (100) heterostructures grown at different ZnO growth temperatures. Oxygen partial pressure was 70 mTorr for all of the samples.

The oxygen pressure dependence of crystallographic orientation for oxide thin films deposited by pulsed laser deposition has been previously reported in the literature.\textsuperscript{13-16} This change in crystallographic orientation of oxides is often attributed to either changes in stoichiometry (which alter the strain energy associated with non-stoichiometric point defects) or decreased kinetic energy of the ablated species with increasing oxygen pressure.\textsuperscript{14, 15}
However, the mechanism underlying this phenomenon is unclear. To understand the role of oxygen pressure in controlling the crystallographic orientation of ZnO, we deposited films where the first few pulses of ZnO were deposited at high pressure (70 mTorr, a condition in which ZnO grows only in r-plane orientation). The remainder of the ZnO deposition was continued at lower oxygen pressure (0.5 mTorr, a condition in which ZnO grows only in the c-plane orientation). The XRD results for these samples are summarized in Figure 7.3.

**Figure 7.3** X-ray diffraction data for ZnO/YSZ/Si (100) heterostructures for which the initial N1 number of ZnO pulses were deposited at a high oxygen pressure of 70 mTorr and the remaining N2 (6000-N1) pulses were deposited at a reduced oxygen pressure of 0.5 mTorr.

The XRD results indicate that growth orientation of ZnO is r-plane even if only the first 5 pulses (~6 Å, based on TEM results) of ZnO are deposited in high oxygen pressure, while the
rest of the pulses are deposited at low oxygen pressure. This finding indicates that high oxygen pressure is important only for the nucleation stage of r-plane ZnO. Once nucleated, r-plane ZnO can grow even at low oxygen pressures. To understand whether kinetics of the ablated species plays a role in controlling the orientation, one deposition was performed in which the sample was annealed in 70 mTorr oxygen after YSZ deposition for two minutes. The oxygen pressure was subsequently reduced to 0.5 mTorr; all of the pulses of ZnO were then deposited at 0.5 mTorr. The orientation of ZnO in this case also was found to be r-plane. This indicates that kinetics of ablated particles does not affect the crystallographic orientation of ZnO since the entire ZnO deposition was carried out at 0.5 mTorr oxygen partial pressure, a condition in which ZnO prefers to grow in c-plane orientation. This result also indicates that oxygen pressure condition just before the deposition of ZnO, rather than that during the deposition of ZnO, is the key factor that controls the crystallographic orientation of ZnO. This can be explained on the basis of different atomic termination of YSZ layer under different oxygen pressure conditions. We propose that at low oxygen pressures the YSZ surface is Zr-terminated while at higher oxygen pressures the YSZ surface is O-terminated. The experimental evidence suggests that c-plane ZnO growth is favored on Zr-terminated YSZ, while r-plane ZnO growth is favored on O-terminated YSZ. To further correlate ZnO orientation with atomic termination of YSZ, we have simulated atomic arrangements of YSZ (002), ZnO (0002) and ZnO (10\bar{1}2) planes. These atomic arrangements are shown in Figure 7.4. From this figure it can be seen that in YSZ, Zr-only and O-only layers alternate along [002]. Although Zr-layers are atomically smooth, O-layers are atomically rough. In c-plane ZnO, Zn-only and O-only layer alternate along a direction normal to (0002). Both of these
planes are atomically smooth. The atomic arrangement in ZnO (10\bar{1}2) plane is more complex, with the planes defining both O and Zn atoms being atomically rough. When YSZ layer is Zr-terminated and is thus atomically smooth, it is likely that first atomic layer of ZnO will be atomically flat O atoms, which is the case for c-plane ZnO. On the other hand, when YSZ is O-terminated and is thus atomically rough, the first atomic layer of ZnO is also likely to be atomically rough, which is the case for r-plane ZnO. This explains the growth of r-plane orientation of ZnO in high oxygen pressure conditions. The coexistence of r- and c-plane orientations in ZnO films deposited at 800 °C with high oxygen pressure (Figure 7.2c) can be explained by the mixed termination of YSZ under these conditions. In thin film growth,
crystallographic orientation of the film is determined by interplay of chemical energy, which depends on the bonding characteristics across substrate-film interface, and the substrate-film misfit strain energy. The chemical energy for the YSZ-ZnO film interface, for a particular orientation of ZnO, depends on the nature of termination of YSZ layer. However, for a given orientation of ZnO, the strain energy will remain the same irrespective of the nature of termination of YSZ layer. Thus, the dependence of orientation of ZnO on nature of termination of YSZ layer indicates that chemical energy, rather than strain energy, is controlling the crystallographic orientation of ZnO on YSZ.

