Growth and characterization of epitaxial tin oxide thin films by laser molecular beam epitaxy

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**NANYANG
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**Growth and Characterization of Epitaxial
Tin Oxide Thin Films**

By

Laser Molecular Beam Epitaxy

Ke Chang

**SCHOOL OF ELECTRICAL AND ELECTRONIC
ENGINEERING**

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**Growth and Characterization of Epitaxial
Tin Oxide Thin Films**

By

Laser Molecular Beam Epitaxy

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School of Electrical and Electronic Engineering

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2011

STATEMENT OF ORIGINALITY

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

Date

Ke Chang (signature)

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SUMMARY

The wide variety of electronic, optical and magnetic properties of metal oxides makes them interesting materials for basic research and technological applications. As a well known binary semiconducting oxide, SnO_2 based materials combine high electrical conductivity with optical transparency in the visible range of the optical spectrum and thus constitute an important component for optoelectronic applications. These properties are sought in a number of applications, notably as electrode materials in solar cells, light emitting diodes, and flat panel displays. On the other hand, the discovery of room temperature ferromagnetism (RTFM) in 3d transition metals doped SnO_2 makes this material more interesting in research and applications, since it combines two important realms of condensed matter physics: magnetism and semiconductor. In this dissertation, the epitaxial growth of SnO_2 thin films, electrical transport properties of SnO_2 thin films, and the ferromagnetism in $\text{SnO}_2\text{:Fe}$ based diluted magnetic semiconductor (DMS) have been systematically investigated.

The epitaxial growth of SnO_2 thin films were achieved using laser molecular beam epitaxy (LMBE) technique. Crystal orientation controlled epitaxy of SnO_2 thin films was realized on sapphire substrates. The phase structure and epitaxial relationships were analyzed by reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD). In addition to the sapphire substrates, we also investigated the

epitaxial growth of SnO₂ thin film on (111) SrTiO₃ (STO) substrate, which is believed to be the first report of SnO₂ epitaxy on perovskite substrate. The microstructure and optical dielectric function of SnO₂ thin film on STO were investigated by transmission electron microscopy (TEM) and ellipsometry, respectively. To study the interface of SnO₂/STO heterostructure, its energy band alignment, which is the determining parameter of the optoelectronic properties, was quantitatively determined by X-ray photoelectron spectroscopy (XPS).

The electrical transport properties of SnO₂ thin films deposited by our LMBE technique were extensively studied. First of all, a crystal orientation dependent anisotropic conduction in SnO₂ thin films was observed. This orientation controlled electrical conduction behavior was attributed to the anisotropic crystal structure of SnO₂. Secondly, the thickness effect on the electrical transport properties of SnO₂ (Sb doped) based conductive oxide thin films was investigated. A thickness induced metal-insulator transition (MIT) was observed. According to the XPS results, this MIT is attributed to the valence state variation of Sb. Finally, by varying the annealing temperature, an anomalous electrical transport behavior of the SnO₂ thin films was observed and explained by the growth of crystal grain and the temperature-dependent variation of oxygen vacancy density.

The ferromagnetism of SnO₂ based DMS was investigated with the Fe acting as magnetic dopant, due to its high solid solubility in SnO₂ (up to 10%). RTFM was achieved in both the SnO₂:Fe bulk and thin film samples, in which no secondary phase or magnetic cluster was observed by XRD and TEM. Using orientation control

technique, a crystal orientation affected ferromagnetism was observed in the differently orientated $\text{SnO}_2\text{:Fe}$ thin films. This crystal orientation dependent ferromagnetism may show an evidence which excludes the possibility that the ferromagnetism in $\text{SnO}_2\text{:Fe}$ thin films originates from the ferromagnetic clusters. In addition, carrier doping (electron- and hole-doping) effects on the ferromagnetic properties of $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ were investigated by changing the dopant M (Sb/Mg). A prominent decrease of saturation magnetization (M_s) was observed in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{Sb}_{0.02}\text{O}_{2-\sigma}$. On the contrary, the M_s was significantly enhanced in the case of Mg doping. Based on the results of XPS characterization, this co-doping tuned ferromagnetism in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ was attributed to the oxidation state transition of Fe and the variation of carrier type.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	i
SUMMARY.....	iii
TABLE OF CONTENTS	vi
LIST OF FIGURES.....	viii
LIST OF TABLES.....	xvi
LIST OF ABBREVIATIONS	xvii
CHAPTER 1 INTRODUCTION	1
1.1 Motivation.....	1
1.2 Objectives.....	4
1.3 Major contributions.....	6
1.4 Organization.....	9
CHAPTER 2 LITERATURE REVIEW	11
2.1 Epitaxial growth of SnO ₂ thin films.....	12
2.1.1 Epitaxial potential of SnO ₂	12
2.1.2 SnO ₂ on TiO ₂	17
2.1.3 SnO ₂ on sapphire.....	21
2.1.4 SnO ₂ on Pt (111)	27
2.1.5 Summary and outlook for SnO ₂ epitaxy	29
2.2 Properties and applications of SnO ₂	30
2.2.1 Electronic structure of SnO ₂	30
2.2.2 Electrical transport properties of SnO ₂	36
2.2.3 Optical properties of SnO ₂	39
2.2.4 SnO ₂ based transparent conductors.....	43
2.2.5 SnO ₂ based gas sensors	45
2.3 Metal oxide (SnO ₂) based diluted magnetic semiconductor	48
2.3.1 Brief history of DMSs.....	48
2.3.2 Origin of ferromagnetism in DMSs	51
CHAPTER 3 EXPERIMENTAL PROCEDURES.....	55
3.1 Laser molecular beam epitaxy (LMBE) technique	55
3.2 X-ray diffraction (XRD)	58
3.3 Vibrating sample magnetometer (VSM)	58
3.4 Atomic force microscopy (AFM)	59
3.5 X-ray photoelectron spectroscopy (XPS)	59
3.6 Transmission electron microscopy (TEM).....	60
3.7 Energy dispersive X-ray spectroscopy (EDX).....	61
3.8 Ellipsometry	62
CHAPTER 4 EPITAXIAL GROWTH OF SnO ₂ THIN FILM BY LMBE.....	65
4.1 Orientation controlled SnO ₂ epitaxial thin film on sapphire substrates....	67
4.1.1 Introduction.....	67
4.1.2 Experimental detail	68
4.1.3 Results and discussions.....	69
4.1.4 Summary	81
4.2 Epitaxial growth of SnO ₂ thin film on (111) perovskite substrate.....	83

TABLE OF CONTENTS

4.2.1	Introduction	83
4.2.2	Experimental detail	84
4.2.3	Results and discussions	85
4.2.4	Summary	97
4.3	Band alignment between SnO ₂ and STO	99
4.3.1	Introduction	99
4.3.2	Experimental detail	100
4.3.3	Results and discussions	100
4.3.4	Summary	106
CHAPTER 5 ELECTRICAL TRANSPORT PROPERTIES OF SnO ₂ THIN FILMS		107
5.1	Anisotropic conduction in SnO ₂ epitaxial thin films	109
5.1.1	Introduction	109
5.1.2	Experimental detail	110
5.1.3	Results and discussions	111
5.1.4	Summary	121
5.2	Electrical transport in Sb-doped SnO ₂ thin films: The thickness effect..	122
5.2.1	Introduction	122
5.2.2	Experimental detail	123
5.2.3	Results and discussions	124
5.2.4	Summary	136
5.3	Thermal annealing induced anomalous electrical transport behavior in SnO ₂ thin films	138
5.3.1	Introduction	138
5.3.2	Experimental detail	139
5.3.3	Results and discussions	140
5.3.4	Summary	146
CHAPTER 6 MAGNETIC PROPERTIES OF TRANSITION METAL DOPED SnO ₂		147
6.1	Ferromagnetism in Fe-doped SnO ₂ : Bulk and Thin film	149
6.1.1	Introduction	149
6.1.2	Experimental detail	150
6.1.3	Results and discussions	151
6.1.4	Summary	163
6.2	Carrier doping tuned ferromagnetism in SnO ₂ :Fe	164
6.2.1	Introduction	164
6.2.2	Experimental detail	165
6.2.3	Results and discussions	166
6.2.4	Summary	178
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS		179
7.1	Conclusions	179
7.2	Recommendations for future work	186
AUTHOR'S PUBLICATION		189
BIBLIOGRAPHY		191

LIST OF FIGURES

Figure 2-1.	Crystal structure of SnO ₂ (cassiterite, isostructural with rutile).....	13
Figure 2-2.	Photograph of a SnO ₂ single crystal grown by a vapor phase transport technique. (from reference [33])	14
Figure 2-3.	Sn-O phase diagram (from reference [34]).	16
Figure 2-4.	SnO ₂ -Al ₂ O ₃ phase diagram (from reference [35,36]).	17
Figure 2-5.	Schematic diagrams of the surface unit cells for various low index SnO ₂ crystalline planes as well as the TiO ₂ substrate. All dimensions indicated are in angstroms.....	18
Figure 2-6.	(a) Cross-sectional HRTEM image of the SnO ₂ thin film grown on TiO ₂ substrate. The incident electron beam was parallel to the [010] direction. The introduced edge dislocations are indicated by white symbols. (b) [001] cross-sectional HRTEM of SnO ₂ film (from reference [38]).	19
Figure 2-7.	AFM images (1×1 μm ²) of atomically smooth TiO ₂ surface with different orientations after cleaning by organic solvents and subsequent HF treatment. (a) (110) surface annealed at 900 °C, (b) (100) at 900 °C, and (c) (001) at 900 °C. The vertical profiles were taken along the lines in the AFM images. (from reference [44]).....	20
Figure 2-8.	Plane-view TEM micrograph and SAED pattern of the SnO ₂ on sapphire (0001) surface (from reference [48]).	22
Figure 2-9.	(a) The crystal structure of the sapphire (0001) plane. (b) Three distinguishable in-plane epitaxial growth orientations by SnO ₂ (100) plane packing on sapphire (0001) plane (from reference [48]).	23
Figure 2-10.	Ball-and-stick models of SnO ₂ and Al ₂ O ₃ illustrating the epitaxial relationship and the lattice mismatch (from reference [52]).	25
Figure 2-11.	(a) HRTEM micrograph of the interface between SnO ₂ and sapphire viewed in the SnO ₂ [010] direction. (b) HRTEM micrograph of the interface between SnO ₂ and sapphire viewed in the SnO ₂ [$\bar{1}$ 01] direction (from reference [23]).	26

Figure 2-12.	AFM images of (0001) sapphire substrates: (a) as-received ($1 \times 1 \mu\text{m}^2$), (b) annealed at 1000°C for 1h ($1 \times 1 \mu\text{m}^2$), and (c) annealed at 1400°C for 1h ($3 \times 3 \mu\text{m}^2$). The vertical profile was taken along the line indicated in the image (from reference [53])......	27
Figure 2-13.	SnO_2 growth on Pt (111). (a) Large scale STM image of SnO_2 (101) crystallites with preferential orientation along the three low symmetry directions of Pt (111). (b) Atomic resolution STM image of SnO_2/Pt , in which the SnO_2 (101) unit cell is indicated by a gray rectangle. (c) Schematic diagram of epitaxial relationship of the SnO_2 (101) unit cell with respect to the Pt (111) lattice (from reference [57])......	28
Figure 2-14.	Band structure of SnO_2 obtained from first principles calculations (from reference [59])......	30
Figure 2-15.	Density of states (DOS) of stoichiometry SnO_2 : blue curves represent s states, red are p states, and green are d states. (a) The total DOS, (b) and (c) shows the partial DOS of Sn and O, respectively (from reference [59])......	32
Figure 2-16.	Total and partial electronic density of states for combined defect $\text{VO}^{\cdot\cdot} + \text{Sn}_{\text{Sn}}''$ in SnO_2 . Sn_{nn} and O_{nn} are tin and oxygen atoms neighboring the vacancy. Gray lines indicate position of the highest occupied state. Blue curves are s, red are p, and green are d states (from reference [59])......	34
Figure 2-17.	Charge density plots for $\text{VO}^{\cdot\cdot} + \text{Sn}_{\text{Sn}}''$ in SnO_2 . (a) Partial charge density from -10 eV to the defect state at contour levels from 0 (blue) to $0.3 \text{ e}/\text{\AA}^3$ (red). (b) Charge density difference between VB of bulk and defective cell at contour levels between -0.1 (red) and $0.1 \text{ e}/\text{\AA}^3$ (blue). (c) Partial charge density of defect state at contour levels between 0 (blue) and $0.05 \text{ e}/\text{\AA}^3$ (red) (from reference [59]).	35
Figure 2-18.	Carrier concentration, Hall mobility, and conductivity between 80 K and 625 K for CVD prepared SnO_2 signal crystal sample (from reference [75]).	37
Figure 2-19.	Electrical transport properties of SnO_2 thin films with different thicknesses as a function of inverse absolute temperature; (a)	

LIST OF FIGURES

	conductivity, (b) electron concentration, (c) mobility, and (d) response to hydrogen (from reference [76])......	38
Figure 2-20.	UV absorption coefficient in SnO ₂ single crystals versus photon energy for radiations polarized parallel and perpendicular to the <i>c</i> axis (from reference [58])......	40
Figure 2-21.	(a) Temperature dependence PL spectra of SX emission from 77 K to 300 K. (b) Evolution of SX emission peak energy with temperature. (c) Dependence of SX emission peak intensity on the reciprocal of temperature (from reference [82])......	41
Figure 2-22.	Schematic diagram of surface localized exciton recombination process and evolution of peak energy with excitation intensity. The arrows indicate the radiative recombination process of surface localized exciton (SX) and free exciton (FX) in different areas of SnO ₂ nanocrystal; SX occurs at the close surface region and FX occurs at the core of the nanocrystals (from reference [82])......	42
Figure 2-23.	Decrease of the resistivity achieved for TCO materials (from reference [91]).	44
Figure 2-24.	Optical transmission spectra of SnO ₂ films with different conductivities (from reference [92])......	45
Figure 2-25.	Schematic density of states with fully spin-polarized (a) conduction band (b) valence band and (c) impurity band (from reference [135]).	51
Figure 2-26.	Schematic band structure of the three different models for exchange mechanism in 3d metal doped SnO ₂ . (a) Impurity band exchange (b) RKKY exchange and (c) Two-electron defect-center exchange (from reference [17]).	52
Figure 2-27.	Magnetic polarons formed in the oxide based DMS. The overlap between the hydrogenic electron and the cations within its orbit leads ferromagnetic exchange coupling. Cation sites are represented by small circles. Oxygen is not shown; the oxygen vacancies are represented by squares (from reference [136])......	53
Figure 3-1.	Schematic diagram of a PLD system. (from reference [138])	56

LIST OF FIGURES

Figure 3-2.	(a) Schematic view of the RHEED geometry. (b) Typical RHEED pattern from a single crystal substrate [140].	57
Figure 3-3.	Schematic illustration of an ellipsometric experiment, showing the polarized light reflected by the surface of the measured sample.	63
Figure 4-1.	(a) XRD 2θ - ω scan of SnO ₂ thin film deposited on (10 $\bar{1}2$) sapphire substrate. (b) XRD phi scans of SnO ₂ thin film and sapphire substrate for the film deposition on (10 $\bar{1}2$) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.	71
Figure 4-2.	ω -scan (rocking curve) of the SnO ₂ (101) peak for SnO ₂ film on (10 $\bar{1}2$) sapphire substrate.	72
Figure 4-3.	(a) <i>in-situ</i> RHEED pattern and (b) <i>ex-situ</i> AFM topography image of the SnO ₂ thin film on (10 $\bar{1}2$) sapphire substrate.	73
Figure 4-4.	(a) XRD 2θ - ω scan of SnO ₂ thin films deposited on (0001) sapphire substrate. (b) XRD phi scans of SnO ₂ thin film and sapphire substrate for the film deposition on (0001) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.	75
Figure 4-5.	ω -scan (rocking curve) of the SnO ₂ (200) peak for SnO ₂ thin film on (0001) sapphire substrate.	77
Figure 4-6.	(a) <i>in-situ</i> RHEED pattern and (b) <i>ex-situ</i> AFM topography result of the SnO ₂ thin film on (0001) sapphire substrate.	78
Figure 4-7.	(a) XRD 2θ - ω scan of SnO ₂ thin film deposited on (10 $\bar{1}0$) sapphire substrate. (b) XRD phi scans of SnO ₂ thin film and sapphire substrate for the film deposition on (10 $\bar{1}0$) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.	79
Figure 4-8.	ω -scan (rocking curve) of the SnO ₂ (002) peak for SnO ₂ film on (10 $\bar{1}0$) sapphire substrate.	80
Figure 4-9.	(a) <i>in-situ</i> RHEED pattern and (b) <i>ex-situ</i> AFM topography result of the SnO ₂ thin film on (10 $\bar{1}0$) sapphire substrate.	81
Figure 4-10.	RHEED patterns of (a) STO (111) substrate, (c) as deposited SnO ₂ thin film, and their corresponding AFM images of (b), (d).	86
Figure 4-11.	XRD patterns of the SnO ₂ thin films fabricated under different growth conditions. (a) $T_{\text{Sub}} = 600\text{ }^{\circ}\text{C}$, P_{Oxy} varied from 1 Pa to 10^{-3} Pa. (b)	

	$T_{\text{Sub}} = 700\text{ }^{\circ}\text{C}$, P_{Oxy} varied from 1 Pa to 10^{-3} Pa. (c) $T_{\text{Sub}} = 750\text{ }^{\circ}\text{C}$, P_{Oxy} varied from 1 Pa to 10^{-3} Pa.	88
Figure 4-12.	(a) 2θ - ω scan result of optimized SnO_2 thin film on STO (111), with rocking curve inserted. (b) symmetric XRD mapping to SnO_2 (200) plane and STO (111) plane.	89
Figure 4-13.	XRD phi scan results of SnO_2/STO structure: (a) (110) plane of SnO_2 , (b) (110) plane of STO. The diffraction peak index and tilt angle are indicated for each measurement.	90
Figure 4-14.	Comparison of crystal structures of (a) STO (111) plane, and (b) SnO_2 (100) plane.	91
Figure 4-15.	Cross-sectional TEM image of SnO_2/STO heterostructure. (a) low magnification image and (b) high-resolution TEM image on the interface region. (c) SAED pattern of SnO_2/STO	93
Figure 4-16.	Comparison of the measured (points) and the best fit (solid line) to the ellipsometric parameters (Ψ, Δ) of the SnO_2 thin film with a 150 nm thickness deposited on STO substrate using the structural model illustrated in Figure 4-17. (for a clear presentation, only the fittings for the incident angles of 65° and 70° are shown).....	95
Figure 4-17.	The extracted dielectric functions $\varepsilon(E) = \varepsilon_r(E) + i\varepsilon_i(E)$ of the SnO_2 thin film on STO substrate. The inset is a schematic structure of the double layer model for the data fitting.	97
Figure 4-18.	The RHEED intensity oscillation of STO epilayer growth with the RHEED pattern (inset).	101
Figure 4-19.	2θ - ω XRD result for the as fabricated 150- SnO_2/STO heterostructure. The insets I and II show the rocking curve and RHEED pattern of SnO_2 layer, respectively.	102
Figure 4-20.	XPS spectra of all three samples. VB (a) in 150- SnO_2/STO and (c) in STO-epi, Sn 3d CL (b) in 150- SnO_2/STO and (f) in 5- SnO_2/STO , Ti2p CL (d) in STO-epi and (e) in 5- SnO_2/STO	104
Figure 4-21.	Schematic energy band diagram of the SnO_2/STO heterostructure, in which a type-II alignment is indicated.	106

LIST OF FIGURES

Figure 5-1.	(a) XRD 2θ - ω scan results of Sample S1, S2, and S3. (b) ω -scan (rocking curve) of the Sample S1, S2, and S3.....	112
Figure 5-2.	Temperature dependence of resistivity in (002)- and (200)-orientated SnO ₂ thin films on different substrates.....	114
Figure 5-3.	(a) Arrhenius plot of the resistivity data of Samples S1, S2, and S3. (b) Mott VRH plot of the resistivity data of Samples S1, S2, and S3...	118
Figure 5-4.	Crystal structure of rutile SnO ₂	120
Figure 5-5.	AFM image of high temperature treated sapphire (10 $\bar{1}2$) substrate (2 $\times$ 2 μm^2). The vertical profile was taken along the line shown in the image, which indicates an atomically flat surface with uniform atomic steps. The observed step height is 0.35 nm, which corresponds to the interplanar spacing of (10 $\bar{1}2$) planes.	125
Figure 5-6.	XRD patterns of SnO ₂ :Sb film on sapphire (10 $\bar{1}2$) substrate. The inset shows the <i>in-situ</i> RHEED pattern of the as-deposited film.....	126
Figure 5-7.	AFM images (2 $\times$ 2 μm^2) of the SnO ₂ :Sb thin films with thickness of: (a) 3.1 nm, (b) 7.9 nm, (c) 31.3 nm and (d) 188 nm, respectively. .	127
Figure 5-8.	Semilogarithmic plot of the temperature-dependent resistivity of SnO ₂ :Sb thin films with varied film thickness.	128
Figure 5-9.	XPS results of the SnO ₂ :Sb films with different thicknesses in the binding energy ranging from -2 to 16 eV. For comparison, the VB spectrum of pure sapphire substrate is also presented. The substrate effect on the VBM denotation and conduction band electron measurement of the SnO ₂ :Sb thin films can be neglected due to little contribution from sapphire below 7 eV.....	129
Figure 5-10.	Core level Sb 3d _{3/2} XPS spectra of SnO ₂ :Sb thin films (filled squares) with different thicknesses: A: 188 nm, B: 31.3nm, C: 7.9nm, and D: 3.1nm. The spectra were fitted to a Shirley background (green solid line) together with the Voigt profiles for Sb(V) (blue dot dash line) and Sb(III) (red dash line). The fitting curves (black solid line) are seen to match well with the experimental data points. The denotation exp., fit., and bg. represent the experimental data, fitting curve, and back ground, respectively.....	132

Figure 5-11.	The E_g of different thickness $\text{SnO}_2\text{:Sb}$ thin films as extracted from the XPS VB spectra. The dash line shows the least-squares fit to a power-law function: $E_g = 3.2 + 2.4/t^{1.16}$, from which a remarkable quantum confinement effect is revealed.....	133
Figure 5-12.	The schematic diagram for the conduction band filling and band alignment in XPS VB measurements for the metallic and insulating $\text{SnO}_2\text{:Sb}$ thin films.....	134
Figure 5-13.	(a) XRD patterns of SnO_2 thin films annealed at different temperatures. (b) Grain size of SnO_2 thin films as a function of the annealing temperature.	141
Figure 5-14.	Carrier concentration and resistivity of SnO_2 thin films versus the annealing temperature.	142
Figure 5-15.	(a) XPS Sn $3d_{5/2}$ and O 1s spectra obtained from the SnO_2 thin films annealed at different temperatures. (b) The $\text{O}_{[2]}/\text{O}_{[1]}$ and Sn/O intensity ratios extracted from Sn $3d_{5/2}$ and O 1s spectra as a function of annealing temperature.....	145
Figure 6-1.	(a) XRD patterns of the $\text{Sn}_{1-x}\text{Fe}_x\text{O}_{2-\sigma}$ bulk samples as x varied from 0.00 to 0.25. (b) Fe doping concentration dependence of the d-spacing of (200) plane calculated from the SnO_2 (200) peaks in (a).....	152
Figure 6-2.	(a), (b) and (c) show the low-magnification TEM image and its corresponding element mappings of Sample $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$, respectively. (d) gives the typical HRTEM image, and (e) presents the SAED pattern.	154
Figure 6-3.	(a) XPS survey spectrum of bulk Sample $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$. (b), (c) and (d) present the core-level Sn 3d, O 1s and Fe 2p spectra, respectively. The spectra are fitted to a Shirley background (green dot line) together with the Voigt profiles. The fitting curves are seen to match well with the experimental data points.....	157
Figure 6-4.	(a) M vs H data of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ bulk sample measured at room temperature. (b) M vs H curve of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ after subtracting the paramagnetic response.	159

LIST OF FIGURES

Figure 6-5.	XRD patterns of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ thin films, S1 and S2 deposited on sapphire (0001) and (10 $\bar{1}$ 0) substrates, respectively.	160
Figure 6-6.	(a) Room-temperature M vs H data of Sample S1. (b) Room-temperature M vs H data of Sample S2.	162
Figure 6-7.	XRD patterns of the bulk polycrystalline samples of Fe_5Mg_2 , Fe_5Sb_2 and Fe_5	167
Figure 6-8.	(a), (b), (c) and (d) show the low-magnification TEM image and its corresponding element mappings of sample Fe_5Mg_2 . (e), (f), (g) and (h) show the low-magnification TEM image and its corresponding element mappings of sample Fe_5Sb_2 . (i) and (j) are the typical HRTEM images of Fe_5Sb_2 and Fe_5Mg_2 . (k) and (l) are the SAED patterns corresponding to Fe_5Sb_2 and Fe_5Mg_2	168
Figure 6-9.	(a) M vs H data of Sample Fe_5Mg_2 , Fe_5Sb_2 and Fe_5 measured at 300 K. (b) M vs H curve after subtracting the paramagnetic response for the sample Fe_5Mg_2 , Fe_5Sb_2 and Fe_5 measured at 300 K.	171
Figure 6-10.	XRD patterns of TF: Fe_5 , TF: Fe_5Sb_2 and TF: Fe_5Mg_2 . The dashed line is a reference for viewing the shift of diffraction peaks.	172
Figure 6-11.	Room-temperature M vs H data of thin film samples TF: Fe_5 , TF: Fe_5Sb_2 and TF: Fe_5Mg_2	173
Figure 6-12.	(a) Core-level Fe 2p XPS spectra of bulk Sample Fe_5Mg_2 , Fe_5Sb_2 and Fe_5 . The spectra were fitted to a Shirley background (green dot line) together with the Voigt profiles for Fe^{2+} (dash line), Fe^{3+} (dash dot line), Sn 3p (dash line) and Fe 2p satellite (short dot line). The fitting curves (solid line) are seen to match well with the experimental data points. (b) VB spectra of the Samples Fe_5Mg_2 , Fe_5Sb_2 and Fe_5	175
Figure 6-13.	Schematic diagrams of band structure of semiconductors in different doping cases.	177
Figure 6-14.	The schematic diagram of the band alignment in XPS VB measurements for a semiconductor.	178