The in-plane orientation of YSZ and ZnO layers in ZnO/YSZ/Si (100) heterostructure was established by x-ray diffraction $\phi$-scans. The $\phi$-scan data for an r-plane ZnO/YSZ/Si (100) heterostructure is shown in Figure 7.5a. The $\phi$-scan for YSZ layer was done at $2\theta = 30.25^\circ$ and $\psi = 54.2^\circ$, which corresponds to (101) peak of tetragonal YSZ. The 4-fold symmetry seen in the $\phi$-scan of YSZ confirms that it is epitaxial and tetragonal. Also, it can be seen that YSZ (101) peaks are at 45 degrees from Si (202) peaks. Hence, the epitaxial relationship of YSZ with silicon substrates can be written as: $[110]_{YSZ} \parallel [100]_{Si}$ and $(001)_{YSZ} \parallel (001)_{Si}$. This observation is consistent with our previous results. The $\phi$-scan for ZnO layer was done at $2\theta = 36.39^\circ$ and $\psi = 18.5^\circ$, which correspond to the $(10\bar{1}1)$ peak of zinc oxide. The $\phi$-scan of ZnO shows four peaks which are 90 degrees apart. This indicates that ZnO grows epitaxially on YSZ. The calculated stereographic projection of $\{10\bar{1}1\}$ planes on $(10\bar{1}2)$ plane for single crystalline ZnO is shown in Figure 7.5b. From this stereographic projection,
Figure 7.5 (a) X-ray diffraction $\phi$-scan data for one of the ZnO/YSZ/Si (100) heterostructure. The ZnO growth temperature was 750 °C, while the oxygen partial pressure was 70 mTorr. (b) Calculated stereographic projection of $\{10\overline{1}1\}$ planes on $(10\overline{1}2)$ plane for single crystalline ZnO.
it can be concluded that in single crystalline ZnO, \{101\} planes should exhibit only 1-fold symmetry. Hence, the observation of four peaks in $\phi$-scan indicates that ZnO has 4 different in-plane orientations. The position of YSZ (101) peak and ZnO (10\bar{1}1) peak at the same angle in the $\phi$-scan indicates that [11\bar{2}0] direction of ZnO is parallel to [100] or [010] directions of YSZ. The [100] and [010] directions in YSZ are equivalent. Thus there are two equally likely orientations of r-ZnO, which are at 90 degrees to each other.

![Diagram of ZnO orientations](image)

**Figure 7.6** (a) Schematic showing (a) two possible orientations of rectangular r-plane ZnO (blue color) on square (001) plane of YSZ (red color) (b) other two orientation of ZnO, which arise because the c-plane of ZnO can be inclined on either side with respect to the r-plane.

These two orientations of ZnO are schematically shown in Figure 7.6a. Here, it should be noted that the atomic arrangement on r-plane of ZnO can be represented by a rectangular lattice, one side of which is along [11\bar{2}0] while other side is along [10\bar{1}1] direction. The
existence of other two peaks in the $\phi$-scan of ZnO can be explained by considering the orientation of c-plane with respect to r-plane of ZnO. The c-plane is inclined at 42.8 degrees with respect to r-plane. The inclination of c-plane can be on either side, which gives rise to two additional orientations of r-plane ZnO; this is schematically shown in Figure 7.6b. As seen from this figure, these two orientations are 180 degrees rotated with respect to each other. Based on this information, the epitaxial relationship for r-ZnO can be written as:

$[11 \overline{2} 0]_{\text{ZnO}}$ or $[10 \overline{1} 1]_{\text{ZnO}} \parallel [100]_{\text{YSZ}}$ and $(10 \overline{1} 2)_{\text{ZnO}} \parallel (001)_{\text{YSZ}}$.

Figure 7.7 An overview TEM image from a cross-section sample of r-plane ZnO/YSZ/Si (100) heterostructure grown at 700 $^\circ$C at 50 mTorr oxygen pressure. The inset shows the electron diffraction pattern obtained from all three layers. The YSZ spots are very close to the Si spots and are not indexed to maintain the clarity.
These results were further confirmed using transmission electron microscopy. Figure 7.7 shows an overview TEM image of the ZnO/YSZ/Si (100) heterostructure and an electron diffraction pattern. The thickness of YSZ layer can be estimated as ~45 nm and the thickness of the ZnO layer can be estimated as ~800 nm from this image. The indexing of electron diffraction pattern shows that spots from ZnO correspond to [100] and [121] zones of ZnO. It should be noted that two variants of [100] zone of ZnO, which are rotated by ~86 degrees from each other, are observed in the electron diffraction pattern. This corresponds to orientation variants of ZnO shown in Figure 7.6b. The electron diffraction pattern also shows that (10 \bar{2} 1) planes of ZnO are tilted by ~2 degrees from (004) planes of Si. The high resolution images of Si/YSZ and YSZ/ZnO interfaces are shown in Figure 7.8. In these images, YSZ is in [100] zone while ZnO is in [121] zone. The high resolution image of YSZ/ZnO surface shows that interface is very sharp; no reaction layer at the interface was observed. In the high resolution image of YSZ/Si interface, a ~ 2 nm thick amorphous layer can be observed. As reported earlier, the YSZ layer grows epitaxially on Si (100); this amorphous layer forms during the later stages (after oxygen is introduced in the chamber) of YSZ and ZnO growth as a result of oxygen diffusion to the YSZ/Si interface.\textsuperscript{12}

It can be seen from Figure 7.6a that the misfit between r-plane ZnO and tetragonal YSZ is 9.7% in one direction and 6.7% in the perpendicular direction. Epitaxy with such large misfits can be explained in the framework of domain matching epitaxy (DME), in which matching of planes instead of matching of lattice is considered.\textsuperscript{17} Along the [11 \bar{2} 0] direction
Figure 7.8 High resolution TEM images from (a) YSZ/Si (100) interface and (b) ZnO/YSZ interface from a cross-section sample of r-plane ZnO/YSZ/Si (100) heterostructure grown at 700 °C at 50 mTorr oxygen pressure. In these images, Si, YSZ, and ZnO are in [110], [100] and [121] zones, respectively.

of ZnO, 9.7% misfit can be completely accommodated by two type of domains. In one domain, 10 ZnO planes match 9 YSZ planes. In the other domain, 11 ZnO planes match 10 YSZ planes. The misfit will be completely relaxed if these domains alternate with a relative
frequency of 5:2. Along the [10\bar{1}1] direction of ZnO, 6.7% misfit can be accommodated by a single domain in which 15 ZnO planes match 16 YSZ planes.

The room temperature photoluminescence spectra for r-plane ZnO/YSZ/Si (100) and c-plane ZnO/YSZ/Si (100) samples grown under similar conditions are shown in Figure 7.9. Both of these spectra exhibit near band emission at 3.3 eV. Near band emission in ZnO is attributed to excitonic recombination.\textsuperscript{18} The excitonic emission in r-plane ZnO is approximately five times stronger than that in c-plane ZnO. The stronger excitonic emission observed in r-ZnO can be attributed to the higher probability of radiative recombination in r-plane ZnO due to reduced polarization effects.

![Figure 7.9 Photoluminescence spectra of r-plane ZnO/YSZ/Si (100) and c-plane samples deposited at similar conditions. The first 50 pulses of ZnO for c-ZnO were deposited at low oxygen pressure of 0.5mTorr to nucleate the c-orientation of ZnO.](image)

\textbf{Figure 7.9} Photoluminescence spectra of r-plane ZnO/YSZ/Si (100) and c-plane samples deposited at similar conditions. The first 50 pulses of ZnO for c-ZnO were deposited at low oxygen pressure of 0.5mTorr to nucleate the c-orientation of ZnO.
Another important feature in the spectra shown in Figure 7.9 is the prominent broad emission band in c-ZnO, which peaks at 2.35 eV. This emission, termed as green band emission, is often attributed to mid gap point defect levels such as charged oxygen vacancies or zinc interstitials.\textsuperscript{19,20} It is interesting to note that green band emission is completely suppressed for r-plane ZnO, which indicates that the density of defects responsible for green band emission is minimal in these films. The reduced green band in r-ZnO films can also contribute to stronger excitonic emission observed in r-ZnO films since the probability of excitonic recombination is increased because of reduced mid gap states. The strong excitonic emission, with negligible emission in visible range, in r-plane ZnO indicates the good optical quality of these films.