LIST OF TABLES

Table 2-1.	Surface energies of stoichiometric SnO ₂ surface in (J m ⁻²).	13
Table 2-2.	Tin oxide based sensors.....	47
Table 2-3.	Metal oxide based diluted magnetic semiconductors.....	50
Table 4-1.	Parameters of the SnO ₂ thin film extracted from the best fitting to ellipsometry experimental data by TL-Drude model.	96
Table 4-2.	Binding energies of the XPS CLs and VBM for all the three samples.	105
Table 5-1.	Thickness t , valence band maximum (VBM), room temperature electron concentration (N_{300K}), conduction band filling (E_{fill}) and energy band gaps (E_g) for the four SnO ₂ :Sb films with different thickness.	130
Table 6-1.	Lattice parameters (a and c), cell volume (V), saturation magnetization (M_s), net contribution (Bohr magneton) per Fe atom and Fe ³⁺ to Fe ²⁺ ratio (Fe ³⁺ /Fe ²⁺).....	167

LIST OF ABBREVIATIONS

a_B	Bohr radius
AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
BM	Burstein-Moss
CB	Conduction Band
CBM	Conduction Band Minimum
CBO	Conduction Band Offset
CL	Core Level
CVD	Chemical Vapor Deposition
DFT	Density Functional Theory
DMS	Diluted Magnetic Semiconductor
DOS	Density of State
E_A	Activation Energy
EDAX	Energy Dispersive X-ray Analysis
EELS	Electron Energy Loss Spectroscopy
E_f	Fermi Level
E_g	Energy Band Gap
EMA	Effective Medium Approximation
FET	Field Effect Transistor
FWHM	Full Width Half Maximum

LIST OF ABBREVIATIONS

FX	Free Exciton
GGA	Generalized Gradient Approximation
HCP	Hexagonal Close Packing
HRTEM	High Resolution Transmission Electron Microscopy
k_B	Boltzmann constant
LMBE	Laser Molecular Beam Epitaxy
MBE	Molecular Beam Epitaxy
MIT	Metal-Insulator Transition
M_s	Saturation Magnetization
n_c	Mott Critical Density
PAMBE	Plasma-Assisted Molecular Beam Epitaxy
PL	Photoluminescence
PLD	Pulsed Laser Deposition
PPMS	Physical Property Measurement System
RHEED	Reflection High-energy Electron Diffraction
RMS	Root Mean Square
RTFM	Room Temperature Ferromagnetism
SAED	Selected Area Electron Diffraction
SE	Spectroscopic Ellipsometry
STO	SrTiO ₃
STM	Scanning Tunneling Microscope
SX	Surface-localized Exciton
T_c	Curie Temperature
TCO	Transparent Conductive Oxide

LIST OF ABBREVIATIONS

TEM	Transmission Electron Microscopy
TL	Tauc Lorentz
UV	Ultraviolet
UHV	Ultra-High Vacuum
VB	Valence Band
VBM	Valence Band Maximum
VBO	Valence Band Offset
VSM	Vibrating Sample Magnetometer
VRH	Variable Range Hopping
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

CHAPTER 1 INTRODUCTION

1.1 Motivation

Within the class of inorganic materials, metal oxides display perhaps the most diverse range of functionality. The fascinating properties of metal oxides continue to inspire and drive materials scientists to master both understanding and synthesis of the materials, with the goal of exploiting these properties in applications. As a well known wide energy band gap semiconducting metal oxide, SnO_2 based materials combine high electrical conductivity with optical transparency in the visible range of optical spectrum and thus constitute an important component for optoelectronic applications. These properties have been investigated in a number of applications, notably as electrode materials in solar cells [1,2], light emitting diodes [3-6], flat panel displays [7], and other optoelectronic devices where an electrical contact needs to be made without obstructing photons from either entering or escaping the optical active area. Gas sensor is another important application of SnO_2 . Over the past

decades, a great deal of research effort has been dedicated to the development of miniature gas sensing devices, particularly for toxic gas detection and for pollution monitoring. Solid state metal oxides offer a wide spectrum of materials and sensitivity selections for different gaseous species, making it a better choice over other options. Among the materials studied for gas-sensing, SnO₂ dominates over other metal oxides and has been extensively studied. Its gas sensing properties have been widely reported in literatures. The well-known advantages of this material include low cost and high sensitivity for different gas species. A large number of methods, such as doping, surface treatment, nanotechnology, have been employed to improve its response time, operation temperature, selectivity, and so on [8-10].

Recently, a new research area, metal oxide based diluted magnetic semiconductor (DMS), arose dramatically and attracted intensive research interest [11-15]. Perhaps one of the most surprising and potentially significant claims made in magnetism is that nonmagnetic semiconductors and insulators such as ZnO or TiO₂ become ferromagnetic at and/or above room temperature when doped with just a few percent of a transition-metal cation such as V, Cr, Mn, Fe, Co or Ni. As a wide energy band gap, multi-functional oxide semiconductor material, SnO₂ based DMS is becoming one of the most important host systems for 3d elements, after the first report on high temperature ferromagnetism in SnO₂ thin film published by S. B. Ogale *et al.* in 2003 [14]. In S. B. Ogale's work, 5% Co-doped SnO₂ thin film exhibited ferromagnetism with a Curie temperature of 650K and astonishingly large moment of 7.5 μ_B per Co ion. After that, a series of work on realization of ferromagnetism in SnO₂ by doping with 3d transition elements, such as, Fe, Cr, and Ni, has been reported [16-18].

As mentioned in the foregoing discussion, SnO_2 is such a unique material, in which, gas sensing effect, optical transparency, semiconductivity, and ferromagnetism can be combined simultaneously. Intensive and continuous research interests on this material are motivated by its applications as a solid state gas sensor, transparent conductor, oxidation catalyst, and promising candidate material for spintronic device. Since the thin film is one of the most common forms in the applications of SnO_2 based materials, the fabrication of SnO_2 thin films is extensively studied in this dissertation. Although polycrystalline oxide films have plentiful properties for applications and have been studied extensively, the epitaxial growth of highly crystalline films is attracting more and more attention recently, due to their superior properties for oxide electronics applications and for fundamental studies. Accordingly, the fabrication of SnO_2 in this dissertation is focused on the epitaxial growth of SnO_2 and its based materials using our laser molecular beam epitaxy (LMBE) system. The electrical transport properties of the SnO_2 thin films fabricated by LMBE are systemically investigated.

In most applications, SnO_2 is modified by additives to either increase the charge carrier concentration by donor atoms, or incorporates ferromagnetic property by 3d transition elements doping. The effect of doping and oxygen defects on transport behavior, optical property, and band structure should be systematically studied. Furthermore, for the unexpected high temperature ferromagnetism in 3d element doped SnO_2 , its mechanism is still an open question. There are many disagreements among the results reported in different research groups [14,19-21]. Another motivation of this project is to explore the ferromagnetism in $\text{SnO}_2\text{:Fe}$ based DMS

samples. The effects of crystal orientation and carrier doping on the ferromagnetism of $\text{SnO}_2\text{:Fe}$ based DMS are comprehensively investigated.

1.2 Objectives

Driven by above motivations, the goal of this dissertation is to achieve epitaxial growth of SnO_2 thin films using LMBE technique and to investigate their electrical transport/magnetic properties. The primary objectives include:

1. To epitaxially deposit SnO_2 thin films on sapphire substrates using LMBE technique.

Differently orientated sapphire single crystal substrates were used to get crystal orientation controlled epitaxy of SnO_2 thin films. Detailed structural information and epitaxial relationship were investigated by X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED).

2. To study the epitaxial growth of SnO_2 on perovskite structural substrate.

The epitaxial growth of SnO_2 on perovskite structural substrate such as SrTiO_3 (STO) may open a way to integrate these two multifunctional materials together and to explore new applications. The deposition conditions were varied to obtain the optimum parameters to fabricate high quality epitaxial thin

film on (111) STO substrate. Epitaxial relationships and microstructure were investigated by XRD and transmission electron microscopy (TEM), respectively. The optical property of SnO_2/STO , i.e. its dielectric function in the optical range, was studied by ellipsometry. Using X-ray photoelectron spectroscopy (XPS), the energy band alignment between SnO_2 and STO was quantitatively determined.

3. To extensively study the electrical transport properties of SnO_2 thin films deposited by LMBE technique.

As one of the most important properties of SnO_2 , the electrical transport behavior attracted long-term research interests, and has been utilized in many applications. In this dissertation, the electrical transport properties of SnO_2 thin films were extensively investigated, which include: (a) the crystal orientation effect, (b) thickness effect, and (c) thermal annealing effect.

4. To explore the ferromagnetism in the $\text{SnO}_2:\text{Fe}$ based DMS materials.

The magnetic properties of Fe-doped SnO_2 were investigated in the form of both polycrystalline bulk and single crystal thin film. The crystal orientation effect on the ferromagnetism in $\text{SnO}_2:\text{Fe}$ epitaxial thin films was studied. The carrier doping (electron- and hole-doping) tuned ferromagnetism in $\text{SnO}_2:\text{Fe}$ based DMS was comprehensively investigated.

1.3 Major contributions

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

1. Using differently orientated sapphire substrate, i.e. the $(10\bar{1}2)$, (0001) , and $(10\bar{1}0)$ sapphire substrates, the crystal orientation controlled epitaxial growth of SnO_2 thin films was achieved. The single crystallinity of the SnO_2 thin films was confirmed by XRD and RHEED results. Comprehensive XRD characterizations revealed the in-plane epitaxial relationships between SnO_2 films and the sapphire substrates. The surface morphology was investigated by atomic force microscopy (AFM), from which smooth surface was observed in all three differently orientated SnO_2 thin films.
2. SnO_2 thin films were epitaxially deposited on the (111) plane of STO single crystal substrate, which was believed to be the first report of epitaxial growth SnO_2 on perovskite substrate. Detailed analyses with *in-situ* RHEED, *ex-situ* XRD, AFM and TEM confirm the possibility of epitaxial growth of SnO_2 on perovskite substrate under a wide range of deposition conditions, despite of the large lattice mismatch and hetero structure between the films and substrate. The optimum deposition parameters for SnO_2 thin film on STO were found to be $T_{\text{Sub}} = 700\text{ }^\circ\text{C}$ and $P_{\text{Oxy}} = 10^{-2}\text{ Pa}$. The epitaxial relationship between SnO_2 and STO was also determined according to XRD characterizations.
3. A TL-Drude model was developed to describe the dielectric function of SnO_2

thin film on STO in the UV-Vis-NIR range, and this model fitted the ellipsometry data very well. The energy band alignment between SnO₂ and STO has also been quantitatively determined using XPS.

4. Crystal orientation affected in-plane electrical transport property was observed in SnO₂ epitaxial thin films. This orientation controlled electrical conduction behavior can be understood on the basis of the anisotropic crystal structure of rutile SnO₂.
5. SnO₂:Sb based conductive oxide thin films were fabricated on sapphire substrate using LMBE. By precisely controlling the laser ablation counts, thickness effect on the electrical transport behavior of SnO₂:Sb thin films was studied. A thickness induced metal-insulator transition (MIT) was observed from the electrical transport measurement, and was further confirmed by the XPS valence band (VB) study. This transition was attributed to the oxidation state variation of Sb from Sb(V) to Sb(III), which was revealed by XPS core level analyses.
6. The influence of thermal annealing on the structure and electrical transport properties of LMBE deposited SnO₂ thin films were investigated using the XRD, Hall measurement, and XPS. By varying the annealing temperature, an anomalous electrical transport behavior of the SnO₂ thin films was observed and explained by the crystal grain size growth and annealing temperature dependent oxygen vacancy density variation.

7. $\text{SnO}_2\text{:Fe}$ based DMS materials in the form of both polycrystalline bulk and epitaxial thin film were fabricated, in which prominent RTFM was observed. Using crystal orientation control technique, magnetic anisotropy was observed in (200)- and (002)-orientated $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ thin films which were deposited on sapphire (0001) and (10 $\bar{1}$ 0) substrates, respectively. This crystal orientation dependent ferromagnetism suggests that the ferromagnetism in $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ unlikely originates from Fe clusters or magnetic secondary phase.
8. Carrier doping (electron- and hole-doping) effect on the magnetic property of $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ by varying the dopant M (Sb/Mg) was comprehensively studied. A prominent carrier doping tuned ferromagnetism is observed, i.e., the saturation magnetization (M_s) was decreased by electron-doping and was increased in the case of hole-doping. XPS results demonstrated that the concentration of high spin state Fe ions [Fe(III)] increased in the hole- (Mg) doped sample and decreased in the electron- (Sb) doped one. The oxidation state transition of Fe and carrier type variation are believed to be responsible for the carrier doping tuned ferromagnetism in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$.

1.4 Organization

This dissertation emphasizes on the epitaxial growth of SnO₂ thin films by LMBE, as well as the extensive studies on the electrical transport and magnetic properties of SnO₂ based materials. The dissertation is organized as follows:

In **Chapter 1**, the motivations for epitaxial growth and characterization study of SnO₂ thin films are explained. Then, the objectives, major contributions, and organization of the thesis are presented.

Chapter 2 is devoted to discussions on the fundamental knowledge and related literature review with respect to the fabrications, properties and applications of SnO₂. The fundamental basis for the work and proposals of this dissertation are also provided in this chapter.

In **Chapter 3**, the experimental methods used in this research work are presented. The working principle of LMBE technique for the preparation of SnO₂ thin films and the material characterization methods used in this project are described in detail.

Chapter 4 presents the investigation of epitaxial growth of SnO₂ thin films by LMBE technique. Firstly, crystal orientation controlled epitaxy of SnO₂ thin films were achieved on the sapphire single crystal substrates. Detailed epitaxial relationship was determined by XRD characterizations. The second section of this chapter provides the epitaxial growth of SnO₂ thin film on (111) STO substrate. The optimum deposition

conditions, crystal structure, and optical dielectric function were studied. The last section presents the energy band alignment between SnO_2 and STO, which is measured by XPS.

Chapter 5 focuses on the study of electrical transport property of SnO_2 thin films. A crystal orientation dependent electrical transport behavior in SnO_2 thin films was observed. This orientation dependence is attributed to the anisotropic crystal structure of SnO_2 . The second section presents a thickness induced MIT in $\text{SnO}_2\text{:Sb}$ based conductive oxide thin films. The last section in Chapter 5 studies the thermal annealing effect on the electrical transport property of SnO_2 thin films deposited on quartz substrate.

Chapter 6 gives a comprehensive investigation on the ferromagnetism in $\text{SnO}_2\text{:Fe}$ based DMS materials. Two sections are included in this chapter. The first one presents the study on the ferromagnetism of $\text{SnO}_2\text{:Fe}$ in the form of both polycrystalline bulk and epitaxial thin films. The second section shows the study of carrier doping (electron and hole) effect on the magnetic properties of $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ by varying the dopant M (Sb/Mg). A prominent carrier doping tuned ferromagnetism was observed, i.e. the M_s was decreased by electron-doping and was increased in the case of hole-doping.

Finally, the conclusions and recommendations are presented in **Chapter 7**.

CHAPTER 2 LITERATURE REVIEW

In this chapter, the fundamental knowledge and related literature review with respect to the fabrications, properties and applications of SnO_2 are presented. This chapter also provides an extensive fundamental basis for the work and proposals of this dissertation. It is organized as follows: The first section provides the background and underlying principles related to fabrication of SnO_2 epitaxial thin films, and reviews the current state of epitaxial growth of SnO_2 on different substrates. The second section gives a brief summary on the properties, i.e. electronic structure, electrical transport properties and optical properties of SnO_2 , and its applications such as transparent conducting oxides (TCOs) and gas sensor. The last section provides the background and principle of the SnO_2 based DMS which is an emerging topic in recent years.

2.1 Epitaxial growth of SnO₂ thin films

Oxides display a wide range of functionality in inorganic materials. The interplay between localized and itinerant character yields metal oxide materials a lot of interesting electronic properties. Attracted by the applications and fundamental studies, significant efforts have been made to the growth of single crystalline oxides thin films [22]. For SnO₂, there have been several efforts to fabricate epitaxial thin films on various substrates, using techniques such as: pulsed laser deposition (PLD) [23], reactive r.f. sputter deposition [24], molecular beam epitaxy (MBE) [25], atomic layer deposition (ALD) and chemical vapor deposition (CVD) [26].

2.1.1 Epitaxial potential of SnO₂

As a mineral, SnO₂ is also called cassiterite. It possesses the rutile structure, [tetragonal structure, with a space group symmetry of D_{4h}^{14} ($P4_2/mnm$)] [27] as several other metal oxides, e.g. TiO₂, RuO₂, GeO₂, VO₂, and CrO₂. Under pressure, SnO₂ also exists as an orthorhombic high-pressure phase which is slightly denser than the rutile phase. Figure 2-1 shows the bulk unit cell of SnO₂. Large red balls represent oxygen atoms and light gray balls are tin atoms. It consists of SnO₆ octahedra that are connected via opposite edges along the rutile *c*-axis.

Figure 2-1. Crystal structure of SnO_2 (cassiterite, isostructural with rutile).

In bulk SnO_2 single crystal, the naturally occurring growth faces are (110), (101) [equivalent to (011)], and (100) [equivalent to (010)]. For these bulk terminated SnO_2 surface, i.e. surfaces with surface-tin atoms in their bulk Sn (IV) oxidation state, the (110) surface exhibits the lowest energy surface followed by the (100), (101), and (001) surfaces. The surface energies of low index SnO_2 surface with a termination that maintains the bulk composition have been calculated. Table 2-1 shows the results of these theoretical calculations.

Table 2-1. Surface energies of stoichiometric SnO_2 surface in ($\text{J}\cdot\text{m}^{-2}$).

Surface	B3LYP [28]	GGA [29]	LDA [30,31]	GGA [32]
(110)	1.20	1.04	1.30-1.40	1.21
(100), (010)	1.27	1.14	1.66-1.65	1.29
(101), (011)	1.43	1.33	1.55	1.60
(001)	1.84	1.72	2.36	-

The fact that the (110) surface is the lowest energy surface can be appreciated by investigating the crystallographic orientations of the bulk termination of single crystals. Figure 2-2 shows the photograph of a single crystal grown by a vapor phase transport technique. As it can be seen in the picture, the {110} surfaces make up the majority of the surface area followed by the {101} faces and small {100} faces. No {001} faces are observed. Although this crystal does not necessarily represent an ideal crystal one would obtain from a Wulff's construction, it nevertheless clearly demonstrates the preferential terminations of a SnO_2 single crystal.

Figure 2-2. Photograph of a SnO_2 single crystal grown by a vapor phase transport technique. (from reference [33])

Different from the growth of bulk single crystal, the fabrication of single crystalline thin films (epitaxial growth) can be artificially controlled using different substrates and deposition parameters. In the process of epitaxial growth, the substrate acts as a seed crystal, the deposited film takes on a lattice structure and orientation identical to those of the substrate. As a result, the substrate selection and surface treatment are

critical steps in any attempt at producing epitaxial SnO₂ films. Film/substrate lattice mismatch, thermal expansion match, and chemical compatibility are the most relevant factors when the only consideration is film property. SnO₂ has a tetragonal, rutile structure with lattice constants of $a = b = 4.74 \text{ \AA}$ and $c = 3.19 \text{ \AA}$ [27]. Favorable heteroepitaxy could be expected for growth on another rutile-structured material with similar lattice constants. The rutile phase of titania, TiO₂, represents such a material with lattice constants of $a = b = 4.59 \text{ \AA}$ and $c = 2.96 \text{ \AA}$. However, for planar applications, e.g. gas sensor and photodetector, it would be preferable to have a substrate much less conductive than the SnO₂ films. TiO₂ has semiconducting properties similar to SnO₂ and is therefore a less promising candidate for a device substrate. Sapphire, however, is an especially desirable material since it is not only electrically insulating, but also quite inert chemically, and therefore should not interfere with the electrical action of SnO₂ overlayers. Furthermore, the high thermal conductivity, low absorption in light transmission, and high quality of sapphire substrate will be beneficial for thin film growth, as well as for optical, electrical, and magnetic properties measurements. On the other hand, motivated by the requirements of STM investigation and other vertical study of electrical transport properties of SnO₂ thin film, a metal, platinum, was also used as a substrate for SnO₂ epitaxy. The growth on those three substrates is summarized in the following.

Knowledge of the relevant phase diagrams provides information about the epitaxial problems that would limit the material quality. Non-stoichiometric material or unwanted impurities due to solid solubility prevent high-quality single phase films. Figure 2-3 shows the reported phase diagrams of the Sn-O system.

Figure 2-3. Sn-O phase diagram (from reference [34]).

According to the Sn-O phase diagram (Figure 2-3), the SnO, which is formed by a $(\beta\text{Sn}) + (\text{Sn}_3\text{O}_4) \rightarrow \text{SnO}$ peritectoid reaction, exists in its stable state from 298 K up to about 543 K. It can also be noticed that the triclinic Sn_3O_4 is a stable compound between 410 K and 730 K. Finally, SnO_2 which adopts a tetragonal symmetry is stable from room temperature to 2273 K. Based on this phase diagram, the most frequently used LMBE growth temperature in this dissertation was 973 K.

Figure 2-4. $\text{SnO}_2\text{-Al}_2\text{O}_3$ phase diagram (from reference [35,36]).

Figure 2-4 presents the phase diagram of $\text{SnO}_2\text{-Al}_2\text{O}_3$ system. It is worthy to note that the eutectic reaction between SnO_2 and Al_2O_3 happens when the temperature is higher than 1893 K. The maximum LMBE growth temperature used in this dissertation was 1023 K. Therefore, the Al_2O_3 and SnO_2 should not mix when depositing the SnO_2 thin film on Al_2O_3 substrate, for all growth conditions.

2.1.2 SnO_2 on TiO_2

TiO_2 is isostructural to SnO_2 , and possesses the similar lattice constants as SnO_2 . Accordingly, TiO_2 can serve as the substrate for the epitaxy of SnO_2 with different orientations. Till now, SnO_2 thin films have been grown on the (100) [37-39], (110) [24,40,41], and (001) [42] planes of rutile TiO_2 substrates. Although SnO_2 and TiO_2

have the same structure, the lattice constant mismatch is still substantial between these two materials:

$$(a_{\text{SnO}_2} - a_{\text{TiO}_2})/a_{\text{TiO}_2} = (4.74 - 4.59)/4.59 = 3.3\%$$

$$(c_{\text{SnO}_2} - c_{\text{TiO}_2})/c_{\text{TiO}_2} = (3.19 - 2.95)/2.95 = 7.7\%$$

Consequently the interface between substrate and film has to accommodate this lattice mismatch. The schematic drawings of the surface unit cells of TiO_2 substrate are shown in Figure 2-5 along with in-plane structure of several low index SnO_2 planes.

Figure 2-5. Schematic diagrams of the surface unit cells for various low index SnO_2 crystalline planes as well as the TiO_2 substrate. All dimensions indicated are in angstroms.

Due to the large lattice mismatch between SnO_2 and TiO_2 , the possibility of heteroepitaxial growth is still obscure. For SnO_2 (100)/ TiO_2 (100) epitaxy, high resolution TEM, RHEED, and AFM have been employed to investigate the defects structure and surface morphology [38]. The misfit-induced large biaxial compressive stress in the SnO_2 thin film was almost fully relaxed to yield high-density interfacial

misfit dislocations and related planar defects, when the thickness of thin films surpass 200 nm. Illustrated in Figure 2-6 (a), this [010] cross-sectional HRTEM image of SnO₂ film shows that the film contains high density dislocations at the interface, due to the relaxation of the lattice mismatch between $b_{\text{SnO}_2} = 4.75 \text{ \AA}$ and $b_{\text{TiO}_2} = 4.59 \text{ \AA}$, and a wedge-shaped planar defect existing on two crystallographically equivalent (101) and ($\bar{1}01$) planes. The interfacial dislocations were classified into two types: partial edge dislocations with Burgers vectors of $\mathbf{b} = 1/2[101]$ or $\mathbf{b} = 1/2[\bar{1}01]$ involving ($\bar{1}01$) or (101) anti-phase boundaries, respectively; and perfect edge dislocations with Burgers vectors of $\mathbf{b} = [101]$. Figure 2-6 (b) shows the [001] cross-sectional HRTEM image of SnO₂ film. There exist high density of dislocations at the interface and planar defects penetrating the film, due to the large lattice misfit. These observed dislocations were identified as $\mathbf{b} = 1/2[110]$ and $\mathbf{b} = 1/2[\bar{1}10]$ partial edge dislocations accompanying (010) planar defects normal to the film surface, and perfect edge dislocations with Burgers vectors of $\mathbf{b} = [010]$.