\textbf{7.4 Summary}

To summarize, we have demonstrated heteroepitaxial growth of semipolar r-plane zinc oxide films on YSZ buffered Si (100) substrates. It was found that on YSZ buffered silicon, ZnO grows in r-plane orientation at a high oxygen pressure of 70 mTorr. On the hand, the ZnO films deposited at lower oxygen pressures were c-plane oriented. It is envisaged that the chemical free energy dominates strain free energy in controlling the orientation of ZnO on YSZ. The oxygen pressure dependence of crystallographic orientation of ZnO films has been explained by considering the nature of the atomic termination of the YSZ layer. Detailed x-ray diffraction and TEM studies indicated that r-plane ZnO films exhibited four in-plane orientations. The epitaxial relationship of r-plane ZnO with YSZ buffer layer was established
to be: $[10\bar{1}0]_{ZnO} \parallel [100]_{YSZ}$ or $[01\bar{1}1]_{ZnO} \parallel [100]_{YSZ}$ and $(10\bar{1}2)_{ZnO} \parallel (001)_{YSZ}$. The r-plane ZnO films showed strong excitonic emission, which is indicative of good optical quality.
References


8. Integration of Epitaxial ZnO/La$_{0.67}$Sr$_{0.33}$MnO$_3$ Heterostructures with Si (100) Substrates

The objective of this chapter is to demonstrate epitaxial integration of ZnO/LSMO heterojunctions with Si (100) substrates. In the first part of this chapter, growth of epitaxial La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO) films on Si (100) substrates using yttria stabilized zirconia (YSZ) and cerium oxide (CeO$_2$) buffer layers has been discussed. Results on structural, electrical and magnetic characterization of LSMO/CeO$_2$/YSZ/Si (100) heterostructures are presented. In the second half of the chapter, results on growth and characterization of epitaxial ZnO/LSMO heterostructure are presented. It has been shown that nonpolar a-plane ZnO films can be epitaxially grown on LSMO/CeO$_2$/YSZ/Si (100) heterostructures. Finally, experimental results on electrical characteristics of ZnO/LSMO junction will be discussed.

8.1 Introduction

Recently, perovskite manganites have attracted considerable research interest because of their colossal magnetoresistance (CMR) phenomena and spin dependent high efficiency tunneling. Due to high spin polarization, the manganites show a great potential for applications in magnetic tunnel junctions (MTJs), which are promising candidates for nonvolatile magnetic random access memory. The p-n junctions based on the colossal magnetoresistance (CMR) oxides are of special interest, because their electrical and magnetic properties can be modulated by external electric and magnetic fields. It is possible to fabricate electronic devices with high electric and magnetic sensitivity, which can be used for various applications such as magnetic field detector and magnetic storage.$^{1-5}$
Among manganites, $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) has been studied extensively because of its high Curie temperature. LSMO is a ferromagnetic metal at low temperature while it becomes a paramagnetic insulator above its Curie temperature. High quality LSMO thin films can be grown on perovskite substrates such as $\text{SrTiO}_3$. However, for practical devices it is imperative to grow high quality LSMO films on Si (100) substrates. Also, there has been significant interest in creating p-n junctions based on p-type LSMO and n-type wide band gap semiconductor such as ZnO. In such junctions carrier concentration can be modulated by applying external field or light across the junction. Though there are a few reports in the literature on fabrication of polycrystalline ZnO/LSMO junctions, it is desirable to develop epitaxial junctions for device applications. Hence the objective of the present work is to develop an epitaxial ZnO/LSMO junction. This objective has been achieved by first integrating epitaxial LSMO films with Si (100) substrates, followed by growth of epitaxial a-plane ZnO films on LSMO.

### 8.2 Experimental Details

Pulsed laser deposition (KrF excimer laser, $\lambda = 248$ nm) technique was used to grow LSMO/CeO$_2$/YSZ/Si (100) and ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructures. Prior to deposition, silicon substrates were ultrasonically cleaned with acetone and methanol. High-purity solid state targets were used for all the materials. The laser fluence used in this study was $\sim 3 \text{ J/cm}^2$. A target-substrate distance of 4.5 cm and a laser pulse rate of 5 Hz were utilized. The growth temperature was maintained at 800 °C for deposition of YSZ and CeO$_2$ layers. To remove the oxide layer on silicon, 400 pulses of YSZ were deposited in vacuum.
Oxygen was subsequently introduced in the chamber. 600 pulses of YSZ were then deposited at an oxygen partial pressure of 0.5 mTorr. After adjusting the substrate temperature to LSMO growth temperature, 1000-2000 pulses of LSMO were deposited. Growth of LSMO was performed at temperatures in the range 750 - 800 °C and with oxygen pressures in the range 100 - 300 mTorr. ZnO layer was grown in the temperature range 600-750 °C. X-ray diffraction studies were done using Philips X’Pert PRO x-ray diffractometer with Cu Kα radiation. Cross-sectional samples of the LSMO/CeO₂/YSZ/Si (100) heterostructures were characterized using JEOL 2000FX and 2010F high resolution transmission electron microscopes. Electrical characterization was performed using an HP8545 semiconductor parameter analyzer. Resistivity was measured as a function of temperature by four-probe method. The field and temperature-dependent magnetization of the LSMO films was examined using a vibrating sample magnetometer.

8.3 Results and Discussion

8.3.1 Growth and Characterization of LSMO/CeO₂/YSZ/Si (100) Heterostructures

Being sensitive to stoichiometry and strain, the properties of LSMO vary with film deposition conditions such as oxygen pressure and temperature. Hence, in the present study, we have studied deposition of LSMO thin films under many different conditions. To illustrate the dependence of LSMO properties on deposition conditions, the data of four samples A, B, C and D is presented. Deposition conditions for these samples are summarized in Table 8.1. The XRD patterns for these samples are shown in Figure 8.1. From the XRD patterns, it is very clear that LSMO grows only in the (001) orientation in cubic phase for all
Table 8.1 Deposition conditions and measured lattice parameters for LSMO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>LSMO Deposition Temperature</th>
<th>$P_{O_2}$ (m Torr)</th>
<th>LSMO lattice parameter measured by XRD (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>All 1000 pulses at 750 °C</td>
<td>350</td>
<td>3.86</td>
</tr>
<tr>
<td>Sample B</td>
<td>All 1000 pulses at 815 °C</td>
<td>350</td>
<td>3.86</td>
</tr>
<tr>
<td>Sample C</td>
<td>Initial 100 pulses at 815 °C + 900 pulses at 750 °C</td>
<td>350</td>
<td>3.86</td>
</tr>
<tr>
<td>Sample D</td>
<td>Initial 100 pulses at 815 °C + 900 pulses at 750 °C</td>
<td>80</td>
<td>3.88</td>
</tr>
</tbody>
</table>

Figure 8.1 XRD patterns for LSMO/CeO$_2$/YSZ/Si (100) heterostructures prepared at different deposition conditions. Details of samples A, B, C and D are given in Table 8.1.
the deposition conditions used in the present study. No other orientations of LSMO are observed. Also, both CeO$_2$ and YSZ grow only in (002) orientations. Based on the 2θ values of the LSMO (002) peaks we have calculated the cubic lattice parameters for LSMO. The measured out-of-plane lattice parameters are given in Table 8.1. The measured lattice parameters of LSMO vary in the range 3.86-3.88 Å. The bulk lattice parameter of LSMO is 3.87 Å. This indicates that LSMO films grown in the present study are relaxed (residual strain being very small, ~0.25 %).

Further structural characterization of LSMO/CeO$_2$/YSZ/Si (100) heterostructure was done by transmission electron microscopy studies on sample ‘C’. A Bright field TEM image of sample ‘C’ is shown in Figure 8.2. From this image, the estimated thicknesses of YSZ, CeO$_2$ and LSMO layers are ~60, 35 and 105 nm thick, respectively. This image shows that LSMO growth is columnar with a grain size of ~ 50 nm. The high resolution TEM image of LSMO/CeO$_2$ interface (Figure 8.3) shows that this interface is clean and sharp. The plan-view electron diffraction pattern (Figure 8.4) of sample ‘C’ clearly shows the four-fold symmetry and epitaxial nature of the LSMO films. Based on the XRD (including φ-scan data presented in the next section) and TEM results, the epitaxial relationship of the LSMO films can be written as:

\[ \text{LSMO}(001) \parallel \text{CeO}_2(001) \parallel \text{YSZ}(001) \parallel \text{Si}(001) \text{ \ AND} \]

\[ \text{LSMO}[110] \parallel \text{CeO}_2[100] \parallel \text{YSZ}(110) \parallel \text{Si}[100] \]
Figure 8.2 A bright field cross sectional TEM image of LSMO/CeO$_2$/YSZ/Si (100) heterostructure (Sample C). Inset shows an electron diffraction pattern from all the layers of the heterostructure.

Figure 8.3 High resolution TEM image of LSMO/ CeO$_2$ interface in LSMO/CeO$_2$/YSZ/Si (100) heterostructure (Sample C).
Figure 8.4 A plan-view electron diffraction pattern from LSMO layer of LSMO/CeO2/YSZ/Si (100) heterostructure (Sample C).