Figure 2-6. (a) Cross-sectional HRTEM image of the SnO₂ thin film grown on TiO₂ substrate. The incident electron beam was parallel to the [010] direction. The introduced edge dislocations are indicated by white symbols. (b) [001] cross-sectional HRTEM of SnO₂ film (from reference [38]).

The quality of substrate is one of the crucial parameters for thin film epitaxy. In many cases, attractive substrate materials have been prepared that possess smooth surfaces with only unit cell high steps as revealed by scanning force microscopy [42,43]. Oxide materials of which surface termination and atomic steps have been reproducibly demonstrated are the perovskite-related materials, such as SrTiO_3 , LaAlO_3 and NdGaO_3 . The first work of atomically smooth rutile TiO_2 (110), (100), (001) and (101) surfaces was reported by Yamamoto [44]. By appropriate cleaning and subsequent thermal treatment, ultra smooth TiO_2 substrate with atomic steps can be obtained, as shown in Figure 2-7.

Figure 2-7. AFM images ($1 \times 1 \mu\text{m}^2$) of atomically smooth TiO_2 surface with different orientations after cleaning by organic solvents and subsequent HF treatment. (a) (110) surface annealed at 900 °C, (b) (100) at 900 °C, and (c) (001) at 900 °C. The vertical profiles were taken along the lines in the AFM images. (from reference [44])

The epitaxial growth of SnO_2 on atomically smooth TiO_2 substrate was seldom reported, and the defects behavior of SnO_2 on TiO_2 other planes, such as (110), and (001), are also not very clear till now. Furthermore, due to the intersolubility of TiO_2 and SnO_2 [45], the intermixing at the interface particularly at elevated growth temperature is possible. As a result, the Ti contamination on SnO_2 film should be taken into consideration.

2.1.3 SnO_2 on sapphire

Sapphire (α - Al_2O_3) has a hexagonal structure which is totally different from SnO_2 , but it is still the mostly used substrate for SnO_2 epitaxy, not only because of the fairly low lattice mismatch between SnO_2 and sapphire, but also the sophisticated single crystal growth technique of sapphire and its good physical properties, which usually are beneficial for electrical and optical measurements. SnO_2 films have been grown on sapphire (0001) and on sapphire ($10\bar{1}2$) substrates. In the first case, predominantly (100) oriented SnO_2 thin films were obtained [24,46-48]. Characterized by XRD and HRTEM, the SnO_2 film on sapphire (0001) was found to be single-phase rutile and epitaxial, but showed variant structures. The epitaxial relationship of $\text{SnO}_2(100) // \text{Al}_2\text{O}_3(0001)$ with $\text{SnO}_2[100] // \text{Al}_2\text{O}_3\langle 1\bar{2}10 \rangle$ between the film and substrate was obtained in the microstructure investigation.

Figure 2-8. Plane-view TEM micrograph and SAED pattern of the SnO_2 on sapphire (0001) surface (from reference [48]).

The plane-view TEM micrograph and the corresponding selected-area electron diffraction (SAED) pattern for the film grown on the (0001) surface of sapphire are shown in Figure 2-8. It is clear that the entire film is composed of grains with rectangular shape and 120° relative angle between them. The average width and length of these rectangular grains are different, but both are in the range of about a few tens of nanometers. Diffraction spots are diffused and show streaks in the azimuthal direction, making them somewhat overlapped and less distinguishable. The 60° angle separating streaks in the SAED pattern indicate that the in-plane orientations of grains in the film are not random, but can be classified into six different groups with each having a different but equivalent in-plane orientation.

The main cause for the observed structural variant is the symmetry difference between the substrate and the film. A sapphire (0001) surface has been found to have six equivalent in-plane directions for the deposited SnO_2 to nucleate, so that the initial

rutile (100) islands are expected to nucleate epitaxially in six different in-plane directions and would coalesce into six different variants 60° apart from one another. A crystallographic model has been proposed by Donhang Liu *et al.* to explain the film morphology [48].

Figure 2-9. (a) The crystal structure of the sapphire (0001) plane. (b) Three distinguishable in-plane epitaxial growth orientations by SnO_2 (100) plane packing on sapphire (0001) plane (from reference [48]).

Figure 2-9 gives the crystallographic construction of the possible in-plane epitaxial relationships between the rutile SnO_2 (100) plane and the sapphire (0001) plane. Figure 2-9 (a) shows the surface atom arrangement of sapphire (0001) plane, which has O^{2-} anions in an approximately hexagonal close packing (hcp) arrangement, while cations occupy two-thirds of the octahedral interstices. Three distinguishable epitaxial growth directions which result from SnO_2 (100) plane-packing on sapphire (0001) are shown in Figure 2-9 (b). Based on this model, the three distinct in-plane epitaxial relationships are determined as:

The thickness dependent crystal morphology of SnO₂ on sapphire (0001) fabricated by femtosecond PLD was reported by J. E. Dominguez *et al* [46]. The critical value for appearance of (101) oriented grains is about 60 nm. Furthermore, the electrical transport properties are also strongly dependent on the film thickness.

Most of the efforts of SnO₂ thin film epitaxy were made on the (10 $\bar{1}$ 2) plane of sapphire, a variety of techniques, including reactive sputter deposition [24], PLD [23], pulsed electron beam deposition [49], atomic layer CVD [50,51], and oxygen plasma assisted MBE [25] have been used. For the SnO₂ (101) films on sapphire (10 $\bar{1}$ 2), an epitaxial relationship of $[\bar{1}01]_{\text{SnO}_2} // [101\bar{1}]_{\text{Al}_2\text{O}_3}$ and $[010]_{\text{SnO}_2} // [12\bar{1}0]_{\text{Al}_2\text{O}_3}$ has been determined.

Figure 2-10 shows the ball-and-stick models for the epitaxy of rutile SnO₂ film on sapphire (10 $\bar{1}$ 2) substrate. From this representation, it is apparent that the similar symmetry of SnO₂ (101) and sapphire (10 $\bar{1}$ 2) facilitates this epitaxial growth. However, the lattice mismatch between these two crystal structures is also considerable. Along $[010]_{\text{SnO}_2}$ direction, the lattice constants are very close, with a small misfit of $(\text{SnO}_{2[010]} - \text{Al}_2\text{O}_{3[12\bar{1}0]}) / \text{Al}_2\text{O}_{3[12\bar{1}0]} = (4.74 - 4.76) / 4.76 = -0.2\%$. Along the SnO₂ $[\bar{1}01]$ direction the lattice mismatch with Al₂O₃ $[101\bar{1}]$ is, however,

considerably large. The misfit along this direction is calculated to be $(\text{SnO}_2_{[\bar{1}01]} - \text{Al}_2\text{O}_3_{[101\bar{1}]})/\text{Al}_2\text{O}_3_{[101\bar{1}]} = (5.71-5.13)/5.13 = 12\%$, which is a big obstacle for high quality epitaxy.

Figure 2-10. Ball-and-stick models of SnO₂ and Al₂O₃ illustrating the epitaxial relationship and the lattice mismatch (from reference [52]).

In order to compensate the large lattice mismatch between the SnO₂ film and sapphire substrate along the SnO₂ $[\bar{1}01]$ direction, high-density interfacial dislocations and related planar defects should accumulate in this direction, and low or no defect will be observed along SnO₂ $[010]$, due to the small lattice mismatch. HRTEM has been employed to investigate the epitaxy SnO₂ film on sapphire $(10\bar{1}2)$ plane [23], and the results are shown in Figure 2-11.

Figure 2-12. AFM images of (0001) sapphire substrates: (a) as-received ($1 \times 1 \mu\text{m}^2$), (b) annealed at 1000 °C for 1h ($1 \times 1 \mu\text{m}^2$), and (c) annealed at 1400 °C for 1h ($3 \times 3 \mu\text{m}^2$). The vertical profile was taken along the line indicated in the image (from reference [53]).

Figure 2-12 gives the AFM results of the (0001) sapphire substrates before and after annealing at different temperatures. It is clear that atomic steps formed after treatment.

2.1.4 SnO_2 on Pt (111)

Platinum (111), as a metal, usually was employed as the substrate for SnO_2 in scanning tunneling microscope (STM) investigation, due to its good conductivity [54-57]. Deposition of multilayer-Sn in an oxidizing atmosphere on Pt (111) substrates at 600 K followed by subsequent annealing to 900 K resulted in the formation SnO_2 crystallites [57]. STM investigations illustrate that the crystallites are aligned along the three $\langle 110 \rangle$ directions of the Pt (111) substrate, as shown in Figure 2-13 (a). The growth of tin oxide on Pt (111) proceeds via a pseudo-Stranski-Krastanov growth

mode, i.e. formation of a wetting layer followed by the growth of three dimensional crystallites. Atomic resolution STM image of the SnO_2 crystallite on Pt (111) substrate shown in Figure 2-13 (b) exhibits the structure of the SnO_2 (101) surface. The out-of-plane epitaxial relationship between SnO_2 and Pt substrate can be determined as: $(101)_{\text{SnO}_2} // (111)_{\text{Pt}}$. In the structure point of view, the growth of (101) orientated SnO_2 on Pt is stabilized by the low mismatch of this orientation with the Pt (111) substrate with a mismatch of 0.5% and 3% in the $[0\bar{1}0]$ and $[\bar{1}01]$ SnO_2 directions, respectively. This is indicated in Figure 2-13(c).

Figure 2-13. SnO_2 growth on Pt (111). (a) Large scale STM image of SnO_2 (101) crystallites with preferential orientation along the three low symmetry directions of Pt (111). (b) Atomic resolution STM image of SnO_2/Pt , in which the SnO_2 (101) unit cell is indicated by a gray rectangle. (c) Schematic diagram of epitaxial relationship of the SnO_2 (101) unit cell with respect to the Pt (111) lattice (from reference [57]).

2.1.5 Summary and outlook for SnO₂ epitaxy

Compared with polycrystalline samples, epitaxially deposited SnO₂ thin film may offer a way for atomic scale characterization of the surface structure and properties. Although SnO₂ can be grown on sapphire and TiO₂ substrates with fairly good quality, the lattice mismatch between them is still an obstacle for layer by layer epitaxy. Differently orientated SnO₂ thin films can be deposited on TiO₂ substrates, but the interdiffusion of Ti and Sn at the interface is considerable. Substrates with closer lattice constants to SnO₂ are still being sought. Furthermore, conductive substrates, such as metal or metallic oxide, are also in demand, which are beneficial for electrical characterizations and applications.

2.2 Properties and applications of SnO₂

2.2.1 Electronic structure of SnO₂

SnO₂ is known as one of the few wide band gap materials which simultaneously possess electrical conductivities. The energy band structure of SnO₂ on the basis of experimental results was firstly investigated by R. Summitt *et al.* [58]. Based on the ultraviolet (UV) absorption edge spectrum of pure single crystal SnO₂, they concluded that SnO₂ is a dipole-forbidden direct band material which has an energy band gap around 3.6 eV.

Figure 2-14. Band structure of SnO₂ obtained from first principles calculations (from reference [59]).

The detailed electronic structure of SnO₂ has been widely studied by first-principles calculations. Figure 2-14 shows the calculated energy band structure of SnO₂ using

generalized gradient approximation (GGA) corrections as the exchange-correlation functional within the implementation of Perdew, Burke, and Ernzerhof. According to the calculated band structure, the energy band gap is 0.6 eV, which is much lower than the experimental value of 3.6 eV. This disagreement is expected as density functional theory (DFT) is known to greatly underestimate the band gaps of metal oxides, despite the fact that the ground-state properties are well described [60]. From Figure 2-14, it can be seen that both the minimum of conduction band and the maximum of VB are located at the Γ point in the Brillouin zone. This implies that the undoped SnO_2 is a direct-gap material in which the electrons can be excited to the conduction band without the help of phonons to conserve the crystal momentum. This is consistent with the experimental result and other calculations [58,61,62]. A large dispersion in the lowest lying conduction band at Γ of approximately 5 eV can also be observed, consistent with previous calculations. This has been suggested to be one of the important band structure features of a good transparent conducting oxide as it limits optical absorbance in the visible and infrared regions of the spectrum. This large dispersion of conduction band also provides a light effective electron mass for carrier transport [63].

The density of states (DOS) of stoichiometry SnO_2 is shown in Figure 2-15. According to the calculated DOS, the VB of SnO_2 is mainly contributed by O 2p states. A significant density of Sn 5s states is seen in the VB between -8 and -6 eV. Sn 5p states contribute to the VB from -6 to -2 eV. Due to a small amount of mixing between the Sn 4d states and O 2p states, there is a slight contribution from Sn 4d states in the upper part of the VB from -5 to -1 eV. As for the conduction band (CB),

it is consisted by Sn 5s, 5p, and O 2p states. The bottom of the CB is more than 90% s type.

Figure 2-15. Density of states (DOS) of stoichiometry SnO_2 : blue curves represent s states, red are p states, and green are d states. (a) The total DOS, (b) and (c) shows the partial DOS of Sn and O, respectively (from reference [59]).

The intrinsic band gap of SnO_2 is as large as 3.6 eV and stoichiometric SnO_2 is a fairly good insulator. However, in semiconducting oxide, the defects usually act as effective carrier donors which may significantly change the electrical transport

properties. As for SnO₂, either oxygen vacancies ($V_O^{\bullet\bullet}$), or interstitial tin atoms, ($Sn_i^{\bullet\bullet\bullet}$), are expected to be electron donors in undoped SnO₂, according to the following defect reactions:[64-67]

To experimentally determine the dopant in SnO₂, S. Samson and C. G. Fonstad investigated the conductivity of SnO₂ as a function of oxygen partial pressure at elevated temperatures. Their experimental data suggested that the cause of the nonstoichiometry in SnO₂ is oxygen vacancies rather than tin interstitials [65]. This result also has been confirmed by the work of J. Maier and W. Göpel [66].

K. G. Godinho *et al.* analyzed the energetic and electronic structure of the intrinsic defects in SnO₂ [59]. It was found that the most stable defect in SnO₂ is $V_O^{\bullet\bullet}$ with charge compensated by the reduction of a Sn(IV) ion to Sn(II) ($Sn_{Sn}^{\bullet\bullet}$). In the neutral defect cluster ($V_O^{\bullet\bullet} + Sn_{Sn}^{\bullet\bullet}$), formation of the oxygen vacancy leads to the loss of coordination of three neighboring tin ions and their relaxation away from the vacancy. The DOS for $V_O^{\bullet\bullet} + Sn_{Sn}^{\bullet\bullet}$ defect is shown in Figure 2-16 with the VB maximum at 0 eV.

Figure 2-16. Total and partial electronic density of states for combined defect $V_{\text{O}} + \text{Sn}_{\text{Sn}}''$ in SnO_2 . Sn_{nn} and O_{nn} are tin and oxygen atoms neighboring the vacancy. Gray lines indicate position of the highest occupied state. Blue curves are s, red are p, and green are d states (from reference [59]).

It is notable that the Fermi level of oxygen deficient SnO_2 is just below the conduction band minimum (CBM), which implies the *n*-type conductivity. The defect state of $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}^{\prime\prime}$ is mainly contributed by the Sn 5s and O 2p respectively from the tin and oxygen ions neighboring the vacancy. The location of this defect state agrees qualitatively with experimental evidence which places donor levels of oxygen vacancies 0.03-0.15 eV below the CBM [65,68]. Similar defect state character also have been observed on reduced SnO_2 surface by resonant photoemission spectroscopy due to the reduction of Sn(IV) ions neighboring oxygen vacancies to Sn(II) [69].

Figure 2-17. Charge density plots for $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}^{\prime\prime}$ in SnO_2 . (a) Partial charge density from -10 eV to the defect state at contour levels from 0 (blue) to $0.3 \text{ e}/\text{\AA}^3$ (red). (b) Charge density difference between VB of bulk and defective cell at contour levels between -0.1 (red) and $0.1 \text{ e}/\text{\AA}^3$ (blue). (c) Partial charge density of defect state at contour levels between 0 (blue) and $0.05 \text{ e}/\text{\AA}^3$ (red) (from reference [59]).

The charge density maps of $V_{\text{O}}^{\bullet\bullet} + \text{Sn}_{\text{Sn}}^{\prime\prime}$ in SnO_2 have been calculated and shown in Figure 2-17. The partial charge density from -10 eV up to the defect state (i.e. VB) shows that most of the density is located on the oxygen atoms with some spherical 5s

character on Sn atoms [Figure 2-17 (a)]. The three Sn atoms surrounding the vacancy show lone-pair-like density. The charge density difference between the VB of the defect-free and defective cell [Figure 2-17 (b)] shows an increase in electron density on the tin ions neighboring the defect. This is consistent with the reduction of Sn(IV) to Sn(II). Figure 2-17 (c) shows the partial charge density of the defect state which is 0.3 eV below the CBM. The density is mainly on O ions near the defect with some lone-pair-like density on the neighboring Sn ions.

2.2.2 Electrical transport properties of SnO₂

The determination of the intrinsic conductivity is difficult due to the difficulty in preparing stoichiometric SnO₂ [70-72]. Various groups, e.g. M. Nagasawa *et al.* [73] and C. G. Fonstad *et al.* [74] fabricated SnO₂ single crystals and investigated the optical and electrical properties. Figure 2-18 shows the carrier concentration, Hall mobility, and conductivity between 80 K and 625 K for CVD prepared SnO₂ single crystal sample [75]. Based on the electrical transport properties shown in Figure 2-18, the effective mass m_p^* can be determined from the following relations

$$\frac{n(n+N_A)}{N_D-N_A-n} = \left(\frac{2\pi m_p^* k_B T}{h^2} \right)^{3/2} \exp\left(-\frac{E_D}{k_B T}\right) \quad (2-3)$$

$$m_p^* = (m_{p\perp}^* m_{p\parallel}^{*2})^{1/3} \quad (2-4)$$

where N_A and N_D are the acceptor and the donor concentrations, respectively. E_D is the activation energy of the donor equal to 27.5 meV, and m_p^* is fitted to be $0.39m_0$ [75]. This value is very close to the result obtained by cyclotron resonance method [74].

Figure 2-18. Carrier concentration, Hall mobility, and conductivity between 80 K and 625 K for CVD prepared SnO₂ signal crystal sample (from reference [75]).

Compared with Si ($m_p^* = 0.33m_0$), the conduction electrons in SnO₂ are as light as those in Si. According to Figure 2-18, the mobility is $2.4 \times 10^{-2} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K. Though it differs from sample to sample, this value is not as large as in Si ($1.6 \times 10^{-1} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$), InSb ($7.7 \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$) and PbS ($6.0 \times 10^{-2} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$) at 300 K. The smaller mobility is supposed to be attributed to the iconicity of SnO₂.

Compared with the single crystal sample, SnO₂ is mostly used in the form of thin film. J. E. Dominguez *et al.* have investigated the electrical transport properties of SnO₂ thin films fabricated by femtosecond PLD [46,76]. Figure 2-19 shows temperature dependent electrical transport properties of SnO₂ thin films with different thicknesses.

Figure 2-19. Electrical transport properties of SnO₂ thin films with different thicknesses as a function of inverse absolute temperature; (a) conductivity, (b) electron concentration, (c) mobility, and (d) response to hydrogen (from reference [76]).

The conductivity of SnO₂ thin film shows a strong dependence on the thickness. A difference of about 4 orders of magnitude is observed between the 6 nm and 100 nm thick films [Figure 2-19 (a)]. The carrier density and mobility decrease with the reduction of film thickness. According to the Arrhenius conduction equation:

$$\sigma(T) = \sigma_0 \exp\left(\frac{E_A}{k_B T}\right) \quad (2-5)$$

where σ_0 is the residual electrical conductivity, k_B is Boltzmann constant, and E_A is the activation energy, values of the activation energy were calculated to be 0.52 eV, 0.11 eV and 0.07 eV for 6 nm, 60 nm, and 100 nm thick films, respectively. The difference in transport properties of the films is attributed to: (a) the interaction

between electrons and crystal defects in thin films, (b) the effect of the film surface, and (c) the film/substrate interface [76]. The electrical transport properties of SnO₂ films were also found to strongly depend on the preparation conditions, i.e. temperature, pressure and fabrication techniques [49,77,78].

2.2.3 Optical properties of SnO₂

SnO₂ is transparent in the UV to visible range. The first investigation of optical properties of SnO₂ single crystals was carried out in 1962 by E. E. Kohnke on natural cassiterite [79]. From the short wavelength cutoff, a fundamental optical energy gap, E_g , is found to be ≥ 3.5 eV. Kohnke also observed a sharp absorption at the wavelength of 3.07 μm which he attributed to the presence of O-H groups oriented in a plane perpendicular to the c axis of the crystal. The UV absorption coefficient of synthetic SnO₂ as a function of photon energy was measured by R. Summitt *et al.* and is shown in Figure 2-20 [58]. As can be seen from the figure, pronounced dichroism exists in the UV region. The absorption edge for radiation polarized parallel and perpendicular to the c axis is separated by approximately 0.3 eV. As is well known, the absorption coefficient is related to photon energy for direct transition:

$$K = K_0(h\nu - E_g)^{1/2} \quad (2-6)$$

where E_g is the vertical separation between valence and conduction bands, and K_0 is a constant. By plotting the experimental values of K^2 versus photon energy and extrapolating to zero absorption, the width of the energy gap can be obtained. Using

this method, the parallel and perpendicular gaps of SnO₂ were determined to be 3.93 and 3.57 eV, respectively.

Figure 2-20. UV absorption coefficient in SnO₂ single crystals versus photon energy for radiations polarized parallel and perpendicular to the c axis (from reference [58]).

R. Summit *et al.* also investigated the temperature dependence of the UV absorption edges in SnO₂ crystals in the range between 20 and 1300 K. Their results showed that, above room temperature, both edges (parallel and perpendicular) shifted linearly with temperature, where $\Delta E_g / \Delta T = 1.2 \times 10^{-3} \text{ eV/K}$. Between 20 and 300 K, the shift in the parallel polarized edge was about 1.4 times larger than that in the perpendicular edge. Experimental results were fitted by the expression:

$$E_g(T) = E_g^0 - c \left[\exp\left(\frac{\theta}{T} - 1\right) \right]^{-1} \quad (2-7)$$

where E_g^0 corresponds to $T = 0$, and c is a constant. The best fits were obtained when $\theta = 196 \text{ K}$ and 414 K for parallel and perpendicular edges, respectively.

Besides the wide direct-band gap, SnO_2 also has high exciton binding energy (130 meV) at room temperature [76]. Consequently, it is considered as a potential host material for constructing next generation nonpolar UV optoelectronic devices, e.g. UV light-emitting diodes or laser diodes [80]. However, the intrinsic band edge transition of SnO_2 , i.e., exciton or band to band recombination, can hardly be obtained, due to the dipole-forbidden nature of energy band structure [81]. S. S. Pan *et al.* reported the room temperature exciton-type radiative recombination in a high quality undoped SnO_2 nanocrystalline thin film, as the nanostructuring changed the symmetry of the wave function and broke the dipole forbiddances [82].

Figure 2-21. (a) Temperature dependence PL spectra of SX emission from 77 K to 300 K. (b) Evolution of SX emission peak energy with temperature. (c) Dependence of SX emission peak intensity on the reciprocal of temperature (from reference [82]).

Figure 2-21 shows the photoluminescence (PL) spectra of the SnO_2 nanocrystal film from 3.1 eV to 3.64 eV measured at different temperatures. It can be seen that the shapes of PL band are typically asymmetric and with an extended low energy tail. The

surface localized excitation (SX) peak shifts toward lower energy side with temperature increasing and still exists at room temperature [Figure 2-21 (b)]. The temperature dependence of the PL intensity shown in Figure 2-21 (c) can be well described by the equation:

$$I(T) = \frac{I(0)}{[1 + c \exp(-E_\alpha/k_B T)]} \quad (2-8)$$

where $c = \tau_R/\tau_0$, which is related to the radiative lifetime of the recombination channels, τ_R is the radiative lifetime, τ_0 is a constant, E_α is the activation energy for the thermal quenching process, k_B is the Boltzmann constant, and T is the temperature [83]. The activation energy $E_\alpha = 54.8 \text{ meV}$, deduced from the SX emission, can be attributed to the surface donor (such as surface oxygen vacancy) binding energy.

Figure 2-22. Schematic diagram of surface localized exciton recombination process and evolution of peak energy with excitation intensity. The arrows indicate the radiative recombination process of surface localized exciton (SX) and free exciton (FX) in different areas of SnO_2 nanocrystal; SX occurs at the close surface region and FX occurs at the core of the nanocrystals (from reference [82]).

The SX emission peak is found to show a blueshift trend with increasing excitation intensity. A schematic diagram shown in Figure 2-22 is proposed by S. S. Pan *et al.* to understand the PL properties in nanocrystal SnO₂ film. From the diagram, the FX emission comes from the inner region of the SnO₂ nanocrystal, and SX originates from the outer surface area in which there exists a large fraction of local disorder and surface defects, such as oxygen vacancies or interstitial Sn atoms in the near-surface region. These defects form band tail states close to the conduction band minimum, shown in Figure 2-22. The SX process corresponds to the recombination of the exciton localized by the band tail. The red shift of SX emission with increasing temperature can be understood by temperature induced band gap shrinkage. The excitation power increasing induced SX emission peak blue shift can be understood by the occupation of conduction band tail due to a large number of electron-hole pairs generated under high excitation intensity.

2.2.4 SnO₂ based transparent conductors

TCOs are degenerately doped semiconductor oxides that are transparent to visible light. These simultaneous properties enable numerous applications, such as flat-panel displays, photovoltaic devices, and light-emitting diodes [84-86]. As mentioned previously, SnO₂ belongs to the important family of oxide materials that combine low electrical resistance with high optical transparency in the UV to visible range. This exotic property makes SnO₂ an important TCO. Fluorine (F), antimony (Sb), niobium (Nb), and tantalum (Ta) are most commonly used additives in SnO₂ to achieve high *n*-type conductivity while remaining high optical transparency [87-90]. Besides SnO₂,

ZnO and In_2O_3 are other two most commonly used binary systems for TCOs. Figure 2-23 shows the progress that has been made in reducing the resistivity of these three TCOs systems.

Figure 2-23. Decrease of the resistivity achieved for TCO materials (from reference [91]).

The transmission window of TCOs is between wavelength of 400 nm and 1500 nm. At short wavelengths (high photon energies), the electron-interband transitions (valence to conduction band) limit the transmission. While for the long wavelengths (low photon energies) light is absorbed by the electron-intraband transitions (plasma edge). The increase of conductivity will decrease the long wavelengths transmission due to a blue shift of the plasma frequency, which is a direct consequence of the increase in charge carriers. The plasma frequency is give by:

$$\omega_p = (ne^2/\epsilon_0\epsilon_\infty m^*)^{1/2} \quad (2-9)$$

where n is the carrier density, e is the electron charge, ϵ_0 is the permittivity of free space, ϵ_∞ is the high frequency permittivity, and m^* is the effective mass. Figure 2-24 shows the optical transmission spectra of SnO_2 based TCO films with different conductivities. It is apparent that more highly conductive sample has lower transmission in long wavelength range due to the plasma frequency shift.

Figure 2-24. Optical transmission spectra of SnO_2 films with different conductivities (from reference [92]).

2.2.5 SnO_2 based gas sensors

Among different materials studied for gas-sensing applications, SnO_2 has dominated over all other metal oxides and is most extensively studied. The gas-sensing properties of this material have been widely reported in literatures. Well known advantages of this material include its low cost and high sensitivities for different gas species. Furthermore, a large number of dopants have been introduced into the SnO_2 to

improve response times, temperature of operation, selectivity, and so on. Surface morphology has also been studied to enhance and explain the sensing properties by many researchers. Table 2-2 gives a brief review on the SnO₂ based sensing devices.

The exact fundamental mechanisms that cause a gas response are still controversial, but essentially trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are responsible for the conductivity change. When a molecule adsorbs at the surface, the electrons can be transferred to this molecule if the lowest lying unoccupied molecular orbital lies below the Fermi level of the solid and vice versa electrons are donated to the solid if its Fermi level is higher than the highest occupied orbit in the molecule. As a result, the absorption of molecule on the surface may induce a net charge and cause an electric field. The presence of this surface electrostatic field will result in a bending of the energy bands in the solid consequently. Accordingly, the sheet conductance of the surface layer of the adsorbed solid changes due to band bending effect, and the gas sensing mechanism appears. In polycrystalline gas sensing materials, another effect, i.e. the Schottky barriers formed at the grain boundary, is often considered to contribute to and improve the gas sensing response.

Table 2-2. Tin oxide based sensors

Tin oxide with additives	Sensing gas	Operating temperature range (°C)	Range of detection limits	Sensing element form	Response time	Reference
SnO ₂	NO ₂	131 – 313	0.01 – 0.25 ppm	Thick films	~1h	[93]
	CO	25 – 400	200 – 3000ppm	Thin films	~1min	[94]
	CO ₂	450	9%	Thin films	<1min	[95]
	C ₂ H ₅ OH	500	2.1%			
	H ₂ S	300 – 450	0 – 9 ppm	Thin films	-	[96]
	H ₂	27 – 650	62 – 101 ppm	Powder	-	[97]
	O ₂	150 – 300	300mbar	Thin films	-	[98]
	Humidity	Room Temp.	30 – 90%	Thick films	6 – 8s	[99]
	CH ₄	320	1%	Bulk	<1min	[100]
SnO ₂ -Pt	NH ₃	450 – 550	100 – 1000ppm	Thin films	~3min	[101]
	CO	50 – 250	10 – 1000ppm	Thin films	~200s	[102]
SnO ₂ -Pd	NH ₃	35 – 160	-	FET	-	[103]
	Co					
	CH ₄	200 – 450	0.5 vol%	Thick & thin films	1 -2 min	[104]
	H ₂					
SnO ₂ -Sb	O ₂	225 – 500	-	-	-	[105]
	CO	500 – 1000	200ppm	Single crystal	-	[106]

2.3 Metal oxide (SnO_2) based diluted magnetic semiconductor

2.3.1 Brief history of DMSs

DMSs, also known as semimagnetic semiconductors, are materials in which rare earth or transition metal ions replace a considerable number of the native ions in the semiconductor lattice [107]. This substitution of magnetic ions for constituent ions results in a close relationship between the state of magnetization and the electronic properties of the material, which has been a consistent source of scientific interest since the initial report on Mn doped CdTe by A. V. Komarov *et al.* in 1977 [108]. Although this II-VI semiconductors based DMS has an advantage in material synthesis, it is difficult to be doped to *n*- and *p*-type.

In contrast to II-VI semiconductors, the species and concentrations of carrier in III-V semiconductors can be easily controlled. Among the III-V based DMSs, GaAs doped with Mn is one of the most intensively investigated systems [109-111]. The Mn dopants provide holes by substituting for Ga sites as well as spins as a magnetic element. The mobile holes are known to mediate the Mn localized spins, giving rise to ferromagnetism. From the polarized light emission and anomalous Hall effect [111], this material was proved to be an intrinsic ferromagnetic semiconductor. The ferromagnetism of (Ga,Mn)As is relatively well established, but its applications are

still restricted due to its low Curie temperature (T_c). Till now, most of the DMSs based on Group IV [112], III-V [111,113], and II-VI [114] exhibited *p*-type electrical behavior and low Cuire temperature ($T_c < 180$ K), making them impractical for use in real devices. Successful spintronic applications have to concentrate on fabricating ferromagnetic semiconductors in which ferromagnetism will persist at higher temperatures.

Recently, it has been found that Curie temperature was closely related to the energy band gap of semiconductor, and RTFM realized in oxide based semiconductor hosts has been intensively reported. Table 2-3 lists references to typical early studies on a variety of oxides, with data on Curie temperature and moment per dopant cation.

So much work has already been done to investigate the ferromagnetism in metal oxides, but little agreement was reached by different groups. Furthermore, majority of the previous work about the oxide based DMSs was concentrated on the ferromagnetic property by doping single 3d elements. Motivated by combing semiconductive and ferromagnetic properties into one material, the wide band gap semiconductor oxide, SnO_2 system, was chosen and its electrical and magnetic properties were investigated by doping two different elements spontaneously, in this dissertation.

Table 2-3. Metal oxide based diluted magnetic semiconductors.

Material	$E_g(\text{eV})$	Dopant & concentration	Moment(μ_B)	$T_c(\text{K})$	Reference
TiO_2	3.2	V – 5%	4.2	>400	[115]
		Co – 1-2%	0.3	>300	[116]
		Co – 7%	1.4	>650	[117]
		Fe – 2%	2.4	300	[118]
		Ni – 5%	3.0	>400	[119]
ZnO	3.3	V – 15%	0.5	>350	[120]
		Mn -2.2%	0.16	>300	[121]
		Fe – 5%	0.75	550	[122]
		Cu – 5%	1.45	>300	[123]
		Co – 10%	2.0	280-300	[124]
		Ni – 0.9%	0.06	>300	[125]
SnO_2	3.6	Fe – 5%	1.8	610	[16]
		Co – 5%	7.5	650	[14]
		V – 0 ~10%	~0.5	350	[126]
		Mn – 5%	0.5	>300	[127]
		Ni – 5%	2	627	[128]
Cu_2O	2.0	Co -5%	0.2	>300	[129]
		Mn – 0.3%	0.6	>300	[130]
In_2O_3	3.7	Fe – 5%	1.4	>600	[131]
		Cr – 2%	1.5	900	[132]
$(\text{In}_{1-x}\text{Sn}_x)_2\text{O}_3$	3.5	Mn – 5%	0.8	>400	[133]
CeO_2	3.4	Co – 3%	6.0	800	[134]

2.3.2 Origin of ferromagnetism in DMSs

According to the work of J.M.D. Coey *et al.* [135], we can imagine three ways of making a magnetic semiconductor, which are shown in Figure 2-25. For model one, shown in Figure 2-25 (a), the interaction between magnetic ions and conduction electrons produce an *n*-type semiconductor with a spin-split conduction band. This is the situation in the europium chalcogenides, where a red shift of band gap absorption occurs on cooling below the Curie point because of the spin splitting of the *5d/6s* conduction band. Figure 2-25 (b) gives the spin-split of VB, which can be used to explain the ferromagnetism in III-V materials. The third possibility, illustrated in Figure 2-25 (c), in heavily defective material is a spin-split impurity band.

Figure 2-25. Schematic density of states with fully spin-polarized (a) conduction band (b) valence band and (c) impurity band (from reference [135]).

For the SnO_2 based DMS, the mechanism and origin of ferromagnetism are still an open question, due to the complexity caused by heterogeneity, secondary phases, contamination, and even measurement artifacts. As one of the most important properties for intrinsic magnetic material, anomalous Hall effect hasn't been observed

in SnO₂ based DMS up to now, which brings on many controversies on the origin of ferromagnetism and the exchange coupling mechanism in this system. Three approaches for understanding the exchange coupling and high Curie temperature have been proposed by C. B. Fitzgerald *et al.*[17].

Figure 2-26. Schematic band structure of the three different models for exchange mechanism in 3d metal doped SnO₂. (a) Impurity band exchange (b) RKKY exchange and (c) Two-electron defect-center exchange (from reference [17]).

According to Figure 2-26 (a), electrons in Bohr-like donor orbitals form magnetic polarons spanning several 3d dopant ions, and the magnetic polarons overlap to make a spin-split impurity band. The model B, shown in Figure 2-26 (b), corresponds to the situation that the donor states lie very close to the bottom of the 5s (Sn) conduction band, and cause a spin-split conduction band. This is equivalent to the RKKY exchange interaction for low electron densities. However, based on these two models, the high Curie temperature and large moment per dopant ion are still hard to understand. In order to deal this problem, the model C, shown in Figure 2-26 (c), was proposed, in which the defects were assumed to have moments. In this frame, two-hole defect or more extended oxygen hole orbits can be envisaged. The two-hole

triplets can themselves form spin-split impurity band, in the same way as the hydrogenic donor or F center electrons, and large extra orbital moment may be introduced depending on the symmetry of the defect state.

Figure 2-27. Magnetic polarons formed in the oxide based DMS. The overlap between the hydrogenic electron and the cations within its orbit leads ferromagnetic exchange coupling. Cation sites are represented by small circles. Oxygen is not shown; the oxygen vacancies are represented by squares (from reference [136]).

As an *n*-type oxide, the doping elements tend to form shallow donors in SnO_2 . The donated electron associated with a particular defect will be confined in a hydrogenic orbital, and form hydrogenic electrons in the impurity band. Driven by the interaction of the magnetic dopants with that hydrogenic electron, the donors tend to form bound magnetic polarons, coupling the 3d moments of the ions within their orbits. This concept has been presented in Figure 2-27 [136]. Based on this idea, the doped cations will present an extra random potential, which extends the localized region as the increase of doping concentration. The ferromagnetic exchange coupling will be

realized when the hydrogenic electron overlap with the cations within its orbit [137]. Generally, this coupling is ferromagnetic when the 3d shell is less than half full, and antiferromagnetic when the 3d shell is half full or more.

CHAPTER 3 EXPERIMENTAL PROCEDURES

This chapter describes the practical aspects of the work performed in this dissertation, outlining the experimental procedures carried out in detail.

3.1 Laser molecular beam epitaxy (LMBE) technique

One of the most versatile techniques for oxide thin film fabrication is the PLD [138,139]. Though significant development of this technique began only in the late 1980s, PLD is now a widely used deposition approach for thin film growth, especially in the oxide research. It was not until PLD was popularized as an oxide film growth technique through its success in growing epitaxial high temperature superconducting films that widespread attention and development were given. In this technique, shown

in Figure 3-1, a pulsed laser is focused onto a target of the material to be deposited. For sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material. The ablated material is ejected from the target in a forward directed plume.

Figure 3-1. Schematic diagram of a PLD system. (from reference [138])

PLD has several attractive features, including stoichiometric transfer of material from the target, generation of energetic species, hyperthermal reaction between the ablated cations and molecular oxygen in the ablation plasma, and compatibility with background pressure ranging from ultra-high vacuum (UHV) to 100 Pa. Epitaxial oxide films can be deposited with PLD using single, stoichiometric targets of the material of interest, or with multiple targets for each element. As with evaporation, the film-growth process can be controlled at the atomic level using PLD. In addition, epitaxial growth with deposition rates in the order of $100 \text{ \AA/s}$ has been demonstrated with this technique.

RHEED has become an important tool in surface science because of its high surface sensitivity, and the ability of *in-situ* monitoring of film growth [140,141]. A RHEED equipped PLD system, alternatively named laser molecular beam epitaxy (LMBE), has been established in our lab and atomic layer by layer epitaxy has been realized according to the RHEED oscillation.

The principle of RHEED is utilizing the diffraction of electrons by surface atoms to provide information of the periodic arrangement of the surface atoms. Figure 3-2 (a) shows a schematic drawing of the RHEED geometry. The incident electron beam (e-beam) strikes the sample surface at a grazing angle θ_i . The electrons are monoenergetic with a typical energy of $E \sim 10\text{-}50$ keV. The electron gun and phosphor screen (which acts as the detector) are located far from the sample to avoid any interference with the deposition process. In this geometry, electrons are scattered from the crystal surface, resulting in a characteristic diffraction pattern on the phosphor screen, shown in Figure 3-2 (b). This pattern is instantaneously displayed and can be used to define the crystallographic surface structure of, for instance, a growing tin film.

Figure 3-2. (a) Schematic view of the RHEED geometry. (b) Typical RHEED pattern from a single crystal substrate [140].

3.2 X-ray diffraction (XRD)

XRD is a standard analytical technique for analyzing the crystalline properties of films. The applications of XRD include phase identification, thin film analysis, lattice parameter determination, purity or quality control of materials, determination of crystallinity of polycrystalline materials, stress analysis, orientation of single crystals, crystallinity quality determination, and analysis of superlattice structures [142].

Powder XRD (Siemens 5005) and high-resolution triple axis XRD (Philips X'pert Pro) were employed for the bulk materials and epitaxially grown thin film samples, respectively.

3.3 Vibrating sample magnetometer (VSM)

The magnetic properties of 3d elements doped SnO₂ were measured by a vibrating sample magnetometer (VSM) attached to the physical property measurement system (PPMS) by Quantum Design Inc. The operating temperature range is from 2.1 to 400 K, and the magnetic field can be as high as 10 Tesla. The sensitivity of the VSM system can go to 10⁻⁶ emu with 1 sec averaging, and the resolution of the field is around 0.1 G [143].

3.4 Atomic force microscopy (AFM)

In order to observe the surface roughness and topography of substrates and the deposited thin films, atomic force microscopy (AFM) micrographs were taken with a Digital Instruments, Inc. Nanoscope III A. The surface morphology was taken in tapping mode using Si_3N_4 tips. Typical data taken from AFM include atomic steps and root mean square (RMS) roughness [144].

3.5 X-ray photoelectron spectroscopy (XPS)

XPS is a broadly applicable general surface analysis technique because of its surface sensitivity, combined with quantitative and chemical state analysis capabilities. It can detect all elements except hydrogen and helium. XPS analysis was performed using a ESCALab 220i-XL with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation. The survey spectra in the range of 0-1200 eV were recorded in 1 eV step for each sample, followed by high-resolution spectra over different element peaks in 0.1 eV steps, from which the peak shift and detailed compositions were calculated. Curve fitting was performed after a Shirley background subtraction by a Lorentzian-Gaussian method [145].

3.6 Transmission electron microscopy (TEM)

In TEM, electrons can be accelerated from 100 kV up to 1 MV, and projected onto a thin specimen (usually less than 200 nm) by means of the condenser lens system. The greatest advantage that TEM offers over SEM is the high magnification ranging from 50 to 10^6 and its ability to provide both image and diffraction information from a single sample. The high magnification of TEM is a result of the small effective electron wavelength λ , which is given by the de Broglie relationship:

$$\lambda = \frac{h}{\sqrt{2mqV}} \quad (3-1)$$

where m and q are the electron mass and charge, h is Planck's constant, and V is the potential difference through which electrons are accelerated. The higher the operating voltage of a TEM instrument, the greater its lateral spatial resolution and the less interaction with matter. So, it is possible to work with thicker samples using a high-voltage TEM. One shortcoming of TEM is its limited depth resolution.

Selected-area electron diffraction (SAED) offers a unique capability to determine the crystal structure of individual nanomaterials. Since electron scattering is exceedingly sensitive to the target element, various spectroscopy techniques have been developed for the chemical composition analysis such as energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). In addition to the capability of structural characterization and chemical analyses, TEM has also been applied to measuring the thermal and mechanical properties of nanomaterials [146].

In this dissertation, TEM/high-resolution TEM (HRTEM) studies were performed using TEM, JEOL JEM-2010 and JEM-2010F, both operating at 200 kV. TEM operates on the basic principles of the optical microscope; however, it takes advantage of the much shorter wavelengths of electron beams than that of light beams. JEM-2010 provides resolution of the order of 2 Å, rather than 2000 Å for the optical microscope. The electron source is LaB₆ and the magnification can vary from 50 to 1,200,000. The JEM-2010F is equipped with a field emission electron gun that produces high brightness (100 times greater than LaB₆ tip). This feature is essential for nanoscale ultrahigh resolution and analysis. The JEM-2010F incorporates an EDX system allowing simple and integrated data acquisition. As the electron flux is high, other experiments related to irradiation effect can also be done. The point resolution is 1.9 Å and the lattice resolution is 1 Å. The magnification can vary from 50 to 1,500,000.

3.7 Energy dispersive X-ray spectroscopy (EDX)

EDX is an analytical tool predominately used for element analysis or chemical characterization. Samples can be investigated through the interactions between the electromagnetic radiation and matter by analyzing X-rays emitted from the matter in response to the probing charged particles. Since each element has a unique atomic structure which allows characteristic X-ray emission, an element's atomic structure can be identified uniquely from each other. In this dissertation, the EDX installed with TEM (JEM-2010F) was used [146].

3.8 Ellipsometry

Ellipsometry is a very sensitive surface and thin film measurement technique that uses polarized light. Ellipsometry measures the change in polarization state of light reflected from the surface of the measured sample. Fundamentally, ellipsometry refers just to the measurements of the polarization state of a light beam. However, ellipsometric measurements are usually performed in order to describe an optical material system that modifies the polarization state of a light beam. The exact nature of the polarization modification is determined by the properties of the measured sample (i.e., thickness, dielectric function or complex refractive index). Although optical techniques are inherently diffraction limited, ellipsometry exploits phase information and the polarization state of light, and can achieve angstrom resolution [147,148].

In ellipsometry, linearly polarized light falls on the sample and is reflected from the surface of the measured sample. The reflected light passes through a polarizer, which is called analyzer, and falls into the detector. The measured values (ellipsometric angles) are expressed as ψ and Δ , which are related to the ratio of Fresnel reflection coefficient R_p and R_s for p and s polarized components (the s component is oscillating perpendicular to the plane of incidence and parallel to the sample surface, and the p component is oscillating parallel to the plane of incidence), respectively, which is described by the fundamental equation of ellipsometry:

$$\rho = R_p/R_s = \tan(\Psi) \exp(i\Delta) \quad (3-2)$$

where $\tan(\psi)$ denotes the amplitude ratio upon reflection, and Δ is the phase shift. For any angle of incidence greater than 0° and less than 90° , p -polarized light and s -polarized light will be reflected differently. Because ellipsometry measures the ratio of two values, it can be highly accurate and very reproducible. Because the ratio is a complex number, it also contains “phase” information, which makes the measurement very sensitive. In ellipsometric experiment, it is common to use the so-called p and s directions as two orthogonal basis vectors used to express beam polarization states, as shown in Figure 3-3. This figure illustrates the general idea of ellipsometric polarized light beam system.

Figure 3-3. Schematic illustration of an ellipsometric experiment, showing the polarized light reflected by the surface of the measured sample.

Ellipsometry is an indirect method, i.e. in general, the measured Ψ and Δ cannot be converted directly into the dielectric function or optical constants of the sample. Normally, a model analysis must be performed. Direct inversion of Ψ and Δ is only possible in very simple cases of isotropic, homogeneous and infinitely thick films. In all other cases a layer model must be established, which considers the optical constants (refractive index or dielectric function tensor) and thickness parameters of all individual layers of the sample including the correct layer sequence. Using an iterative procedure (least-squares minimization), unknown optical constants and/or thickness parameters are varied, and Ψ and Δ values are calculated using the Fresnel equations. The calculated Ψ and Δ values, which match the experimental data best, provide the dielectric function and thickness parameters of the sample.

CHAPTER 4 EPITAXIAL GROWTH OF SnO₂ THIN FILM BY LMBE

In recent years, interest in exploring the properties of SnO₂ has resulted in thin films being realized by a wide range of growth methods on a variety of substrates. Epitaxial growth of high quality SnO₂ thin films not only benefits the study of this material's intrinsic properties, but also facilitates the exploration of SnO₂ based device applications. In this chapter, we present in detail the epitaxial growth of SnO₂ thin films on different substrates using LMBE technique. Orientation controlled epitaxial growth of SnO₂ thin films was realized on sapphire substrates. The phase structure and epitaxial relationships were analyzed by RHEED and XRD. Besides the sapphire substrates, we also investigated the epitaxial growth of SnO₂ film on (111) SrTiO₃ (STO) substrate, which is believed to be the first report of SnO₂ epitaxy on perovskite substrate. RHEED and XRD were employed to investigate the crystal structure and epitaxial relationship. The microstructure and optical dielectric function of SnO₂ film on STO were investigated by TEM and ellipsometry, respectively. To study the

interface of SnO₂/STO, its band alignment, which is believed to be the determining parameter for the optoelectronic properties, was quantitatively determined by XPS.

This chapter is divided into three sections. The first section presents the epitaxial growth of orientation controlled SnO₂ thin films on sapphire substrates. It includes the (101) SnO₂ on (10 $\bar{1}$ 2) sapphire, (200) SnO₂ on (0001) sapphire and (002) SnO₂ on (10 $\bar{1}$ 0) sapphire. Their detailed crystal structures were obtained by RHEED and XRD. The second section focuses on the epitaxial growth of SnO₂ on (111) STO substrate. The thin film crystal quality, epitaxial relationship, microstructure and optical dielectric function are studied in this section. The band alignment of the interface between SnO₂ and STO is discussed in the third section.

4.1 Orientation controlled SnO₂ epitaxial thin film on sapphire substrates

4.1.1 Introduction

As an important wide band gap transparent oxide semiconductor, SnO₂ has attracted much attention for both fundamental research and various technological applications [4,33,149-151]. Among the various forms of SnO₂, thin film form seems to be the most important one for device applications, e.g. transparent electrodes for flat panel displays, semiconductor gas sensors, as well as dye-sensitized solar cells [150,152]. Accordingly, the interest in exploring the properties of SnO₂ resulted in thin films being realized by a range of thin film deposition methods on a variety of substrates. SnO₂ thin films have been fabricated by plasma-assisted molecular beam epitaxy (PAMBE) [25], ALD [153], CVD [154], sol-gel coating [155], radio-frequency magnetron sputtering [24], and LMBE [156].

LMBE differs significantly from the conventional physical vapor deposition methods. First of all, it is distinguished by the formation of high temperature plasma mixed with ejected target species with high kinetic energies, followed by a forward-directed nature of the ablated materials. The high energetic characteristic of laser beam induced plasma gives LMBE the advantages that the bulk stoichiometry can be transferred to the deposited thin films and the chemical composition of the films can be artificially controlled. Secondly, the RHEED in LMBE allows the user to monitor

surface structure and morphology in real time during the thin film growth. On the other hand, LMBE also offers control of reactive ambience gas and introduction of external applied field in the deposition chamber.

Although the SnO₂ thin films in the form of polycrystal and amorphism have attractive properties for applications and also been extensively studied, the epitaxial growth of highly crystalline films are attracting more attention recently, due to their superior properties for oxide electronics applications, and fundamental studies of material. As mentioned in the Chapter 2, epitaxial SnO₂ thin films have been grown on various substrates, such as TiO₂, sapphire and Pt (111) [23,41,56]. However LMBE is still not a widely used method for SnO₂ epitaxial film deposition. Moreover, no systematic microstructure characterization has been carried out for SnO₂ films deposited by LMBE. In this section, we present the growth of orientation controlled SnO₂ thin films by LMBE and their detailed microstructure analyses.