The electrical properties of the LSMO films were characterized by electrical resistivity measurements as a function of temperature. These results are shown in Figure 8.5. From these results, it can be seen that both the peak resistivity temperature ($T_R (\text{Peak})$) and ratio of minimum to maximum resistivity are very sensitive to deposition conditions. $T_R (\text{Peak})$ is an indicator of semiconductor-to-metal transition (SMT) temperature; LSMO films are metallic below $T_R (\text{Peak})$, while semiconducting behavior dominates above this temperature. Since both electrical and magnetic transitions in LSMO are correlated, $T_R (\text{Peak})$ is also related to ferromagnetic-to-paramagnetic transition. From Figure 8.5, it can be observed that for the samples C and D, which were deposited at identical temperature conditions but with different oxygen pressures, there is a huge difference in $T_R (\text{Peak})$; it is $\approx 350 \text{K}(P_{O2} = 350 \text{ mTorr})$ for
sample C and ~115 K for sample D ($P_{O2} = 80 \text{ mTorr}$). The $T_{R(Peak)}$ value of 350 K is close to that reported for bulk LSMO samples. From the resistivity trend, it can be concluded that quality of the LSMO films deposited by two step growth method is better, as these films exhibit bulk-like properties. We propose that the high temperature deposition step, in which a thin nucleation layer is deposited, improves the crystallinity of LSMO. The low temperature growth step leads to improved stoichiometry. Though stoichiometry is known to affect SMT temperature, low $T_{R(Peak)}$ is often attributed to residual strain in LSMO films. The present results indicate that both the strain and the deposition conditions are important parameters which control SMT temperature in the LSMO films.

Figure 8.5 Normalized resistance as a function of temperature for LSMO films deposited under different conditions. Refer Table 8.1 for details of samples A, B, C and D.
We have also characterized magnetic behavior of one of the LSMO/\(\text{CeO}_2/\text{YSZ/Si}\) (100) heterostructure (Sample A). These results are shown in Figure 8.6. The magnetization curves demonstrate strong ferromagnetic behavior of LSMO films at \(\sim\)250 K. The saturation magnetization drops sharply with increasing temperature. This behavior is consistent with the results on resistivity measurements which indicate a SMT temperature of around 280K for sample A.

**Figure 8.6** Magnetization curves for LSMO films at different measurement temperatures for \(\text{LSMO/\text{CeO}_2/\text{YSZ/Si}}\) (100) heterostructure (Sample A).

### 8.3.2 Growth and Characterization of ZnO/LSMO/\(\text{CeO}_2/\text{YSZ/Si}\) (100) Heterostructures

With the objective of making an epitaxial n-ZnO/ p-LSMO junction, we deposited ZnO/LSMO/\(\text{CeO}_2/\text{YSZ/Si}\) (100) heterostructures. XRD patterns for these heterostructures, in
which ZnO films were deposited at four different temperatures, are shown in Figure 8.7. Indexing of these diffraction patterns shows that for the ZnO growth temperatures in the range 640-720 °C, both c- and r- orientations of the ZnO are present. However, ZnO films exhibited pure a- plane orientation when the ZnO deposition temperature was lowered to 610 °C. Visual inspection of ZnO/LSMO/CeO$_2$/YSZ/Si (100) samples, in which ZnO films were deposited in the temperature range of 640-770 °C, showed signs of interfacial reaction. It is possible that an amorphous reaction layer at the ZnO/LSMO interface results in c-orientation of the ZnO films for the samples in which ZnO deposition temperature was above 640 °C. This can be attributed to the tendency of ZnO to grow in c-orientation on amorphous templates.

![Figure 8.7 XRD patterns for ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructures. The ZnO layer was deposited at different temperatures as indicated, while LSMO layer was deposited at 810 °C. ZnO was deposited in oxygen deficient base pressure conditions.](image)

Figure 8.7 XRD patterns for ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructures. The ZnO layer was deposited at different temperatures as indicated, while LSMO layer was deposited at 810 °C. ZnO was deposited in oxygen deficient base pressure conditions.
To establish epitaxy in the ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructure, we performed $\phi$-scans on the sample in which ZnO was grown at 610 °C. From the $\phi$-scan data shown in Figure 8.8, it can be seen that well defined peaks are seen in $\phi$-scan for all the layers in ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructure. This indicates that all the layers in this heterostructure are epitaxial. It should be noted that eight peaks for ZnO (110) indicate two in-plane orientations for ZnO films. This is expected because of two-fold ZnO can grow in two equally likely orientations on four-fold (001) plane of LSMO.