4.1.2 Experimental detail

SnO₂ thin films were deposited using the LMBE system in which a pulsed KrF-excimer laser (Lambda Physik LPX 305, $\lambda = 248$ nm, 30 ns full width at half maximum) was used. During the film growth, the energy density of laser beam and the laser ablation rate was fixed at 1.5 J/cm² and 1 Hz, respectively. A homemade target prepared from SnO₂ (Sigma Aldrich, 99.99%) powder via standard solid state ceramic process was employed. The background pressure of LMBE chamber was

maintained at $\sim 10^{-5}$ Pa, and the target-to-substrate distance was fixed at 7 cm. To control the crystal orientation of SnO₂ thin film, three different orientated single crystal sapphire substrates, (10 $\bar{1}$ 0), (10 $\bar{1}$ 2) and (0001) were used. Prior to the thin film deposition, the substrates were cleaned in ultrasonic bath to remove contaminations. SnO₂ thin films with thickness around 100 nm were deposited at a substrate temperature (T_{Sub}) of 700 °C and oxygen pressure (P_{Oxy}) of 0.1 Pa, respectively. The growth condition adopted in this section was optimized according to SnO₂ films on (10 $\bar{1}$ 2) sapphire substrate. The surface morphologies of the thin films were investigated by AFM. The *in-situ* RHEED was operated in anti-Bragg condition using 20 keV electron beam under a grazing incidence angle of 1°-3° towards substrate surface. Epitaxial characterization was carried out *ex-situ* using XRD.

4.1.3 Results and discussions

a) SnO₂ thin film on (10 $\bar{1}$ 2) sapphire substrate

Figure 4-1 (a) shows the 2θ - ω XRD scan pattern of SnO₂ thin film deposited on (10 $\bar{1}$ 2) sapphire substrate in the 2θ angle ranging from 20° to 80°. As shown in the figure, except for the strong substrate peaks located at 25.6° and 52.5°, which corresponds to the (10 $\bar{1}$ 2) and (20 $\bar{2}$ 4) reflection of sapphire, respectively, the other two peaks are located at 33.9° and 71.3°. These two peaks can be assigned to the (101) and (202) reflections of the rutile phase SnO₂. From this 2θ - ω XRD scan result, the out-of-plane epitaxial relationship is SnO₂(101) // sapphire (10 $\bar{1}$ 2). Information concerning the in-plane epitaxial relationships between the SnO₂ film and the sapphire

substrate can be obtained from XRD phi scan after bringing the SnO₂ (110) and sapphire (0006) off-axis reflections to the Bragg condition of diffractometer as illustrated in Figure 4-1 (b). The tilt angle (ψ), which is the angle between the reflection plane and substrate surface plane, for SnO₂ (110) and sapphire (0006) are 66.7 ° and 57.6 °, respectively. According to the phi scan results, the SnO₂ thin film on (10 $\bar{1}$ 2) sapphire substrate has a well in-plane alignment which confirms the single crystallite of the thin film. Based on the crystal structures of SnO₂/sapphire and above XRD results, the in-plane epitaxial relationships can be determined as: $[010]_{\text{SnO}_2} // [\bar{1}2\bar{1}0]_{\text{sapphire}}$ and $[\bar{1}01]_{\text{SnO}_2} // [\bar{1}011]_{\text{sapphire}}$, which is consistent with previously reported epitaxial relationships of SnO₂ thin film on (10 $\bar{1}$ 2) sapphire utilizing PAMBE [157].

Figure 4-1. (a) XRD 2θ-ω scan of SnO₂ thin film deposited on (101̄2) sapphire substrate. (b) XRD φ scans of SnO₂ thin film and sapphire substrate for the film deposition on (101̄2) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.

The crystalline quality of the SnO₂ thin film on (10 $\bar{1}2$) sapphire substrate was investigated by X-ray ω -scan (rocking curve), as shown in Figure 4-2. Quantifying the film quality can be achieved by measuring the full width at half maximum (FWHM) of the rocking curve. For our LMBE fabricated SnO₂ thin film, FWHM of the rocking curve is 0.7°. This relatively small FWHM value indicates a high crystalline quality for the LMBE deposited SnO₂ thin film.

Figure 4-2. ω -scan (rocking curve) of the SnO₂ (101) peak for SnO₂ film on (10 $\bar{1}2$) sapphire substrate.

RHEED is a powerful tool for *in-situ* investigation of the film quality and growth process by monitoring the RHEED patterns. Figure 4-3 (a) presents the RHEED pattern of SnO₂ thin film on (10 $\bar{1}2$) sapphire substrate. The spotty but well defined RHEED pattern indicates single crystalline form of the SnO₂ thin film, and the three dimensional (3D) growth mode of SnO₂ thin film. Figure 4-3 (b) gives the AFM (topography) image of the as deposited SnO₂ thin film. The surface root mean square

(RMS) roughness determined from the Figure 4-3 (b) is 0.7 nm, which indicates a smooth surface of SnO₂ thin film on (10 $\bar{1}2$) sapphire substrate.

Figure 4-3. (a) *in-situ* RHEED pattern and (b) *ex-situ* AFM topography image of the SnO₂ thin film on (10 $\bar{1}2$) sapphire substrate.

b) SnO₂ thin film on (0001) sapphire substrate

XRD 2θ - ω scan pattern of the SnO₂ thin film grown on the (0001) sapphire substrate is shown in Figure 4-4 (a). In the 2θ angle ranging from 20° to 80°, two diffraction peaks were observed in this sample. The strong peak located at 41.7° is attributed to the (0006) reflection of sapphire substrate. Another peak located at 38.5° is assigned to the (200) reflection of rutile SnO₂. Accordingly, the out-of-plane epitaxial relationship can be determined as SnO₂ (200) // sapphire (0001), from the 2θ - ω XRD scan result. Its in-plane epitaxial relationships were obtained from the XRD ϕ scan after bringing the SnO₂ (211) and sapphire (11 $\bar{2}$ 3) off-axis reflections to the Bragg condition of the diffractometer as illustrated in Figure 4-4 (b). In the ϕ scan of SnO₂

thin film on sapphire (0001), the tilt angle ψ , for SnO₂ (211) and sapphire (11 $\bar{2}$ 3) are 41.9 ° and 61.2 °, respectively. From Figure 4-4 (b), the phi scan of sapphire substrate shows a six-fold azimuthal symmetry, which is consistent with the hexagonal structure of sapphire. However, the phi scan of the SnO₂ thin film on (0001) sapphire also shows six-fold azimuthal symmetry, which is not expected in tetragonal rutile structure of SnO₂.

Figure 4-4. (a) XRD 2θ-ω scan of SnO₂ thin films deposited on (0001) sapphire substrate. (b) XRD φ scans of SnO₂ thin film and sapphire substrate for the film deposition on (0001) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.

This six-fold symmetry in SnO₂ thin film on (0001) sapphire has also been observed by other groups [47,158]. It was attributed to the rotation of SnO₂ grains, due to the six equivalent in-plane directions for SnO₂ nucleating on sapphire (0001) plane. Based on the crystal structures of SnO₂/sapphire and the XRD results, the epitaxial relationships of SnO₂ thin film on (0001) sapphire substrate can be determined as:

$$(200) \text{ SnO}_2 // (0001) \text{ sapphire}$$

$$[001] \text{ SnO}_2 // [\bar{1}010] \text{ sapphire} ; [010] \text{ SnO}_2 // [1\bar{2}10] \text{ sapphire}$$

$$[001] \text{ SnO}_2 // [1\bar{1}00] \text{ sapphire} ; [010] \text{ SnO}_2 // [11\bar{2}0] \text{ sapphire}$$

$$[001] \text{ SnO}_2 // [01\bar{1}0] \text{ sapphire} ; [010] \text{ SnO}_2 // [\bar{2}110] \text{ sapphire}$$

Figure 4-5 shows the X-ray rocking curve of SnO₂ (200) peak of the SnO₂ thin film on (0001) sapphire. The FWHM of the rocking curve is found to be 0.03 °. This small FWHM value suggests a high quality epitaxy of (200) SnO₂ grains on the (0001) plane of the sapphire substrate.

Figure 4-5. ω -scan (rocking curve) of the SnO₂ (200) peak for SnO₂ thin film on (0001) sapphire substrate.

Figure 4-6 (a) shows the RHEED pattern of SnO₂ thin film on (0001) sapphire substrate. The well defined RHEED pattern indicates that the SnO₂ film is in single crystalline form. Different from the spotty RHEED pattern of SnO₂ thin film on (10 $\bar{1}$ 2) sapphire substrate [Figure 4-3 (a)], the RHEED pattern in Figure 4-6 (a) shows a streaky feature which implies a higher crystal quality of the SnO₂ thin film on (0001) sapphire. This is consistent with the small FWHM value shown in Figure 4-5. Figure 4-6 (b) presents the AFM topography image of the as deposited SnO₂ thin film on (0001) sapphire substrate. The surface RMS roughness determined from Figure 4-6 (b) is 0.5 nm, which indicates a smooth surface of SnO₂ thin film on (0001) sapphire substrate.

Figure 4-6. (a) *in-situ* RHEED pattern and (b) *ex-situ* AFM topography result of the SnO₂ thin film on (0001) sapphire substrate.

c) SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate

Figure 4-7 (a) shows the 2θ - ω XRD scan result of SnO₂ thin film deposited on (10 $\bar{1}$ 0) sapphire substrate in the 2θ angle ranging from 20 ° to 80 °. As shown in the figure, two peaks located at 57.7 ° and 68.2 ° are observed and they are assigned to the (002) reflection of SnO₂ and (30 $\bar{3}$ 0) reflection of sapphire, respectively. According to this 2θ - ω XRD scan result, the out-of-plane epitaxial relationship can be determined as SnO₂(002) // sapphire (10 $\bar{1}$ 0). To obtain the in-plane epitaxial relationships between the film and substrate, the XRD phi scan has been done after bringing the SnO₂ (112) and sapphire (22 $\bar{4}$ 0) off-axis reflections to the Bragg condition of diffractometer [as illustrated in Figure 4-7 (b)]. The tilt angle (ψ) for SnO₂ (112) and sapphire (22 $\bar{4}$ 0) are 25.4 ° and 30 °, respectively.

Figure 4-7. (a) XRD 2θ-ω scan of SnO₂ thin film deposited on (10 $\bar{1}$ 0) sapphire substrate. (b) XRD φ scans of SnO₂ thin film and sapphire substrate for the film deposition on (10 $\bar{1}$ 0) sapphire substrate. The diffraction peak index and tilt angle are indicated for each measurement.

According to the φ scan results, a set of SnO₂ {112} reflections separated by 90° were detected, confirming the fourfold symmetry along *c*-axis of SnO₂ with a

tetragonal phase. Based on the crystal structures of SnO₂/sapphire and the XRD results, the epitaxial relationships can be deduced as: (002) SnO₂ // [10 $\bar{1}$ 0] sapphire; [010]SnO₂ // [0001] sapphire and [100]SnO₂ // [$\bar{1}$ 010] sapphire, which is consistent with previously reported epitaxial relationships of SnO₂ thin film on (10 $\bar{1}$ 0) sapphire utilizing radio-frequency magnetron sputtering [159]. In addition, the double peaks in the phi scan of SnO₂ film imply a mosaic growth due to the tilting relationship. This mosaic structure helps to release the stress induced by the lattice mismatch.

Figure 4-8 shows the X-ray rocking curve of SnO₂ (002) peak of the SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate. The FWHM of the rocking curve is found to be 1.2°. This FWHM value suggests a fair epitaxial quality of (200) SnO₂ thin film on the (10 $\bar{1}$ 0) plane of the sapphire substrate.

Figure 4-8. ω -scan (rocking curve) of the SnO₂ (002) peak for SnO₂ film on (10 $\bar{1}$ 0) sapphire substrate.

Figure 4-9 (a) shows the RHEED pattern of SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate. The single crystalline form of SnO₂ thin film is indicated by the well defined RHEED pattern. In addition, the spotty RHEED pattern implies that the growth of SnO₂ on (10 $\bar{1}$ 0) sapphire substrate is in 3D mode. Figure 4-9 (b) presents the AFM topography image of the as deposited SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate. The surface RMS roughness determined from the Figure 4-9 (b) is 1.5 nm.

Figure 4-9. (a) *in-situ* RHEED pattern and (b) *ex-situ* AFM topography result of the SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate.

4.1.4 Summary

SnO₂ thin films, with rutile phase, have been epitaxially deposited using LMBE on sapphire substrates. Orientation controlled SnO₂ epitaxial thin films, i.e. (101), (200), and (002), were grown on the (10 $\bar{1}$ 2), (0001), and (10 $\bar{1}$ 0) sapphire substrates, respectively. The epitaxy relationships were determined as: (a) (101) SnO₂ // (10 $\bar{1}$ 2)

sapphire; [010]SnO₂ // [$\bar{1}2\bar{1}0$] sapphire and [$\bar{1}01$]SnO₂ // [$\bar{1}011$] sapphire for the (101) SnO₂ thin film on ($10\bar{1}2$) sapphire; (b) (200) SnO₂ // (0001) sapphire; [001]SnO₂ // $\langle\bar{1}0\bar{1}0\rangle$ sapphire and [001]SnO₂ // $\langle 1\bar{2}10\rangle$ sapphire for the (200) SnO₂ thin film on (0001) sapphire. A six-fold rotation for the SnO₂ grains was observed in the (200) SnO₂ thin film on (0001) sapphire substrate; (c) (002) SnO₂ // ($10\bar{1}0$) sapphire. [010]SnO₂ // [0001] sapphire and [100]SnO₂ // [$\bar{1}010$] sapphire for the (002) SnO₂ thin film on ($10\bar{1}0$) sapphire substrate. The single-crystal nature and smooth surface of all the three SnO₂ thin films were confirmed by RHEED and AFM results.

4.2 Epitaxial growth of SnO₂ thin film on (111) perovskite substrate

4.2.1 Introduction

The wide variety of physical properties of metal oxides makes them interesting materials for technological applications and provides an ideal platform for interdisciplinary scientific explorations and fundamental understanding [160]. As introduced in Chapter 2, SnO₂ is a wide band gap (~3.6 eV at 300 K) *n*-type semiconductor with rutile structure. Owing to its exotic electrical, optical, and electrochemical properties, SnO₂ has been widely used in many applications, such as integrated chemical sensors [9], light emitting devices [3], and transparent electrodes for flat panel displays [7]. As discussed in Section 4.1, the fabrication of SnO₂ in the form of thin film, especially high quality epitaxial films has been studied by various deposition techniques, such as oxygen plasma assisted MBE [161], CVD [48], rf-plasma sputtering [162], and PLD [23]. The most commonly used substrates for epitaxial growth of SnO₂ thin films include isostructural TiO₂ and heterostructural sapphire with (10 $\bar{1}$ 2), (0001) and (10 $\bar{1}$ 0) orientation [23,41,46]. In Section 4.1 of this dissertation, the orientation controlled SnO₂ thin film epitaxy on sapphire substrates has been systematically investigated. However, there is no report on the epitaxial growth of SnO₂ thin films on perovskite structural substrates, which may give rise to the feasibility of hybrid devices design.

Extensive research work has been devoted on perovskites, due to their wide spectrum of physical properties, such as ferroelectricity, ferromagnetism, multiferroics, superconductivity and MIT. There have already been many examples of prototype electronic devices based on the combinations of binary semiconducting oxides and complex perovskite oxides, exploiting phenomena such as current rectification effect [163], photovoltaics [164], colossal magnetoresistance [165], resistive memory switching [166,167], magnetic moment modulation [168] and field effect transistor (FET) [169]. In this light, the integration of SnO₂ on multifunctional perovskite materials will offer an interesting opportunity to the design of new devices with novel functionalities. In this section, single crystal SrTiO₃ (STO) was used as the substrate, which is in general the favorite substrate for the growth of many perovskite thin films. (200)-orientated SnO₂ thin films were deposited on (111) surface of STO using LMBE system, and the epitaxial relationship was proposed from the view point of crystallographic symmetry. Additionally, the optical parameters of the epitaxial SnO₂ thin film in the UV-Vis-NIR range were studied by ellipsometry.

4.2.2 Experimental detail

The same LMBE system described in Section 4.1 was used to grow SnO₂ thin films on (111) STO substrate. Prior to the film deposition, the substrates were heated up to 500 °C for 30 min in high vacuum, and followed by a second annealing step at 700 °C under the oxygen atmosphere with a pressure of 1 Pa for 30 min. A series of SnO₂ thin films with thickness around 150 nm were deposited on those STO substrates at a

substrate temperature (T_{Sub}) range of 600 °C to 750 °C and oxygen pressure (P_{Oxy}) from 10^{-3} Pa to 1 Pa, respectively. The surface morphology of the substrates and films were investigated by AFM. Both substrate holder and heater were rotatable to adjust the azimuthal angle of the incident electron beam. Structural characterization was carried by *ex-situ* XRD. In order to study the optical properties of SnO₂ film deposited on STO substrate, spectroscopic ellipsometry has been equipped to measure the film thickness and dielectric function in the UV-Vis-NIR range.

4.2.3 Results and discussions

Both the substrates and SnO₂ thin films were *in-situ* monitored by RHEED. Figure 4-10 (a) shows the RHEED pattern of the STO (111) substrate, in which the $[11\bar{2}]$ direction of the substrate was aligned parallel to the incoming electron beam. In the RHEED pattern, the diffraction spots lying on 0th Laue zone order were labeled as $(0\bar{1})$, (00) , and (01) reflections, which indicate smooth surface of STO substrate. The AFM image of STO substrate and its typical surface profile are shown in Figure 4-10 (b), which is consistent with the RHEED pattern. Without rotation of the substrate, the RHEED pattern evolved to 3D transmission mode as shown in Figure 4-10 (c), suggesting that the SnO₂ film was grown in the Stranski-Krastanov growth mode. As shown in Figure 4-10 (c), the narrow and elongated RHEED pattern indicates a highly oriented crystal with short and wide grains on the surface. Figure 4-10 (d) gives the AFM image of the as deposited SnO₂ thin film, from which the RMS roughness can be determined as 2.35 nm.

Figure 4-10. RHEED patterns of (a) STO (111) substrate, (c) as deposited SnO_2 thin film, and their corresponding AFM images of (b), (d).

By analyzing the electron diffraction pattern in Figure 4-10 (c), in which the ratio (r_1/r_2) of the spacing of diffraction planes and the angle (ϕ) between the corresponding spots are around 1 and 67° , respectively. The azimuth of the film referring to the electron beam can be determined as $[010]$. The indices of the reflections are also determined as shown in the figure. The substrate and the electron beam have not been rotated when capturing these two RHEED patterns in Figure 4-10 (a) and Figure 4-10 (c). Thus, according to these two electron diffraction patterns, it

can be concluded that the atoms of SnO₂ along [010] direction should lie on the [11 $\bar{2}$] direction of STO, implying that the [010] direction of the thin film is parallel to the [11 $\bar{2}$] direction of the substrate. In addition, the horizontal distance (R) between (00) and (0 $\bar{1}$) in the RHEED pattern is inversely proportional to the inter atomic spacing d by $d = (L \times \lambda)/R$, in which the L and λ correspond to the camera length and electron wavelength, respectively [170]. Similarly, the atomic distance of the film along [001] in Figure 4-10 (c) can also be calculated.

By comparing the RHEED patterns of the substrate and the film, a prominent lattice mismatch can be observed in Figure 4-10, in which two dash lines are added to guide the eyes. Quantitatively, the lattice mismatches between [001]_{film} and [1 $\bar{1}$ 0]_{sub} can be calculated as:

$$\frac{d_{\text{film}} - d_{\text{sub}}}{d_{\text{sub}}} \times 100\% = \frac{R_{\text{sub}} - R_{\text{film}}}{R_{\text{film}}} \times 100\% = 14 \pm 2\% \quad (4-1)$$

In order to explore the phase structure and the epitaxial relationship between the film and substrate, the XRD measurement was carried out. The symmetrical 2 θ - ω scan results for all the twelve SnO₂ thin films fabricated under different temperatures and oxygen pressures are shown in Figure 4-11, in which the Figure 4-11 (a), (b), (c) show the XRD patterns of SnO₂ thin films deposited at the temperature of 600 °C, 700 °C and 750 °C, respectively; for each temperature the oxygen pressure was varied from 10⁻³ Pa to 1 Pa. According to the XRD results, all the SnO₂ thin films show pure (200) orientation. No other phases and other oriented grains were detected, suggesting that the SnO₂ can be epitaxially grown on STO (111) surface with the out of plane

epitaxial relationship of SnO₂ (200) // STO (111) under a wide range of growth conditions. The crystalline qualities of these films were determined using the ω scan (rocking curve) of (200) plane. The optimum conditions for SnO₂ deposition were found to be $T_{\text{Sub}} = 700$ °C and $P_{\text{Oxy}} = 10^{-2}$ Pa.

Figure 4-11. XRD patterns of the SnO₂ thin films fabricated under different growth conditions. (a) $T_{\text{Sub}} = 600$ °C, P_{Oxy} varied from 1 Pa to 10^{-3} Pa. (b) $T_{\text{Sub}} = 700$ °C, P_{Oxy} varied from 1 Pa to 10^{-3} Pa. (c) $T_{\text{Sub}} = 750$ °C, P_{Oxy} varied from 1 Pa to 10^{-3} Pa.

Figure 4-12 (a) shows the 2θ - ω and ω scan (insert) results of the optimized SnO₂ thin film, from which the out of plane lattice constant is calculated to be 4.734 Å. A good crystalline quality is obtained with the FWHM of rocking curve as narrow as 0.3°. Figure 4-12 (b) shows the various 2θ - ω scans with different ω values (symmetrical mapping), indicating a nearly perfect alignment between the (200) plane of the film and the substrate (111) plane.

Figure 4-12. (a) 2θ - ω scan result of optimized SnO₂ thin film on STO (111), with rocking curve inserted. (b) symmetric XRD mapping to SnO₂ (200) plane and STO (111) plane.

To get a closer view on the in-plane epitaxial relationship, phi scan also was performed to the film and the substrate, after bringing the SnO₂ (110) and STO (110) off-axis reflections to the Bragg condition of diffractometer. The tilt angle (ψ), which is the angle between the reflection plane and substrate surface plane, for SnO₂ (110) and STO (110) are 45° and 35.3°, respectively. Figure 4-13 (a) and 4-13 (b) give the

phi scan curves for the (110) plane of SnO_2 thin film and the phi scan for (110) plane of STO substrate, respectively. It is clear from Figure 4-13 (b) that the substrate shows three-fold azimuthal symmetry, which is consistent with the perovskite crystal structure. However, in the phi scan result of SnO_2 film [Figure 4-13 (a)], six-fold symmetry is observed, which is not expected in tetragonal rutile structure (SnO_2). These results imply that six symmetrical in-plane orientations should be present in the (200) SnO_2 thin film. This in-plane rotation of the SnO_2 is believed to be due to the three-fold symmetry of the STO substrate, which is similar with the case of epitaxial growth of SnO_2 on sapphire (0001) plane [46].

Figure 4-13. XRD phi scan results of SnO_2/STO structure: (a) (110) plane of SnO_2 , (b) (110) plane of STO. The diffraction peak index and tilt angle are indicated for each measurement.

To better understand the epitaxial relationship between the film and substrate, Figure 4-14 shows the crystallographic construction of the possible in-plane epitaxial

relationships between the rutile SnO₂ (200) plane and the STO (111) plane. In Figure 4-14 (a), the atomic arrangement of STO (111) plane is presented, in which the atoms are approximately hcp packed. The crystal structure of rutile SnO₂ (200) is illustrated in Figure 4-14 (b). By comparing these two figures, six equivalent directions in STO (111) plane for the nucleation of SnO₂ can be observed [denoted in Figure 4-14 (a) by arrows]. In addition, the lattice mismatch between the film and substrate can be calculated as: $M_{\text{SnO}_2[010]} = -0.8\%$; $M_{\text{SnO}_2[001]} = 16\%$, all of the calculations here are based on the bulk lattice constants [171,172]. It is worth to note that the theoretical lattice mismatch along the SnO₂ [001] (16%) is quite close to the result obtained from RHEED pattern analysis ($14 \pm 2\%$), which confirms the validity of *in-situ* monitoring of lattice mismatch.

Figure 4-14. Comparison of crystal structures of (a) STO (111) plane, and (b) SnO₂ (100) plane.

Based on the above crystallographic model and XRD results, the epitaxial relationship of (200) SnO₂ film on (111) STO substrate can be summarized as following, in which the three distinct in-plane epitaxial relationships are presented.

Out of plane: SnO₂ (100) // SrTiO₃ (111),

In plane: SnO₂ [010] // SrTiO₃ $\langle 1\bar{2}1 \rangle$, SnO₂ (001) // SrTiO₃ $\langle \bar{1}01 \rangle$

Based on the previous results, the epitaxial growth of SnO₂ on STO was confirmed by two diffraction methods (RHEED and XRD). As a direct and powerful technique, TEM was used to investigate the microstructure of the SnO₂ thin film. Figure 4-15 (a) shows a typical low magnification cross-sectional TEM image of the SnO₂/STO heterostructure. From this TEM image, the thickness of SnO₂ layer was found to be 155 ± 2 nm. The high-resolution image of the SnO₂/STO interface is given in Figure 4-15 (b). The epitaxial growth of SnO₂ layer on STO (111) plane was further confirmed. In addition, a sharp interface with no evidence of significant interdiffusion is revealed by this high-resolution TEM image.

Figure 4-15. Cross-sectional TEM image of SnO_2/STO heterostructure. (a) low magnification image and (b) high-resolution TEM image on the interface region. (c) SAED pattern of SnO_2/STO .

The optical properties of SnO_2 have attracted great interests, especially for the optoelectronic applications. In this work, the SnO_2 epitaxial film on STO substrate was studied by ellipsometry, which is an accurate, sensitive, powerful, and

nondestructive method to characterize the optical parameters and thickness of thin film [173]. In the present study, the (Ψ, Δ) spectra for the SnO₂ thin film prepared under the optimized conditions were measured for three incident angles (i.e., 65°, 70°, and 75°) over the range from the 0.6 to 4.3 eV. A double layer model on STO substrate was built to simulate the SnO₂ thin film: a surface rough layer consisting of void and SnO₂ based on the Bruggeman effective medium approximation (EMA) combined with a homogeneous SnO₂ layer, as shown schematically in the inset of Figure 4-17.

In order to fit the measured (Ψ, Δ) spectra, the dielectric function $\varepsilon(E) = \varepsilon_r(E) + i\varepsilon_i(E)$ should be formulated, in addition to the models for layered structure of the films. It has been shown that the Kramers-Kronig-consistent Tauc-Lorentz (TL) model obtained from the Tauc joint density of states and the standard quantum mechanical or Lorentz calculation for ε_i , is suitable to parameterize the dielectric function of semiconductors around the interband transitions region [174]. Considering the native *n*-type conductivity of SnO₂ induced by the possible oxygen vacancies in the film, the interband transitions which happened in the lower energy region of spectral range have to be taken into account in our dielectric function. Therefore, in the data fittings of the present study, the TL dispersion model combined with the Drude expression, which is used to simulate the free electron absorption, is adopted. In our TL-Drude model, the imaginary part (ε_i) of dielectric function is written as:

$$\varepsilon_i(E) = \begin{cases} \frac{A_f^2 \Gamma_f}{E(E^2 + \Gamma_f^2)}, & \text{for } E < E_g \\ \frac{A_b \Gamma_b E_b (E - E_g)^2}{(E^2 - E_b^2)^2 + \Gamma_b^2 E^2} \cdot \frac{1}{E}, & \text{for } E > E_g \end{cases} \quad (4-2)$$

Where the parameters $\{A_b, E_b, \Gamma_b\}$ correspond to the amplitude, resonance energy, and broadening for the interband electron transitions, E_g is the energy band gap, and $\{A_f, \Gamma_f\}$ represent the amplitude and broadening for the intraband (or free) electron transitions [175]. The real part (ε_r) of dielectric function is obtained by Kramers-Kronig integration of ε_i with a fitting constant $\varepsilon_r(\infty)$. Nine parameters, i.e. $A_b, E_b, \Gamma_b, E_g, A_f, \Gamma_f, \varepsilon_r(\infty)$, the thickness of SnO₂ film and its surface roughness, were extracted based on the best fit in the least-square fitting procedure between experimental ellipsometry data and the model simulation results.

Figure 4-16. Comparison of the measured (points) and the best fit (solid line) to the ellipsometric parameters (Ψ, Δ) of the SnO₂ thin film with a 150 nm thickness deposited on STO substrate using the structural model illustrated in Figure 4-17. (for a clear presentation, only the fittings for the incident angles of 65° and 70° are shown)

Figure 4-16 shows the best fit to the (Ψ, Δ) spectra. Based on the least-square fitting, the parameters used in TL-Drude model are summarized in Table 4-1. The thickness of SnO₂ thin film was determined to be 156.9 nm, which agrees well with the thickness (155±2 nm) measured by TEM in Figure 4-15. The value of energy band gap is fitted to be 3.65 eV, which is similar to the result reported by another group [174]. In addition, the surface roughness extracted from ellipsometry data fitting is 2.1 nm, which agrees well with the value (2.5 nm) characterized by AFM. The real (ϵ_r) and imaginary (ϵ_i) parts of dielectric function of SnO₂ thin film on STO substrate are shown in Figure 4-17. It can be seen that the value of ϵ_r investigated in the UV-Vis-NIR region of the epitaxial SnO₂ thin film on STO is in the range of 3.5 to 6. As for the imaginary part, the ϵ_i shows an absorption onset in the near UV, which corresponds to the energy band gap ($E_g=3.65\text{eV}$). A negative curvature at lower energies is revealed in the ϵ_i spectrum, which shows the existence of intraband transitions induced by the free electrons.

Table 4-1. Parameters of the SnO₂ thin film extracted from the best fitting to ellipsometry experimental data by TL-Drude model.

SnO ₂ layer	A_b	E_b	Γ_b	E_g	A_f	Γ_f	$\epsilon_r(\infty)$	Surface	χ^2
Thickness	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)		roughness	
(nm)								(nm)	
156.9	264.33	3.56	32.09	3.65	0.17	1.36	2.08	2.1	3.67

Figure 4-17. The extracted dielectric functions $\epsilon(E) = \epsilon_r(E) + i\epsilon_i(E)$ of the SnO₂ thin film on STO substrate. The inset is a schematic structure of the double layer model for the data fitting.

4.2.4 Summary

In conclusion, LMBE technique has been used to grow epitaxial SnO₂ thin films on perovskite structural STO (111) substrate. Detailed analysis with *in-situ* RHEED, *ex-situ* XRD, AFM and TEM confirm the possibility of epitaxial growth of SnO₂ on perovskite substrate under a wide range of deposition conditions, despite of the large lattice mismatch and hetero structure between the film and the substrate. The dielectric function for this SnO₂ epilayer in the UV-Vis-NIR region has been investigated by ellipsometry. This successful growth of epitaxial SnO₂/STO also

opens a way for combining SnO₂ films with many other materials which are compatible with STO, and consequently gives the feasibility of new hybrid device design.

4.3 Band alignment between SnO₂ and STO

4.3.1 Introduction

As mentioned in Section 4.2, the integration of SnO₂ and multifunctional perovskite materials may offer an interesting opportunity to the design of new devices with novel functionalities. It is well known that the interface of heterostructures plays an important role in determining their properties. Various interesting phenomena, such as quasi-two-dimensional electron gases [176], tunable ferromagnetism [177], colossal magnetoresistance [178], and superconductivity [179] have been observed in the artificially designed interface in perovskite oxides based heterostructures. Previously in Section 4.2, the epitaxial growth of SnO₂ thin film on STO substrate has been investigated. In this section, as for SnO₂/STO heterostructure, the XPS was used to investigate its band alignment, which is believed to be an important issue for the SnO₂/STO interface. In addition, the band alignment between the heterostructure components determines the parameters for their optoelectronic properties, dictating the degree of charge carrier separation and localization. It is important to determine the band alignment of the heterostructure for designing, modeling and analyzing the performance of such devices. As a continuing work of Section 4.2, we have experimentally studied the band alignment of the SnO₂/STO heterostructure using XPS. The valence band offset (VBO) as well as conduction band offset (CBO) are quantitatively determined.

4.3.2 Experimental detail

In the fabrication of SnO₂/STO heterostructure, prior to the growth of SnO₂ layer, a 50-nm-thick layer of STO was homo-epitaxially deposited on the STO (111) substrate. The purpose of this STO epilayer is to have a fresh STO layer in our SnO₂/STO heterostructure, and to avoid the surface contamination on the as-purchased STO substrate. The SnO₂ layer was fabricated according to the parameters determined in Section 4.2. To measure the energy band alignment, three samples were prepared. One is 50-nm-thick STO epilayer on the STO (111) substrate, which is denoted as STO-epi. The others are two SnO₂/STO heterojunction samples for which 5-nm and 150-nm-thick SnO₂ films were deposited on the STO (111) substrate with a 200-nm-thick STO epilayer. These two samples are labeled as 5-SnO₂/STO and 150-SnO₂/STO, respectively.

4.3.3 Results and discussions

The homo-epitaxy of STO was *in-situ* monitored by RHEED which was operated in anti-Bragg condition using 20 keV electron beam under a grazing incidence angle of 1°-3° toward substrate surface. A typical RHEED pattern of the STO epilayer is shown in the inset of Figure 4-18. Both the sharp electron diffraction pattern and clear kikuchi line indicate a smooth surface of the STO epilayer. The RHEED intensity evolution during the STO epilayer growth was recorded and shown in Figure 4-18, in which the RHEED intensity oscillation is presented. The layer-by-layer growth mode

of STO was confirmed by the intensity oscillation. Each cycle of oscillation indicated a completed monolayer of STO deposition. By calculating the average of oscillation periods, the growth rate could be determined to be 17 laser pulses per monolayer (3.91 Å).

Figure 4-18. The RHEED intensity oscillation of STO epilayer growth with the RHEED pattern (inset).

Figure 4-19 shows the symmetrical 2θ - ω XRD pattern of the as prepared 150-SnO₂/STO junction, from which the epitaxial relationship of SnO₂ (200) // STO (111) was confirmed. The insets (I) and (II) in Figure 4-19 give the ω scan (rocking curve) of SnO₂ (200) plane and the *in-situ* RHEED pattern, respectively, from which a good crystal quality of the SnO₂ layer could be observed.

Figure 4-19. 2θ - ω XRD result for the as fabricated 150-SnO₂/STO heterostructure. The insets I and II show the rocking curve and RHEED pattern of SnO₂ layer, respectively.

The determination of band alignment, in particular the VBO and CBO, is of crucial importance for the device design and understanding the transport properties of such device. XPS has been demonstrated to be a direct and powerful tool for measuring the VB discontinuities of heterojunctions [180-184]. To determine the VBO of SnO₂/STO heterojunction, high resolution XPS spectra were taken for the VB, Sn 3d and Ti 2p core levels (CLs) in the above mentioned samples. The VBO can be calculated by the following formula [181,185]:

$$\Delta E_V = E_V^{SnO_2} - E_V^{STO} = \Delta E_{CL} + \left(E_{Sn\ 3d\ 5/2}^{SnO_2} - E_{VBM}^{SnO_2} \right) - \left(E_{Ti\ 2p\ 3/2}^{STO} - E_{VBM}^{STO} \right) \quad (4-3)$$

where $\Delta E_{CL} = E_{Ti\ 2p\ 3/2}^{STO} - E_{Sn\ 3d\ 5/2}^{SnO_2}$ is the energy difference between Ti 2p 3/2 and Sn 3d 5/2 CLs in the 5-SnO₂/STO heterostructure, $E_{Sn\ 3d\ 5/2}^{SnO_2} - E_{VBM}^{SnO_2}$ is the energy difference between Sn_{3d 5/2} and valence band maximum (VBM) in the 150-SnO₂/STO heterostructure, and $E_{Ti\ 2p\ 3/2}^{STO} - E_{VBM}^{STO}$ is the energy difference between Ti_{2p 3/2} and VBM in the STO-epi sample. The CL narrow scans and VB region XPS spectra for STO-epi, 5-SnO₂/STO and 150-SnO₂/STO heterostructure are shown in Figure 4-20. All the CL spectra were fitted to a Voigt (mixed Lorentz-Gaussian) line shape with a Shirley background. The VBM positions were determined by extrapolating a linear fit to the leading edge of the VB photoemission to the background level in order to take account of the finite resolution of the spectrometer.

Figure 4-20. XPS spectra of all three samples. VB (a) in 150-SnO₂/STO and (c) in STO-epi, Sn 3d CL (b) in 150-SnO₂/STO and (f) in 5-SnO₂/STO, Ti2p CL (d) in STO-epi and (e) in 5-SnO₂/STO.

The parameters for fittings to the spectra in Figure 4-20 were extracted and summarized in Table 4-2.

Table 4-2. Binding energies of the XPS CLs and VBM for all the three samples.

Sample	VB (eV)	Sn3d _{5/2} (eV)	Ti2p _{3/2} (eV)
150-SnO ₂ /STO	3.28±0.10	487.01±0.05	
STO-epi	2.29±0.10		458.44±0.05
5-SnO ₂ /STO		487.04±0.05	458.61±0.05

By substituting these values into Equation (4-3), the VBO of SnO₂/STO heterostructure is calculated to be -0.85 ± 0.20 eV. In addition, the CBO (ΔE_C) can be estimated by the formula $\Delta E_C = E_C^{SnO_2} - E_C^{STO} = E_V^{SnO_2} + E_g^{SnO_2} - (E_V^{STO} + E_g^{STO})$. According to the room temperature energy band gap values ($E_g^{SnO_2} = 3.65$ eV and $E_g^{STO} = 3.25$ eV) [156,186], the ΔE_C is calculated to be -0.45 ± 0.20 eV. Based on the above analyses, the energy band diagram is deduced and shown in Figure 4-21, from which a type-II band alignment is revealed for the SnO₂/STO heterostructure.

Figure 4-21. Schematic energy band diagram of the SnO₂/STO heterostructure, in which a type-II alignment is indicated.

4.3.4 Summary

In summary, a SnO₂/STO based heterostructure was fabricated by the LMBE technique. The device fabrication was *in-situ* monitored by RHEED, which indicated a high crystalline quality. Epitaxial growth of SnO₂ on STO was investigated by XRD. Based on the XPS results, the VBO and CBO of this heterostructure were determined to be 0.85 ± 0.20 eV and 0.45 ± 0.20 eV, respectively.

CHAPTER 5 ELECTRICAL TRANSPORT PROPERTIES OF SnO₂ THIN FILMS

The deposition of SnO₂ thin films by LMBE technique was extensively investigated and discussed in Chapter 4. High quality SnO₂ thin films with artificially controllable crystal orientations were achieved on sapphire substrates. On the other hand, as a well known wide band gap semiconductor, most of the applications of SnO₂ utilize the electrical transport properties of this material, e.g. transparent conducting oxide, gas sensor, thin film transistor and light emitting diode. Accordingly, in this chapter, the electrical transport properties of SnO₂ thin films fabricated by LMBE will be extensively studied.

This chapter is organized as follows: The first section presents a crystal orientation dependent anisotropic conduction in SnO₂ epitaxial thin films. This crystal orientation

controlled electrical conduction behavior is attributed to the anisotropic crystal structure of SnO₂. The second section is focused on the thickness effect on the electrical transport properties of SnO₂:Sb based conductive oxide thin films. In this section, the electrical conduction behavior of SnO₂:Sb thin film was found to be strongly affected by the thickness. The last section studies the thermal annealing effect on the electrical transport properties of SnO₂ thin films deposited on quartz substrates. By varying the annealing temperature, an anomalous electrical transport behavior of the SnO₂ thin films was observed and explained based on the crystal grain size growth and temperature-dependent oxygen vacancy density variation.

5.1 Anisotropic conduction in SnO₂ epitaxial thin films

Benefited by the crystal orientation controllable epitaxy technique achieved in Chapter 4, the electrical transport properties in differently orientated SnO₂ thin films are studied in this section.

5.1.1 Introduction

As introduced in Chapter 2, SnO₂ is one of the few wide band gap materials which possess fairly high electrical conductivity. On the basis of these exotic properties, SnO₂ has been widely used as electrical conduction channel in optoelectronic devices such as flat panel displays, thin film solar energy cell, light emitting diodes and transparent thin film transistors [3,7,150]. Another well-known application of SnO₂ is gas sensor, which is designed to utilize the gas induced resistance variation of this material [9]. As a result, the electrical transport properties of SnO₂ single crystals, SnO₂ thin films, SnO₂ nanostructures and impurity doped SnO₂ have been extensively studied [187-190]. The stoichiometric and defect-free SnO₂ is a good insulator with a large energy band gap (~3.6 eV). However, artificially fabricated SnO₂ is usually found to be an *n*-type semiconductor due to the existence of oxygen vacancies which act as effective electron donors in the SnO₂ lattice.

Although the electrical transport properties of SnO₂ have been extensively studied, the investigations on the electrical conduction behavior of SnO₂ epitaxial films are still

limited. On the other hand, the crystal structure of SnO₂ (rutile) is anisotropic in the $a(b)$ -axis and c -axis (Figure 2-1). Studying the crystal orientation effect on the conduction behaviors of SnO₂ epitaxial thin films becomes essential for understanding the electrical transport properties of SnO₂ thin films. In addition, a prominent anisotropic conductivity has been discovered in nonstoichiometric TiO₂ which possesses the identical crystal structure of SnO₂ [191]. The electrical transport properties of (002)- and (200)-orientated SnO₂ thin films were investigated in this study. The resistivity and the activation energy of oxygen vacancy were found to show a strong dependence on the thin film crystal orientation. This orientation controlled electrical conduction behavior can be understood on the basis of the anisotropic crystal structure of SnO₂.

5.1.2 Experimental detail

To investigate the crystal orientation effect, three SnO₂ thin films with two distinct orientations were fabricated, using different substrates (discussed in Chapter 4). One (002)-orientated SnO₂ thin film labeled as S1 was deposited on (10 $\bar{1}$ 0) sapphire substrate. Two (200)-orientated SnO₂ thin films labeled as S2 and S3 were grown on (0001) sapphire and (111) STO substrates, respectively. The reason we specifically choose the (002) and (200) orientations was that the lattice constant of SnO₂ is anisotropic in a and c direction, respectively ($a = b = 4.74$ Å and $c = 3.19$ Å) [27]. This structure anisotropy in SnO₂ may give rise to the electrical transport anisotropy in (200) and (002) orientated SnO₂ thin films. The thin film deposition techniques

have been described in Chapter 4. Considering that stoichiometric SnO₂ is a wide band gap insulator, oxygen vacancies are purposely introduced into the SnO₂ thin films by controlling the oxygen pressure at 0.1 Pa. Besides the oxygen vacancy density, the electrical transport in SnO₂ thin films are also affected by other factors, such as film thickness, deposition temperature, and crystal quality. To focus on the crystal orientation effect, we fabricated all the samples, S1, S2 and S3, simultaneously by keeping three different substrates on the same substrate holder at the same time. Accordingly, the deposition parameters were exactly the same for all three samples: substrate temperature ($T_{\text{Sub}} = 700\text{ }^{\circ}\text{C}$), oxygen pressure ($P_{\text{Oxy}} = 0.1\text{ Pa}$), and laser energy ($E_{\text{Laser}} = 1.5\text{ J/cm}^2$). The film thickness was fixed at 200 nm. The crystal orientation and quality of the thin films were characterized by XRD. Temperature dependent resistivity was measured in Van der Pauw configuration using Hall measurement system.

5.1.3 Results and discussions

Figure 5-1 (a) shows the 2θ - ω XRD scan results of SnO₂ thin films deposited on sapphire (10 $\bar{1}$ 0), sapphire (0001) and STO (111) substrates, respectively. According to the XRD results, Sample S1 [on sapphire (10 $\bar{1}$ 0)] is (002)-orientated. Sample S2 [on sapphire (0001)] and S3 [on SrTiO₃ (111)] are (200)-orientated. These results are consistent with the discussions in Chapter 4. The crystalline quality of the SnO₂ thin films were characterized by the X-ray ω -scan (rocking curve), as shown in Figure 5-1 (b). Quantifying the film quality can be achieved by measuring the FWHM of the

rocking curve. It can be seen that the Sample S1 and S3 have similar crystalline quality due to their very close FWHM values (1.2° for S1 and 1.15° for S3). A much higher crystalline quality was achieved in Sample S2, for which the FWHM was measured as 0.03°.

Figure 5-1. (a) XRD 2θ-ω scan results of Sample S1, S2, and S3. (b) ω-scan (rocking curve) of the Sample S1, S2, and S3.

The in-plane resistivity of the (002)- and (200)-orientated SnO₂ thin films were measured as a function of temperature ranging from 90 K to 400 K. Figure 5-2 shows semilogarithmic plot of the temperature-dependent resistivity of each film. From these results, it can be seen that all three samples show semiconductor behavior from which the resistivity increased with the decrease of the temperature. The majority carriers in the SnO₂ thin films were measured to be electrons. These are consistent with the donor nature of oxygen vacancy in SnO₂, which has been discussed in Chapter 2. On the other hand, it is evident that the resistivity of (002)-orientated SnO₂ thin film on (10 $\bar{1}$ 0) sapphire substrate is much higher than that of (200)-orientated SnO₂ thin films deposited both on (111) STO substrate and on (0001) sapphire substrate. As the temperature decreased from 400 K to 90 K, the resistivity ratio between (200) SnO₂ thin film and (002) SnO₂ thin films increased from $\sim 10^2$ to $\sim 10^3$. It is worth mentioning that the resistivity of (200) SnO₂ thin film on STO substrate is only slightly higher than that of (200) SnO₂ thin film on sapphire substrate. The resistivity ratio between these two (200)-orientated SnO₂ thin films keeps around 2 in the temperature range from 400 K to 90 K.

Figure 5-2. Temperature dependence of resistivity in (002)- and (200)-orientated SnO₂ thin films on different substrates.

According to the temperature dependent resistivity results in Figure 5-2, the resistivity of SnO₂ thin films shows substrate dependence. It is well-known that the resistivity of a semiconductor thin film is usually affected by various factors, e.g. the doping concentration, deposition method, and crystal quality. In our case, the thin film fabrication conditions, including substrate temperature, oxygen partial pressure, target, laser energy density, and target to substrate distance, were kept exactly the same for all the three samples. Although all SnO₂ films were deposited at the same conditions, the oxygen vacancy densities (i.e. electron doping concentration) in these three SnO₂ samples may be still different, since the crystal nucleation orientation will affect the oxygen vacancy density. To determine the oxygen vacancy concentration in the SnO₂ films, XPS measurement has been done to the all three SnO₂ films. From the XPS results, the O/Sn atomic ratio was calculated to be 1.58 ± 0.05 , 1.70 ± 0.05 and

1.67 $\pm$ 0.05 for Sample S1, S2 and S3, respectively. Based on the O/Sn ratio values, it is clear that the oxygen vacancy density is indeed affected by the crystal orientation. XPS results indicate that the Sample S1 has more oxygen vacancy than Sample S2 and S3, since O/Sn ratio of S1 is the lowest. However, the electrical transport measurement results (Figure 5-2) shows that Sample S1 has the highest resistivity. As a result the resistivity difference shown in Figure 5-2 cannot be explained by the oxygen vacancy concentration difference, since more oxygen vacancy will lead to a lower resistivity. In addition, the resistivity difference in Sample S2 and S3, which have the same crystal orientation and similar oxygen vacancy density, could be attributed to the difference of their crystalline quality. As discussed previously, the crystal quality of Sample S2 is higher than Sample S3, due to the smaller FWHM of rocking curve of Sample S2. It means that the electrons in Sample S3 will be more likely scattered by the defects or grain boundaries than those in Sample S2. Consequently, the resistivity of Sample S3 is higher than that of Sample S2. Furthermore, the scattering center (e.g. defect, grain boundary) density is temperature independent. This can be used to explain that the resistivity ratio between Sample S3 and S2 is nearly temperature independent in the range from 400 K to 90 K.

It can be seen that the crystalline quality indeed affects the resistivity of the SnO₂ thin films, but the influence is relatively small. However, compared with the resistivity of (200)-orientated Samples (S2 and S3), the resistivity of Sample S1 [(002)-orientated SnO₂ thin film] is much higher. Although Samples S1 and S2 have the similar crystalline quality [see XRD results in Figure 5-1 (b)], the resistivity of S1 is still ~100 times higher than that of S2. In addition, the SnO₂ thin film deposited on (111)

STO substrate (S2) has a six-fold in-plane grain rotation (discussed in Chapter 4), which would further increase the resistivity. Based on these analyses, the prominent resistivity difference between the (002)-orientated SnO₂ thin film (S1) and (200)-orientated SnO₂ thin films (S2 and S3) cannot be simply attributed to the influence of crystalline quality. It is suspected that this electrical conduction anisotropy should come from the difference in crystal orientation.

To further study the electrical transport properties of these three samples, we have plotted the resistivity data in Arrhenius model, which is shown in Figure 5-3 (a). In the relatively high temperature region, the resistivity data can be fitted by [192]:

$$\rho(T) \approx \rho_0 \exp\left(\frac{E_A}{k_B T}\right) \quad (5-1)$$

where ρ_0 is the residual electrical resistivity, E_A is the activation energy and k_B is the Boltzmann constant. Figure 5-3 (a) gives the fitting results, showing that the E_A of Samples S1, S2 and S3 are 88.2 meV, 17.7 meV and 17.8 meV, respectively. It is evident that the E_A in (002)-orientated SnO₂ film (S1) is much higher than that in (200)-orientated SnO₂ films (S2 and S3). On the other hand, Samples S2 and S3 have very similar E_A , which implies that the crystalline quality difference between S2 and S3 has very small impact on the activation energies. Accordingly, the E_A in SnO₂ thin films seems to be strongly affected by the crystal orientation. In the low temperature region, the electrical transport behavior can be described in terms of variable-range hopping (VRH) conduction. In the VRH model, an electron moves by hopping from one localized state to another. When the density of states is finite and the states are localized at Fermi energy, the Mott VRH occurs. In Mott VRH regime, the three-dimensional VRH mechanism is described by the following equation [193]:

$$\rho(T) \approx \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^m \right] \quad (5-2)$$

where m is the hopping exponent, equal to 0.25 in the Mott VRH regime, and

$$T_0 = \left[\frac{18\alpha^3}{k_B N(E_F)} \right] \quad (5-3)$$

where T_0 is a characteristic temperature coefficient, $N(E_F)$ is the density of localized states at the Fermi level, and α describes the spatial extent of the localized wave function and is assumed to be $0.124 \text{ \AA}^{-1}$ [193]. Figure 5-3 (b) shows a plot of $\ln(\rho)$ against $T^{-1/4}$. It is evident from the straight lines in Figure 5-3 (b) that the electron transport in all the three SnO₂ films can be explained by the Mott VRH model in the low temperature region. According to the Mott VRH conduction mechanism, the $N(E_F)$ can be calculated to be $1.9 \pm 0.03 \times 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$, $9.0 \pm 0.5 \times 10^{23} \text{ cm}^{-3} \text{ eV}^{-1}$ and $1.6 \pm 0.2 \times 10^{23} \text{ cm}^{-3} \text{ eV}^{-1}$ for the Samples S1, S2 and S3, respectively. It is obvious that the density of localized states at the Fermi level is much lower in the (002)-orientated SnO₂ film (S1) than that in the (200)-orientated SnO₂ films (S2 and S3). As for Samples S2 and S3 which have the same orientation but different crystalline quality, their $N(E_F)$ are in the same order but with little difference. This implies that the crystal orientation has strong influence on the $N(E_F)$.