![X-ray diffraction $\phi$-scan data for all the layers in ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructure. The ZnO layer was deposited at 610°C.](image)

**Figure 8.8** X-ray diffraction $\phi$-scan data for all the layers in ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructure. The ZnO layer was deposited at 610°C.
8.3.3 Characterization of ZnO/LSMO Junction

The I-V characteristics of ZnO/LSMO junctions were measured for many samples prepared under different deposition conditions. However, none of the ZnO/LSMO junctions prepared in the present study showed diode-like rectifying behavior. Most of the junctions showed ohmic behavior. The I-V characteristics of one representative sample, which showed ohmic behavior, are shown in Figure 8.9. It can be seen that in this sample equal current flows in both forward and reverse bias. These results suggest that the junction has not formed properly in these samples because of surface states or diffusion at the ZnO/LSMO interface.

Figure 8.9 I-V characteristics of ZnO/LSMO junction. The ZnO layer was deposited at 500°C, oxygen pressure of 150 mTorr was used for LSMO deposition.
The energy band diagram for LSMO and ZnO are schematically drawn in Figure 8.10. From this diagram it should be noted that the work functions (Φ) of LSMO and ZnO are very close, and hence the junction potential of ZnO/LSMO is expected to be small. This can also explain the difficulty in making a rectifying n-ZnO/p-LSMO junction.

![Energy band diagrams for ZnO and LSMO](image)

**Figure 8.10** *Energy band diagrams for ZnO and LSMO.*

Some of the ZnO/LSMO junctions exhibited ‘backward’ diode behavior (Figure 8.11). In these samples, current flowing in reverse bias was much higher than the forward bias current. At low temperatures (< 150 K), current in the forward bias was negligible, and the junction exhibited characteristics of a perfect ‘backward’ diode (Figure 8.11a). It was observed that at higher temperatures, there was appreciable current in forward bias also (Figure 8.11b)
Figure 8.11 I-V characteristics of ZnO/LSMO junction. The ZnO layer was deposited at 740°C, oxygen pressure of 80 mTorr was used for LSMO deposition. Figures (a) and (b) show diode characteristics at four different temperatures for the same sample.
The ‘backward’ diode characteristics have been observed earlier for manganites.\textsuperscript{12-13} In the present study this behavior can be explained by considering that the p-type LSMO is heavily doped and is degenerate. A schematic of p-LSMO/n- ZnO junction energy level diagram for such a case is shown in Figure 8.12. In this type of contact, electrons can easily tunnel across the junction even in reverse bias, giving rising high current in reverse bias.

![Energy level diagram](image)

**Figure 8.12** A schematic of p-LSMO/n- ZnO junction energy level diagram. Fermi energy of LSMO lies below VB edge and indicates it is degenerate.

Based on above observations it can be concluded that LSMO/ZnO junctions prepared in the present study are not rectifying because The I-V measurement results indicate that one of the possible reasons for non-rectifying behavior of LSMO/ZnO junctions in the present study is the heavy doping of LSMO, which makes it a degenerate semiconductor. It is possible to reduce carrier concentration in LSMO by introducing oxygen deficiency. This can be
achieved by depositing LSMO films at lower oxygen partial pressures. This needs further investigation as it is difficult to grow epitaxial LSMO films at lower oxygen pressures.

8.4 Summary

Growth of LSMO films on Si (100) substrates with CeO$_2$ and YSZ buffer layers was investigated. Structural characterization of LSMO films by x-ray diffraction and transmission electron microscopy established that the LSMO films were epitaxial. Electrical and magnetic properties of LSMO films were characterized. Through electrical resistivity measurements, it was established that a two step deposition method gives high quality LSMO films with bulk-like properties. Growth of ZnO films on epitaxial LSMO films was also investigated. It was established that the ZnO grows epitaxially on LSMO in nonpolar a-plane orientation for ZnO deposition temperatures less than ~630 °C. This study has resulted in integration of an epitaxial ZnO/LSMO heterojunction with Si (100) substrates. The I-V characteristics of epitaxial ZnO/LSMO junction indicated ohmic or ‘backward’ diode behavior. This has been explained on the basis of energy band diagrams of ZnO and LSMO.
References