Figure 5-3. (a) Arrhenius plot of the resistivity data of Samples S1, S2, and S3. (b) Mott VRH plot of the resistivity data of Samples S1, S2, and S3.

According to the above electrical transport measurement and analyses, a crystal orientation determined electrical conduction was revealed in SnO₂ epitaxial thin films. In (200)-orientated SnO₂ thin film, the electrons flow in the *a* plane of rutile SnO₂, i.e., electrons move along the *c* and *b* axes. In (002)-orientated SnO₂ films, the electrons

flow in the c plane, i.e., electrons move along the a and b axes. Referring to the crystal structure of SnO₂ (Figure 5-4), the lattice constant along the c axis is remarkably shorter than that along a and b axes. Intuitively, it means that the electron movement along c axis will be easier than a and b axes. As a result, the resistivity in the c orientation should be lower than that in the a and b orientations, which is consistent with experimental results. Similar anisotropic conduction was observed by L. E. Hollander *et al.* in the TiO₂ single crystal [191], which is isostructural with SnO₂. According to the results of L. E. Hollander *et al.*, anisotropy of conduction greater than 10^3 to 1 was observed at room temperature, increasing to more than 10^4 to 1 at -60 °C. This anisotropy conduction in TiO₂ was attributed to the difference of lattice spacing between the c direction and $a(=b)$ direction ($c/a = 0.644$ in TiO₂). Based on a crude hydrogen atom approximation, it was found that the overlap probability of the Bohr orbits in the c direction is three times of that in a direction in the TiO₂. Consequently, this high electron wave function overlap in c direction gives high conductivity. Similarly, in our SnO₂ thin films, the anisotropy can also be examined on the basis of the separation of the Bohr orbits in the a and c directions. From the hydrogen atom approximation, the Bohr radius, a_B , can be obtained from the relation:

$$a_B = \frac{\varepsilon \hbar^2}{m^* e^2} \quad (5-4)$$

where ε is the dielectric constant of the material being examined, m^* is the effective electron mass, e is the electronic charge, and $\hbar$ is the Planck's constant divided by 2π . For SnO₂: (a) the dielectric constants are $\varepsilon_{\parallel a} = 14.0$ and $\varepsilon_{\parallel c} = 9.86$, (b) the effective electron masses are $m_{\parallel a}^* = 0.3m_0$ and $m_{\parallel c}^* = 0.23m_0$, where m_0 is the free electron mass, (c) the lattice constants are $a = 4.74$ Å and $c = 3.18$ Å with a c/a ratio of 0.67. According to Equation 5-4, the overlap probability of the Bohr orbits in the c direction

is ~1.6 times of that in the a direction of SnO₂. This stronger wave function overlap in the c direction leads to a higher density of states near Fermi level and consequently a lower resistivity.

Figure 5-4. Crystal structure of rutile SnO₂.

Furthermore, based on Boltzmann equation, the conductivity can be calculated as:

$$\sigma = \frac{e^2 n \tau_{\text{relax}}}{m^*} = e^2 D N(E_F)$$

for a simple parabolic energy band, where the n is the electron concentration, τ_{relax} is relaxation time, D is diffusion coefficient, and $N(E_F)$ corresponds to the density of state at Fermi level. According to the previous Bohr radius analysis and the crystal structure of SnO₂, the electron concentration n and the density of state $N(E_F)$ will be higher along the c axis than the a/b axis, since the Bohr radius in c axis is higher than it in a/b axis and the lattice of SnO₂ is shorter in c axis than it in a/b axis. Consequently, the high resistivity of (100) SnO₂ film and low

resistivity of (002) SnO₂ film can be explained, according to the conductivity equation deduced from Boltzmann equation.

5.1.4 Summary

In conclusion, (002)- and (200)-orientated SnO₂ thin films were epitaxially deposited on sapphire and STO substrates by LMBE. Temperature dependent electrical transport properties of these SnO₂ films were investigated. The electrical transport properties, including resistivity, activation energy, and density of localized states at the Fermi level, were found to show a strong dependence on the film orientation. This orientation controlled electrical conduction behavior has been explained in the terms of the anisotropic crystal structure of SnO₂.

5.2 Electrical transport in Sb-doped SnO₂ thin films: The thickness effect

In Section 5.1, the electrical transport properties of undoped SnO₂ thin films were studied, with emphasis on the crystal orientation effect. In this section, we investigate the electrical conduction in Sb doped SnO₂ thin films, with the focus on the thickness effect.

5.2.1 Introduction

Long-term research interest has been focused on the semiconductor doping since shallow impurities with donor- or acceptor-type play crucial roles in determining the physical properties of the host. It's generally accepted that the electronic properties are significantly affected when the size of crystal is close to its effective Bohr radius (a_B). Benefited from modern techniques, as the device size is approaching nanometer scale, the role of quantum confinement in the electronic states of shallow impurities becomes outstanding. As a fundamental issue in condensed matter physics, the size dependence of metal-insulator transition (MIT) has been well documented from metals to intrinsic metallic oxides, such as Au, Al, V₂O₃, VO₂ and SrRuO₃ [194-200]. However, a few experimental works have shed light on the size induced MIT in the impurity doped semiconductors, which has been predicted by theoretical calculations [201,202]. Sb-doped SnO₂ (SnO₂:Sb) has been an interesting impurity doped wide band gap semiconductor due to its ability to simultaneously combine a high optical

transparency with a low sheet resistance [203]. By increasing the Sb concentration above the Mott critical density (n_c), metallic electrical transport behavior can be achieved in SnO₂, which favors its applications as a TCO [204]. As the quantum confinement effect is concerned, when will the macroscopic laws that give the metallic conductivity in SnO₂:Sb fail (i.e. the critical thickness for transition from metal to insulator in SnO₂:Sb thin films)? How will the electronic properties of shallow impurity be affected? Addressing these questions is not only important from a fundamental point of view, but also beneficial to the design of miniaturized devices.

We conducted electrical and spectroscopic studies on a series of SnO₂:Sb epitaxial thin films deposited on (10 $\bar{1}$ 2) sapphire substrates. By precisely controlling the film thickness ranging from bulk (~200 nm) to quantum confinement scale ($\sim a_B$), a thickness induced MIT was observed from the temperature-dependent measurements on the electrical transport behavior. Further evidence of this transition was also provided by XPS characterizations. Analyses of the XPS core level spectra yielded conclusion that an oxidation state transition of Sb from Sb(V) to Sb(III) was driven by the thickness reduction in SnO₂:Sb ultrathin films. Consequently, the MIT in these SnO₂:Sb thin films emerged when the critical thickness was reached.

5.2.2 Experimental detail

The SnO₂:Sb thin films were deposited on (10 $\bar{1}$ 2) sapphire substrates by LMBE system. Homemade 5% Sb doped SnO₂ ceramic target was prepared via standard

solid state reaction process. The as-purchased sapphire substrates were treated using high temperature annealing technique described by M. Yoshimoto [53]. Four SnO₂:Sb thin film samples with thicknesses of 188 nm, 31.3 nm, 7.9 nm and 3.1 nm (labeled as A, B, C and D respectively) were fabricated on the sapphire substrates by varying the laser pulse counts at a fixed substrate temperature ($T_{\text{Sub}} = 700\text{ }^{\circ}\text{C}$) and under a constant oxygen partial pressure ($P_{\text{Oxy}} = 10\text{ Pa}$). The thin films were deposited at a growth rate of $0.52\text{ \AA}$ per laser ablation as deduced from the thickness calibration of the thickest SnO₂:Sb film (188 nm) using spectroscopic ellipsometry. Phase structural characterization was carried out by XRD. The electrical transport properties, namely, carrier concentration n , dc resistivity ρ and its temperature dependence were measured in Van der Pauw configuration using Hall measurement system. Considering the gas-sensitive nature of SnO₂, the chamber of Hall measurement was purged with nitrogen and evacuated in order to minimize the influence of ambient gas.

5.2.3 Results and discussions

It is well-known that high quality substrate with clean and flat surface is crucial for getting a high quality thin film in epitaxial growth. On the other hand, achieving a flat interface between the film and substrate is important for investigating the properties of ultrathin films. Accordingly, the as-purchased sapphire (10 $\bar{1}2$) substrates were treated using high temperature annealing technique describe by M. Yoshimoto [53]. Figure 5-5 shows the AFM image of sapphire (10 $\bar{1}2$) substrate annealed in oxygen ambient at the temperature of $1400\text{ }^{\circ}\text{C}$. It is evident that a flat and uniform (10 $\bar{1}2$)

sapphire substrate with surface atomic steps was achieved. The observed step height is 0.35 nm, which corresponds to the interplanar spacing of (10 $\bar{1}2$) planes.

Figure 5-5. AFM image of high temperature treated sapphire (10 $\bar{1}2$) substrate (2×2 μm²). The vertical profile was taken along the line shown in the image, which indicates an atomically flat surface with uniform atomic steps. The observed step height is 0.35 nm, which corresponds to the interplanar spacing of (10 $\bar{1}2$) planes.

The growth process of SnO₂:Sb thin films on sapphire (10 $\bar{1}2$) was *in-situ* monitored by RHEED. Similar RHEED patterns were obtained for all thin films. The inset in Figure 5-6 gives a typical RHEED image of Sample B with a thickness of 31.3 nm. The well-defined RHEED pattern indicates that the film is in single crystalline form [33]. The phase structure was further investigated by XRD. Figure 5-6 gives the 2θ-ω scan result of Sample B, in which pure (101) orientation was achieved with no other detectable foreign phase or other orientated grains. This suggests that the SnO₂:Sb thin film was epitaxially deposited with the out of plane epitaxial relationship of

SnO₂ (101) // sapphire (10 $\bar{1}2$). This is consistent with the results discussed in Chapter 4.

Figure 5-6. XRD patterns of SnO₂:Sb film on sapphire (10 $\bar{1}2$) substrate. The inset shows the *in-situ* RHEED pattern of the as-deposited film.

The surface morphologies of the SnO₂:Sb thin films were also investigated by AFM. Figure 5-7 shows the corresponding AFM images, from which continuous and smooth surfaces of all four SnO₂:Sb films were revealed. The RMS roughness were found to be 0.18 nm, 0.15 nm, 0.23 nm, and 0.31 nm for films with thickness of 3.1 nm, 7.9 nm, 31.3 nm, and 188 nm, respectively.

Figure 5-7. AFM images ($2 \times 2 \mu\text{m}^2$) of the SnO₂:Sb thin films with thickness of: (a) 3.1 nm, (b) 7.9 nm, (c) 31.3 nm and (d) 188 nm, respectively.

The in-plane electrical transport properties of all four thin films were measured as a function of temperature ranging from 90 K to 400 K. Figure 5-8 shows the plot of the temperature-dependent resistivity of each film. From these results, it can be seen that the resistivity of relatively thicker films (Samples A and B) reduces as the temperature decreases, which suggests a metallic behavior. By contrast, prominent semiconducting behavior (insulator ground state) was observed in the ultrathin film (Sample D) with a thickness of 3.1 nm, for which the resistivity increases monotonically with the decrease of the temperature. As for Sample C possessing the thickness (7.9 nm)

between those of Samples B and D, its resistivity shows a very weak dependence on the temperature, which implies that the sample is on the edge of MIT. It is evident that a MIT has been induced by varying the SnO₂:Sb film thickness from bulk value to nanoscale, and the critical thickness for this MIT should be around 7.9 nm.

Figure 5-8. Semilogarithmic plot of the temperature-dependent resistivity of SnO₂:Sb thin films with varied film thickness.

In order to get a better insight into this thickness induced MIT, XPS was employed to investigate the electronic structure of the SnO₂:Sb thin films. Figure 5-9 presents the photoemission spectra of four samples in the binding energy ranging from -2 to 16 eV. This region encompasses the CB, the bulk band gap, and the VB. By zooming into the zero-binding-energy region, a prominent Fermi-Dirac-like cutoff associated with electrons in the conduction band is observed in Samples A to C, which confirms the metallic property of these SnO₂:Sb films at room temperature. These results are consistent with the resistivity measurements shown in Figure 5-8.

Figure 5-9. XPS results of the SnO₂:Sb films with different thicknesses in the binding energy ranging from -2 to 16 eV. For comparison, the VB spectrum of pure sapphire substrate is also presented. The substrate effect on the VBM denotation and conduction band electron measurement of the SnO₂:Sb thin films can be neglected due to little contribution from sapphire below 7 eV.

The electron occupation in the conduction band vanished as the film thickness scaled down to 3.1 nm in Sample D. The absence of a Fermi-edge cutoff clearly indicates its insulator nature. According to these XPS results, the thickness induced MIT in SnO₂:Sb thin films is further confirmed. In addition, the electron emission signal from conduction band region was found to gradually reduce as the film thickness decreased (Figure 5-9). This occupation decrement implies a thickness induced reduction of free electron concentration. To quantitatively verify the above behavior, the room-temperature electron concentrations (N_{300K}) were measured by Hall effect as

summarized in Table 5-1, in which a clear shrinkage of electron concentration is revealed.

Table 5-1. Thickness t , valence band maximum (VBM), room temperature electron concentration (N_{300K}), conduction band filling (E_{fill}) and energy band gaps (E_g) for the four SnO₂:Sb films with different thickness.

Sample	A	B	C	D
t (nm)	188	31.3	7.9	3.1
VBM (eV)	4.07 ± 0.10	4.0 ± 0.10	3.94 ± 0.10	3.77 ± 0.10
N_{300K} (cm ⁻³)	-3.99×10^{20}	-3.09×10^{20}	-1.55×10^{20}	-3.48×10^{17}
E_{fill} (eV)	0.86	0.75	0.51	~0
E_g (eV)	3.21 ± 0.10	3.25 ± 0.10	3.43 ± 0.10	$\sim 3.77 \pm 0.10$

Moreover, by referring to the Fermi level, the VBM shows a red shift to lower energy side with the decrease of film thickness (i.e., the shrinkage of electron concentration shown in Figure 5-9 and Table 5-1). This VBM shift can be interpreted by the Burstein-Moss (BM) effect originated from the filling of the conduction band [205]. Considering a free-electron profile of Sn 5s conduction band for SnO₂, the magnitude of BM induced VBM shift in XPS spectra is directly related to the occupied conduction bandwidth, which can be calculated by E_{fill} [206]:

$$E_{fill} = \int_0^N \frac{h^2}{4(3\pi^2n)^{\frac{1}{3}} \times m^*} dn \quad (5-5)$$

Here, $m^* = (0.192 + 0.0259 \times 10^{-20} \times N) \times m_0$ gives the carrier concentration dependent electron effective mass. m_0 and N represent the electron mass and electron concentration, respectively. The parameters for m^* were obtained from the literature [206,207]. Using Equation (5-5) and electron concentrations obtained from Hall measurements, the values of E_{fill} were calculated and shown in Table 5-1. It can be seen that the lower the electron concentration, the narrower the occupied conduction band. Accordingly, the VBM edge shifts to lower energy side in the XPS spectra, which further confirms the self-consistency of the results in Table 5-1.

From the above-mentioned temperature-dependent resistivity results and XPS VB spectra, the thickness induced MIT in metallic SnO₂:Sb thin films was confirmed. However, questions arise such as: Where have the free electrons gone? What is the origin of this MIT behavior in these thickness varied SnO₂:Sb thin films? To address these questions, the role of Sb in SnO₂ should be investigated, since the metallic properties of SnO₂:Sb originate from the overlapping between the donor level Sb(V) and the SnO₂ conduction band. From a real space point of view, metallic SnO₂:Sb can only be achieved as long as the effective Sb(V) concentration is higher than n_c . The doping concentration of Sb in our 5% SnO₂:Sb target (around $1.4 \times 10^{21} \text{ cm}^{-3}$) is much higher than the theoretical value of $n_c = 9.54 \times 10^{17} \text{ cm}^{-3}$ for SnO₂ [193]. The Sb concentration in film was measured to be 3.5% by XPS. This stoichiometry deviation between target and film can be attributed to the difference of vapor pressure of Sn and Sb. Considering this stoichiometry deviation, the doping concentration of Sb in the film is $9.8 \times 10^{20} \text{ cm}^{-3}$, which is still higher than the theoretical value of n_c . In spite of the stoichiometry deviation between the film and the target, the metallic properties

indeed have been observed in the relatively thicker SnO₂:Sb films (sample A and B). However, Sb is a multivalent element with two common oxidation states of Sb(V) and Sb(III). In SnO₂, only Sb(V) acts as donor while Sb(III) tends to be acceptor compensating the free electrons contributed by Sb(V). Therefore, the oxidation state of Sb should directly relate to the free electron concentration and electrical transport behavior in our SnO₂:Sb thin films. The coexistence of Sb(V) and Sb(III) in SnO₂:Sb films was previously reported in literature [208]. In order to investigate the oxidation state of Sb, high-resolution Sb 3d_{3/2} core level spectra of these thickness-varied SnO₂:Sb films were taken and shown in Figure 5-10.

Figure 5-10. Core level Sb 3d_{3/2} XPS spectra of SnO₂:Sb thin films (filled squares) with different thicknesses: A: 188 nm, B: 31.3nm, C: 7.9nm, and D: 3.1nm. The spectra were fitted to a Shirley background (green solid line) together with the Voigt profiles for Sb(V) (blue dot dash line) and Sb(III) (red dash line). The fitting curves (black solid line) are seen to match well with the experimental data points. The denotation exp., fit., and bg. represent the experimental data, fitting curve, and background, respectively.

The Sample A with thickness of 188 nm only shows a symmetric Voigt profile which corresponds to the Sb(V). On the contrary, the peaks show a well-defined shoulder on the lower binding energy side with the decrease of film thickness. Fitting of the asymmetric core lines into two Voigt components gives a good description of the overall core line shape in which the higher binding energy peak represents the Sb(V) and the lower binding energy component is assigned to Sb(III) [208]. It can be seen that the thinner the SnO₂:Sb film is, the higher concentration of Sb(III) exist in the film. Obviously, this oxidation state transition of Sb will cause the reduction of electron concentration as film thickness shrinks, and consequently a MIT occurs when the effective Sb(V) density is lower than the Mott critical criteria.

Figure 5-11. The E_g of different thickness SnO₂:Sb thin films as extracted from the XPS VB spectra. The dash line shows the least-squares fit to a power-law function: $E_g = 3.2 + 2.4/t^{1.16}$, from which a remarkable quantum confinement effect is revealed.

Depending on the above analyses to Sb 3d_{3/2} core level spectra, Sb(III) is preferred for the ultrathin SnO₂:Sb film, and this oxidation state variation gives rise to the electron concentration reduction and MIT. To understand this film thickness related phenomena, the quantum confinement effect should be considered as the film thickness approached its Bohr radius (~2.54 nm) [193]. Referring to the energy band diagram of the SnO₂:Sb/sapphire structure, as shown in the inset of Figure 5-11, the electrons in the films are confined in the potential well formed by sapphire substrate and vacuum. It is generally accepted that the E_g will be significantly broadened when the electrons are squeezed. Based on the BM model and XPS VB measurements, E_g could be extracted by subtracting the conduction band filling (E_{fill}) from the VBM. Figure 5-12 shows the schematic diagram for the conduction band filling and band alignment in XPS VB measurements for the metallic and insulating SnO₂:Sb thin films.

Figure 5-12. The schematic diagram for the conduction band filling and band alignment in XPS VB measurements for the metallic and insulating SnO₂:Sb thin films.

According to this diagram, the E_g for the metallic SnO₂:Sb thin films (Samples A to C) can be calculated by subtracting the conduction band filling (E_{fill}) from the VBM. As for the Sample D, in which there is no conduction band occupation, we approximate the VBM in VB spectrum to be the value of E_g , due to its *n*-type semiconducting properties revealed in Hall measurements. A prominent increase of E_g with the decrease of film thickness was observed, as shown as in Table 5-1 and Figure 5-11.

It is worth pointing out that the band structure will be renormalized due to the impurity doping. Comparing the calculated E_g (3.21 eV) for 188 nm thick SnO₂:Sb film with the reported bulk value ~ 3.6 eV for pure SnO₂, a narrowing of 0.39 eV is observed, which is consistent with the reported results for SnO₂:Sb ceramic sample [206]. Since the SnO₂:Sb films were deposited using the same target, nearly identical impurity concentration of the films is expected. It is reasonable to assume that all SnO₂:Sb films have the same narrowing values for E_g . Therefore, the variation of E_g should be attributed to the thickness-induced quantum confinement effect. By analytic fitting to the thickness-dependent E_g shown in Figure 5-11, the E_g shift scales as $\sim t^{-1.16}$, here t denotes the thickness of thin film. The magnitude of the scaling power is found to have a similar value with the cases of SnO₂ quantum wires ($\sim d^{-1.20}$) and quantum dots ($\sim d^{-1.26}$) predicted by first principles calculations, where d stands for the radius [209]. It is evident that E_g increases in the ultrathin SnO₂:Sb film due to the quantum confinement effect. More specifically, the quantum confinement induced E_g broadening can be attributed to two distinct effects: the increase of ionization energy and the decrease of electron affinity. This size induced electronic structure variation

has been intensively studied in pure IV, III-V, II-VI and IV-VI semiconductor nanostructures [209-216]. As such, the influence of quantum confinement effect on the physical properties of impurity doped semiconductor nanostructures is expected. Based on the first principles calculations, as the nanocrystal size decreases, (a) the impurity activation energy is enhanced [217,219], (b) effective Bohr radius is squeezed [202,218,219], (c) impurity wavefunction becomes more localized [220-222], (d) a valence state transition for the impurity is driven [202], and (e) the energetic level of impurity is pinned referring to the vacuum level [201]. At present, we look back to the previous analyses of the Sb 3d_{3/2} core level spectra shown in Figure 5-10, the observed oxidation state transition from Sb(V) to Sb(III) can be understood by the enhancement of the activation energy (electron binding energy) and the strong trapping of electrons by the Sb(III) sites. Hence, both the experimental results and theoretical analyses indicate a quantum confinement induced MIT in the SnO₂:Sb ultrathin films and the existence of operational size limit for its nanoelectronic applications.

5.2.4 Summary

In summary, SnO₂:Sb thin films were epitaxially deposited, with the thickness varied from 188 nm to 3.1 nm by LMBE on (10 $\bar{1}$ 2) sapphire substrates. From the electrical and spectroscopic studies, a thickness induced MIT, and the critical thickness for these films evolving from metallic behavior to insulating nature have been discovered. This approach allows one to examine the size scaling limitation for nanoelectronic

applications. High resolution XPS core level spectra of Sb indicate that the thickness reduction induced metal to insulator transition in SnO₂:Sb thin films should be directly related to the oxidation states variation of Sb from Sb(V) to Sb(III). In addition, a prominent quantum confinement effect was observed in our SnO₂:Sb thin films. Based on the first principles calculation results reported by other groups, this quantum confinement is believed to be responsible for the oxidation state variation of Sb.

5.3 Thermal annealing induced anomalous electrical transport behavior in SnO₂ thin films

As a continuous work to the foregoing two sections, the annealing effect on the electrical transport behavior of SnO₂ thin films is reported in this section.

5.3.1 Introduction

Over the past several decades, intensive research activities have been conducted on SnO₂ in the bulk, thin film and nanostructure forms due to its interesting electrical and optical properties, making it a promising material for applications in solar cells [223], flat panel displays [224], light emitting devices [3], and integrated chemical sensors [9,225]. For metal oxide materials, oxygen vacancy usually plays a critical role in determining the physical properties by forming defect states inside the electronic band structure. In the case of SnO₂, low formation energy of the oxygen vacancy, based on first principles calculation, has been claimed to explain the coexistence of high conductivity and insulator-like transparency in the visible range [59,226]. The oxygen related defects model has been widely adopted to understand the electrical transport, optical and magnetic properties [16,76], however, systematical experimental work to reveal the annealing temperature dependence of oxygen behavior in SnO₂ is very limited in literature. In this section, we report the influence of annealing temperatures on the electrical transport properties of as-grown SnO₂ thin films. Anomalous carrier

concentration and conductivity behaviors were observed, and attributed to the grain size growth and temperature-dependent density variation of the oxygen vacancy.

5.3.2 Experimental detail

A series of SnO₂ thin films were deposited on quartz substrates, using LMBE system. Eight samples were deposited on quartz with substrate temperature and oxygen partial pressure respectively fixed at 150 °C and 1 Pa. The samples were then annealed at temperatures ranging from 300 °C to 900 °C for 1 hour in pure oxygen ambience with an increment of 100 °C per step. All eight SnO₂ samples were annealed in a tube furnace. Samples were heated up from room temperature to the preset temperature at a ramping rate of 10 °C/min. After the heat treatment, samples were pulled out from the heating zone to the low temperature zone together with a quartz holder. This annealing procedure is considered as a quench process, as the cooling rate is estimated to be 50 °C/min.

Structural phase identification was carried out by powder XRD. The film thicknesses were measured to be 500 ± 20 nm by a stylus profilometer. The resistivity and carrier concentration were determined by Hall measurement with four-point probe technique using van der Pauw geometry. The chamber for Hall measurement was evacuated, in order to minimize the influence of ambient gas, due to the gas-sensitive nature of SnO₂ [227].