9. Conclusions and Suggestions for Further Work

The research in this dissertation focuses on epitaxial integration of two different functional oxides, ZnO and La$_{0.67}$Sr$_{0.33}$MnO$_3$ (LSMO), with Si (100) substrates. This work has significant technological merit as integration of oxides with silicon substrate is very important to realize solid state devices with enhanced functionality. Yttria stabilized zirconia (YSZ) buffer layer has been used to integrate oxide films with Si (100) substrates. In the present study pulsed laser deposition (PLD) technique was used to grow ZnO/YSZ/Si (100), LSMO/CeO$_2$/YSZ/Si (100) and ZnO/LSMO/CeO$_2$/YSZ/Si (100) heterostructures. In addition to epitaxially integrating ZnO (c-, r- and a-plane orientations) and LSMO with Si (100) substrates, we have been successful in growing an epitaxial ZnO/LSMO heterostructure integrated with Si (100) substrates.

It was established that high quality epitaxial YSZ films on Si (100) substrates can be deposited if at least ~300 pulses of YSZ are initially deposited in oxygen deficient conditions (and rest of YSZ deposited in oxygen environment) in the PLD chamber. Also, deposition temperature should be at least ~800 °C to achieve good crystalline quality of epitaxial YSZ films.

It has been shown that zinc oxide thin films can be epitaxially integrated with Si (100) substrates through use of an YSZ buffer layer. Growth of the zinc oxide thin film on the YSZ buffer layer was found to be biepitaxial with minimal misalignment along c-axis of the zinc
oxide. X-ray diffraction $\phi$-scans showed that for a growth temperature of 800 °C, ZnO grows epitaxially on YSZ in two different orientations, in which one orientation is rotated by thirty degrees from the other. This has been explained on the basis of four-fold symmetry of YSZ and six-fold symmetry of ZnO in the growth plane. For c-ZnO films on YSZ buffered Si (100), it was found that in-plane orientation of ZnO films with respect to YSZ depended on the ZnO growth temperature. These ZnO films exhibited a high mobility value of $\sim 46$ cm$^2$ V$^{-1}$ s$^{-1}$. The high mobility of biepitaxial ZnO films in spite of the high density of 30° grain boundaries has been attributed to the coherent nature of these boundaries. Photoluminescence studies of biepitaxial ZnO films indicated that these films exhibit good optical quality.

Heteroepitaxial growth of semipolar r-plane zinc oxide films on YSZ buffered Si (100) substrates was also demonstrated. It was found that for growth temperatures below $\sim 750$ °C, and at high oxygen pressure ($> 70$ mTorr) conditions, ZnO grows in r-plane orientation instead of c-plane orientation. It has been proposed that the chemical free energy dominates strain free energy in controlling the orientation of ZnO on YSZ. The oxygen pressure dependence of crystallographic orientation of ZnO films was explained by considering the nature of atomic termination of YSZ layer.

Finally, growth of epitaxial LSMO films on Si (100) substrates with fully relaxed, bulk-like properties was demonstrated. Electrical resistivity measurements indicated that two-step growth of LSMO films gives high quality LSMO films with bulk-like properties. It has been proposed that in the two-step growth method, high temperature nucleation step helps to
improve the crystalline quality. Low temperature growth step is important to achieve stoichiometric composition in LSMO films. It was also established that ZnO grows epitaxially on LSMO in nonpolar a-plane orientation for ZnO deposition temperatures less than ~630 °C. This work has led to integration of an epitaxial ZnO/LSMO heterojunction with Si (100) substrates. The I-V characteristics of epitaxial ZnO/LSMO junction indicated ohmic or ‘backward diode’ behavior.

Epitaxial ZnO/LSMO junction integrated with technologically important Si (100) substrates may find use in practical multifunctional devices. It would be worthwhile to further investigate ZnO/LSMO junction. Some suggestions for the further work are as follows:

1. One of the proposed reasons for non-rectifying behavior of ZnO/LSMO junction is high carrier concentration in LSMO which makes it degenerate semiconductor. Carrier concentration in LSMO can be reduced by reducing the oxygen content. This can be achieved by depositing LSMO in lower oxygen pressure. This needs a thorough investigation as LSMO has a tendency for polycrystalline growth at low oxygen pressure conditions.

2. Two-step growth may be another way to reduce carrier concentration in LSMO. A high oxygen pressure nucleation step followed by growth at reduced oxygen pressures may yield epitaxial films with lower carrier concentration.

3. It will also be interesting to investigate effect of external magnetic field on characteristics of ZnO/LSMO junction.