5.3.3 Results and discussions

Figure 5-13 (a) shows the XRD patterns of the SnO₂ thin films annealed at different temperatures, demonstrating that pure rutile phase (JCPDS 21-1250) was developed when the annealing temperature reached 400 °C. The as-deposited and 300 °C annealed samples remained in amorphous phase (these amorphous XRD patterns are not shown in the Figure 5-13). In line with the formation of rutile SnO₂ crystallite, crystal grain growth can be expected. The grain size was quantitatively calculated by the Scherrer's formula, $D \approx 0.9\lambda / \beta \cos\theta$, and shown in Figure 5-13 (b), from which a clear trend of grain growth with the increase of annealing temperature is observed.

Figure 5-13. (a) XRD patterns of SnO₂ thin films annealed at different temperatures. (b) Grain size of SnO₂ thin films as a function of the annealing temperature.

Au/Ti Ohmic-contact electrodes on the SnO₂ films were fabricated by electron beam evaporation. The electrical transport properties, namely dc resistivity (ρ) and carrier concentration (n), were determined via Hall measurement. From Figure 5-14, it can be seen that the dc resistivity shows a strong dependence on the annealing temperature. The as-deposited SnO₂ film has a relatively high resistivity of 169 Ω -cm. As the annealing temperature increases, the resistivity of the films decreases dramatically and reaches a minimum at 500 °C. With further increase of the annealing temperature, a reversed behavior of the resistivity emerged showing a gradual increase as the

annealing temperature rose. The carrier concentration of the electrons in these native *n*-type oxides was found to have an opposite annealing temperature dependence compared to the resistivity, and their correlation can be understood according to the well-known relationship, $\rho = (nq\mu)^{-1}$ for *n* type semiconductor, where *n* stands for the electron concentration and μ represents the mobility. From the Hall measurement results, the electrical transport properties of these annealed SnO₂ films were found to have an anomalous behavior at a transition temperature around 500 °C.

Figure 5-14. Carrier concentration and resistivity of SnO₂ thin films versus the annealing temperature.

From the XRD results in Figure 5-13, a gradual increase of the grain size is observed with the increase of annealing temperature. It is generally accepted that the grain growth plays an important role in determining the electrical transport properties of materials in the following two ways: (a) reducing the electron scattering centers and increasing the carrier mobility; (b) annihilating the grain boundaries and lowering the

energy barrier for carrier transportation [33]. As such, larger grain size resulting from higher annealing temperatures will lead to a lower resistivity of the SnO₂ films. This means the annealing temperature dependence of the resistivity is inversely related to the grain size growth. Indeed, this trend was observed in the relatively low annealing temperature range in Figure 5-14. However, the above rule cannot be applied to explain the conduction behaviors when the annealing temperature was above 500 °C.

Considering the inevitable oxygen vacancy (or uncoordinated Sn) in the SnO₂ films and its donor nature, annealing induced variation of oxygen vacancy density should be taken into account to understand the transition of electrical transport behavior which occurred at 500 °C. In order to verify this, the oxygen behavior was investigated by XPS measurements. High resolution Sn 3d_{5/2} and O 1s core-level spectra obtained from all eight SnO₂ thin films are shown in Figure 5-15 (a). Referring to the Sn 3d_{5/2} spectra, two peaks corresponding to Sn(IV) and Sn(II) respectively can be expected due to the existence of oxygen vacancies. However, discrimination between SnO and SnO₂ in photoemission studies was reported to be very difficult due to the small shift in the Sn 3d binding energy for Sn (II) and Sn (IV) [33]. Indeed, only one peak in the Sn 3d_{5/2} spectra was observed in this work [Figure 5-15 (a)]. As a result, it is difficult to obtain the oxygen vacancy information only from the Sn 3d_{5/2} spectra. As for the O 1s spectra, a prominent peak and a well-defined shoulder on higher binding energy side were observed. A fit of the asymmetric core lines to two Voigt components gives good description of the overall core line shape. The lower binding energy peak located at around 530.8 eV, denoted as O_[1], is assigned to the oxygen in SnO₂ lattice, while the higher binding energy component centered around 532.0 eV, denoted as O_[2],

is reported to be surface adsorbed oxygen species and hydroxyl ion [228]. It has been reported that higher oxygen vacancy density will induce more surface adsorbed oxygen species [229-231]. Therefore, it is reasonable to estimate the variation of oxygen vacancy concentration in the SnO₂ films by calculating the intensity ratio of O_[1] to O_[2] [231,232]. As summarized in Figure 5-15 (b), the O_[1] to O_[2] intensity ratio, as well as the oxygen deficiency in the films, increased when the films were annealed from 150 °C to 500 °C and then decreased when the annealing temperature reached 600 °C. To consolidate the evidence for the oxygen vacancy density, we also calculated the normalized intensity (after calibration by XPS atomic sensitivity factor and transmission function) ratio between Sn 3d_{5/2} and lattice O 1s peak (O_[1]). It is obvious that, higher Sn to O ratio indicates more oxygen vacancies. The calculated Sn to O ratio is shown in Figure 5-15 (b). Compared to the O_[1] to O_[2] intensity ratio, a similar annealing temperature dependence of Sn to O ratio was observed, which confirms the behavior of oxygen vacancy at different annealing temperature. The annealing temperature dependent oxygen vacancy behavior revealed by XPS agrees well with the carrier concentration variations obtained from the Hall measurement. Therefore, it can be concluded that the annealing process induced oxygen vacancy variation was responsible for the anomalous electrical transport properties in our SnO₂ thin films. Based on the above discussion, both the grain growth and oxygen vacancy generation were responsible for the decrease of resistivity in the low annealing temperature range. However, above a certain temperature the crystal size induced resistivity decrease became relatively weak while a large amount of oxygen vacancies were compensated by ambient oxygen gas. That is, the reduction of electron concentration at high annealing temperature became the key factor for the

conductivity. Consequently, the resistivity increased although the grain size still increases.

Figure 5-15. (a) XPS Sn 3d_{5/2} and O 1s spectra obtained from the SnO₂ thin films annealed at different temperatures. (b) The O_[2]/O_[1] and Sn/O intensity ratios extracted from Sn 3d_{5/2} and O 1s spectra as a function of annealing temperature.

5.3.4 Summary

In summary, the influence of annealing temperature on the structure and electrical transport properties of LMBE deposited SnO₂ thin films was investigated using the XRD, Hall measurement and XPS. By varying the annealing temperature, an anomalous electrical transport behavior of the SnO₂ thin films was observed and was explained by the crystal grain size and temperature-dependent oxygen vacancy density variation.

CHAPTER 6 MAGNETIC PROPERTIES OF TRANSITION METAL DOPED SnO₂

As a well-known metal oxide, SnO₂ has been actively studied for several decades, due to its potential applications in optoelectronic devices and chemical sensors. Recently, great new attention to this old material emerges, since robust RTFM was discovered in Fe-doped SnO₂ by J.M.D. Coey *et al.* The oxide based RTFM semiconductors not only play an important role in the development of spintronics, but also are interesting from the viewpoint of fundamental physics since they combine two important realms of condensed matter physics: magnetism and semiconductor. Previously in Chapter 4 and 5, the thin film fabrication and transport properties of SnO₂ have been extensively investigated, respectively. In this chapter, we have focused our work on the magnetic properties of SnO₂ based ferromagnetic semiconductor. In detail, this chapter includes the following two sections: The first section presents Fe doping in SnO₂ and the magnetic properties of SnO₂:Fe bulk samples and films deposited on different

substrates. The second section is focused on the carrier doping effect on the magnetic properties of SnO₂:Fe.

6.1 Ferromagnetism in Fe-doped SnO₂: Bulk and Thin film

6.1.1 Introduction

As mentioned in Chapter 2, diluted magnetic semiconductors (DMSs), also known as semimagnetic semiconductors, are materials in which rare earth or transition metal ions replace a considerable number of the native ions in the semiconductor lattice. These resulting DMS materials could thus maintain their electrical properties and possibly incorporate a magnetic dimension as well. Substantial success has been obtained by inducing ferromagnetism in compound semiconductor through transition metal doping, e.g. Mn-doped CdTe, and Mn-doped GaAs. However, their Curie temperatures were still lower than room temperature, which made them impractical for use in practical devices. In attempting to achieve high Curie temperature in DMS, some wide band gap oxide compounds were attempted, since the RTFM was predicted in certain transition metal doped oxides by first principle calculations. For instance, based on Zener model, high Curie temperature (>300 K) was predicted in Mn-doped ZnO by T. Dietl *et al.* [233], and experimental evidences of RTFM in transition metal-doped ZnO were reported by a number of research groups [121,234-238]. Yuji Matsumoto *et al.* reported RTFM in transparent transition metal-doped TiO₂ [115]. Recently, the SnO₂ based DMSs attracted great attention, since the observation of giant magnetic moment in transparent Co- and Fe-doped SnO₂ thin films by S. B. Ogale *et al.* and J.M.D. Coey *et al.*, respectively.

In this section, we systematically investigated the doping of Fe in SnO₂. According to the doping induced lattice parameters variation, the solubility limit of Fe in SnO₂ is determined to be up to 10%. Robust RTFM was observed in the 5% Fe doped SnO₂ bulk sample, in which no secondary phase or small cluster was observed using XRD and HRTEM. The magnetic properties of Fe-doped SnO₂ thin films were investigated. Using orientation control technique described in Chapter 4, a crystal orientation affected ferromagnetism was discovered in the differently orientated SnO₂:Fe thin films. This crystal orientation dependence of ferromagnetism may show an evidence excluding the ferromagnetism in Fe doped SnO₂ films originating from the ferromagnetic clusters.

6.1.2 Experimental detail

To experimentally determine the solid solubility of Fe in SnO₂, six Sn_{1-x}Fe_xO_{2-σ} polycrystalline samples, with x = 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25, were prepared from stoichiometric SnO₂ and Fe₂O₃ powders. The powders were first weighed and mixed by ball milling for 10 hours to reduce the particle size and enhance the powder mixing. Then, the powders were presintered at 900 °C for 24 hours. After that, the powders were shaped into six pellets by compressing, and sintered in air at 1200 °C for 48 hours. The phase structures of all six samples were characterized by powder XRD at room temperature. The magnetic properties of sample Sn_{0.95}Fe_{0.05}O₂ was investigated by a physical property measurement system at 300 K. HRTEM together with selected area electron diffraction (SAED) and energy dispersive X-ray analysis

(EDX) mapping attachment were used to study the microstructure and doping homogeneity of sample Sn_{0.95}Fe_{0.05}O_{2-σ}. The XPS spectra were obtained by a VG ESCALAB. Two Sn_{0.95}Fe_{0.05}O_{2-σ} thin films were deposited on sapphire (0001) and (10 $\bar{1}$ 0) by LMBE, as the Sn_{0.95}Fe_{0.05}O_{2-σ} polycrystalline pellet was used as target. To minimize the substrate contribution in the magnetic property measurement, all of the sapphire substrates were purchased from same company (MTI, KJ Group) and carefully cleaned prior to the thin film depositions. The deposition parameters were the same for all two thin film samples: substrate temperature ($T_{\text{sub}} = 900\text{ }^{\circ}\text{C}$), oxygen pressure ($P_{\text{Oxy}} = 0.1\text{ Pa}$), laser energy ($E_{\text{Laser}} = 1.5\text{ J/cm}^2$). The film thickness was fixed at 500 nm. Their crystal structures were characterized by XRD. The magnetic properties of all three Sn_{0.95}Fe_{0.05}O_{2-σ} thin films were measured by PPMS at room temperature.

6.1.3 Results and discussions

The XRD results of all the six Sn_{1-x}Fe_xO_{2-σ} bulk samples with gradually varied Fe concentration from 0.00 to 0.25 are shown in the Figure 6-1 (a). Pure SnO₂ rutile phase (JCPDS 21-1250) was observed in the XRD patterns of sample $x = 0.00, 0.05$ and 0.10 , in which no trace of Fe metal, oxides or other phases could be detected. With the increase of Fe concentration, the trace of impurity phase [α -Fe₂O₃, denoted by red dash line and plane indices in Figure 6-1 (a)] appears for the sample Sn_{0.85}Fe_{0.15}O_{2-σ} and becomes more obvious in the samples of Sn_{0.8}Fe_{0.2}O_{2-σ} and Sn_{0.75}Fe_{0.25}O_{2-σ}.

Figure 6-1. (a) XRD patterns of the Sn_{1-x}Fe_xO_{2-x} bulk samples as x varied from 0.00 to 0.25. (b) Fe doping concentration dependence of the d-spacing of (200) plane calculated from the SnO₂ (200) peaks in (a).

According to the XRD patterns shown in Figure 6-1 (a), the solid solubility of Fe in SnO₂ should be around 10~15%, since the α -Fe₂O₃ phase appears as the Fe

concentration reached 15%. To confirm this conclusion, the doping induced lattice distance variation was analyzed. Figure 6-1 (b) shows the Fe doping concentration dependence of the d-spacing of (200) plane, which was calculated from the XRD results in Figure 6-1 (a). It is obvious that the lattice of SnO₂ is expanded with the doping of Fe, which means the Fe ions have been doped into the SnO₂ lattice and caused the lattice distance variation. As the Fe concentration was increased to 10%, the lattice reached its maximum value and was saturated in the higher doped sample. This lattice saturation implies that the Fe ions cannot get inside the SnO₂ lattice when the Fe doping concentration reached 15%. Consequently, the excess Fe existed as α -Fe₂O₃, which is shown in the XRD patterns in Figure 6-1 (a). Based on the above analyses, the solid solubility of Fe in SnO₂ can be determined to be 10~15%. This value is in a good agreement with the result reported by A. Punnoose *et al.* [239].

Since the possible magnetic impurity phase and undesirable ferromagnetic metal clusters make the origin of ferromagnetism in the 3d transition metal doped DMS very complicated and controversial [240-247], to minimize the possibility of undesired secondary phase and clusters, the doping concentration of Fe in our SnO₂ based DMS samples was selected as 5%, which is remarkably lower than the solid solubility of Fe in SnO₂ previously determined. In addition to the XRD measurement, HRTEM equipped with EDX mapping attachment was used to investigate the local microstructure and doping homogeneity of polycrystalline sample Sn_{0.95}Fe_{0.05}O_{2- σ} . Figure 6-2 (b) and (c) show the typical Sn and Fe maps, respectively, corresponding to the low-magnification TEM image shown in Figure 6-2 (a). These element mapping results provide the evidence that Fe ions are homogeneously distributed in the

SnO₂ matrix. HRTEM images and SAED patterns of sample Sn_{0.95}Fe_{0.05}O_{2-σ} were taken to verify whether Fe clusters or other impurity phases exist, which will make the magnetic properties of Sn_{0.95}Fe_{0.05}O_{2-σ} ambiguous. Several randomly selected regions of sample Sn_{0.95}Fe_{0.05}O_{2-σ} were investigated by HRTEM. Figure 6-2 (d) shows a representative HRTEM image, in which there is no nanocluster or other undesired phase observed. A typical SAED pattern of sample Sn_{0.95}Fe_{0.05}O_{2-σ} is presented in Figure 6-2 (e), according to which pure rutile SnO₂ phase is confirmed. Based on the above analyses, it can be concluded that the Fe ions have most probably been doped into the SnO₂ lattice instead of existing as a secondary phase.

Figure 6-2. (a), (b) and (c) show the low-magnification TEM image and its corresponding element mappings of Sample Sn_{0.95}Fe_{0.05}O_{2-σ}, respectively. (d) gives the typical HRTEM image, and (e) presents the SAED pattern.

To study the composition and electronic state for each element, XPS spectra of the sample Sn_{0.95}Fe_{0.05}O_{2-σ} were recorded. Figure 6-3 (a) shows the XPS survey scan spectrum. The results reveal the main existing elements of Sn and O, together with the trace of Fe. The core-level spectra of Sn 3d, O 1s, and Fe 2p peaks are shown in Figure 6-3 (b), 6-3 (c), and 6-3 (d), respectively. All of the spectra have been corrected by the C 1s peak at 285.0 eV. As shown in Figure 6-3 (b), the core lines show symmetric profile which can be well described by single Voigt component together with Shirley background. Accordingly, the Sn ions in Sn_{0.95}Fe_{0.05}O_{2-σ} have the same chemical state, and can be identified to be +4, since the separation between the Sn 3d_{5/2} and Sn 3d_{3/2} levels is around 8.5 eV [155]. As for the O 1s spectrum in Figure 6-3 (c), a prominent peak and a well-defined shoulder on higher binding energy side are observed. A fit of the asymmetric core lines to two Voigt components gives good description of the overall core line shape. The lower binding energy peak located at around 530.8 eV, denoted as O_[1], is assigned to the oxygen in SnO₂ lattice, while the higher binding energy component centered around 532.4 eV, denoted as O_[2], is reported to be surface adsorbed oxygen species and hydroxyl ion [228]. The lattice oxygen O_[1] at 530.8 eV assigns the valence of oxygen to be the normal chemical state -2. As for the magnetic dopant Fe, high-resolution Fe 2p core level spectrum was recorded and shown in Figure 6-3 (d). Fitting of the asymmetric core lines into four Voigt components together with Shirley background gives a good description of the overall core line shape. The peaks located around 711.1 eV and 713.7 eV are assigned to the Fe²⁺ and Fe³⁺, respectively. The Sn 3p peak (716.5 eV) is also observed since its binding energy is very close to the Fe 2p. The peak with highest binding energy in

the spectra corresponds to the Fe 2p satellite. From these XPS results, we can see that both Fe³⁺ and Fe²⁺ co-exist in the sample Sn_{0.95}Fe_{0.05}O_{2-σ}.

Figure 6-3. (a) XPS survey spectrum of bulk Sample Sn_{0.95}Fe_{0.05}O_{2-σ}. (b), (c) and (d) present the core-level Sn 3d, O 1s and Fe 2p spectra, respectively. The spectra are fitted to a Shirley background (green dot line) together with the Voigt profiles. The fitting curves are seen to match well with the experimental data points.

Figure 6-4 (a) presents the room-temperature magnetization (M , emu/g) versus magnetic field (H , Oe) result of sample Sn_{0.95}Fe_{0.05}O_{2-σ}, in which prominent ferromagnetic hysteresis behavior can be observed. In addition, this M - H curve shows a linear component superimposed on a saturating ferromagnetic magnetization, which implies a co-existence of paramagnetic response and ferromagnetic behavior. Similar result has been reported by other groups, and the paramagnetic response was attributed to the Fe atoms which did not participate in the ordered magnetic state [239,248]. According to the discussion of J.M.D. Coey *et al.* [16] and A. Punnoose *et al.* [239], these irons did not participate in an ordered magnetic phase, due to: (a) the lack of Fe³⁺ neighbors and/or oxygen vacancies, and (b) the antiferromagnetic exchange interaction of Fe³⁺-O²⁻-Fe³⁺. By subtracting the linear component, the M - H curve of the ferromagnetic phase is extracted as shown in Figure 6-4 (b). The saturation magnetization (M_s) of sample Sn_{0.95}Fe_{0.05}O_{2-σ} is determined to be 0.08±0.001 emu/g, which is in good agreement with the value reported by A. Punnoose *et al.* [239].

Figure 6-4. (a) M vs H data of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ bulk sample measured at room temperature. (b) M vs H curve of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ after subtracting the paramagnetic response.

To further study the ferromagnetism in $\text{SnO}_2\text{:Fe}$ based DMS, two thin film samples labeled as S1 and S2 were grown on the sapphire (0001) and $(10\bar{1}0)$ substrates, respectively, using the $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ polycrystalline pellet as target. Figure 6-5 shows the XRD patterns of S1 and S2, in which pure SnO_2 rutile phase is observed. The epitaxy relationships are determined as SnO_2 (200)//Sapphire (0001) and SnO_2 (002)//Sapphire($10\bar{1}0$), which are consistent with the results discussed in Chapter 4.

Figure 6-5. XRD patterns of $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_{2-\sigma}$ thin films, S1 and S2 deposited on sapphire (0001) and $(10\bar{1}0)$ substrates, respectively.

Figure 6-6 (a) and (b) present the room-temperature M - H results of Sample S1 and S2, respectively. It is evident that both S1 and S2 show ferromagnetic behavior at room temperature. The saturation magnetization of S1 and S2 are measured to be 2.3 ± 0.2 emu/cm^3 and 3.5 ± 0.2 emu/cm^3 , respectively. This prominent difference of M_s in S1 and S2 seems unexpected, since these two samples have the same Fe concentration,

thickness and thin film preparation conditions. On the other hand, the coercivities of these two samples also show a remarkable difference, as shown in Figure 6-6 (S1: 765 ± 5 Oe, S2: 160 ± 5 Oe). In the PPMS measurement, the applied magnetic field was perpendicular to the sample surface. Taking into account the distinct crystal orientations of S1 and S2 determined from XRD patterns in Figure 6-5, the M - H results were measured along the [100] and [001] direction of SnO₂ for sample S1 and S2, respectively. Accordingly, the difference of M_s and coercivity in sample S1 and S2 could be treated as an anisotropy phenomenon. Similar anisotropy in magnetic properties was also observed by Jun Zhang *et al.* in the vanadium-doped SnO₂ thin film, and was interpreted by a symmetry-breaking mechanism [126,249]. In addition, the anisotropy in our Sn_{0.95}Fe_{0.05}O_{2- σ} single crystal thin films may also suggest that the ferromagnetism unlikely originates from Fe clusters or magnetic secondary phase. It is reasonable to assume that the Fe clusters or secondary phase is randomly distributed in the film with no preferred orientation. Therefore, there should be no magnetic anisotropy observed, if the ferromagnetic behavior is only contributed by the Fe clusters or secondary phase. Accordingly, we can concluded that the magnetization and coecivity anisotropy observed in the thin film samples give evidence that the ferromagnetism originates from the intrinsic properties of Sn_{0.95}Fe_{0.05}O_{2- σ} .

Figure 6-6. (a) Room-temperature M vs H data of Sample S1. (b) Room-temperature M vs H data of Sample S2.

6.1.4 Summary

In conclusion, the ferromagnetism in SnO₂:Fe based DMS were studied in both bulk and thin film samples. Based on the XRD results, the solid solubility of Fe in SnO₂ was determined to be up to 10%. In 5% Fe doped SnO₂ bulk sample, robust RTFM was achieved, in which no secondary phase or small cluster was observed using XRD and HRTEM. Using orientation control technique described in Chapter 4, magnetic anisotropy was discovered in Sn_{0.95}Fe_{0.05}O_{2-σ} thin films deposited on sapphire (0001) and (10 $\bar{1}$ 0) substrates. This anisotropy suggests that the ferromagnetism in Sn_{0.95}Fe_{0.05}O_{2-σ} unlikely originates from Fe clusters or magnetic secondary phase.

6.2 Carrier doping tuned ferromagnetism in SnO₂:Fe

6.2.1 Introduction

Driven by the demand of miniaturization in semiconductor industry, the feature size of silicon-based devices is approaching the physical limit where macroscopic scale law breaks. To overcome such difficulty, researchers never cease to explore multifunctionalized materials and more sophisticated technologies. As discussed in section 6.1, the emerging technology of DMS has attracted intensive interest due to its promising applications in spintronics [240]. In the DMS-based materials, an additional degree of freedom of the electron (spin) can be realized by doping ferromagnetic 3d transition metals. Various transition-metal-doped systems such as Ge, GaAs, TiO₂, SnO₂ and ZnO have been reported to show robust ferromagnetic response [16,250-254]. Specifically, RTFM which favors the device applications has been achieved in several wide energy band gap metal oxides, i.e., TiO₂, SnO₂, ZnO and In₂O₃. However, the origin of ferromagnetism is still controversial, due to the complicated defect states, possible secondary magnetic phases and special role of oxygen non-stoichiometry in oxide based DMS [240,246,255,256]. By varying the electron doping concentration and controlling the oxygen vacancy (V_O) density, S. C. Li *et al.* reported that the RTFM in bulk polycrystalline $(\text{In}_{0.85-x}\text{Sn}_x\text{Fe}_{0.15})_2\text{O}_3$ is directly related to the oxygen vacancies [257]. Similar oxygen non-stoichiometry dependent ferromagnetism in $\text{Sn}_{0.95}\text{Fe}_{0.05}\text{O}_2$ was also observed by A. Thurber *et al.* by annealing the sample under controlled atmosphere with varied oxygen concentrations

[258]. Compared with electron-doping, hole-doping was found to be more effective in stabilizing the ferromagnetism in ZnO based DMS, according to the theoretical calculations and experimental results [259,260].

In this section, we have investigated both electron- and hole-doping effects on the ferromagnetic properties of Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} by changing the dopant M (Sb/Mg). A prominent decrease of M_s was observed in Sn_{0.93}Fe_{0.05}Sb_{0.02}O_{2-σ} bulk samples. On the contrary, the M_s was significantly enhanced in the case of Mg doping. The same behavior of the M_s under Sb and Mg doping was also observed in the Sn_{0.93}Fe_{0.05}Sb_{0.02}O_{2-σ} thin films. Based on the results of XPS characterization, this carrier doping (electron- and hole-doping) tuned ferromagnetism in Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} is attributed to the oxidation state transition of Fe and the variation of carrier type.

6.2.2 Experimental detail

In this study, the Sb and Mg are chosen to be the electron- and hole-dopant, respectively, based on the following formula:

Three polycrystalline bulk samples, Sn_{0.95}Fe_{0.05}O_{2-σ} (Fe5), Sn_{0.93}Fe_{0.05}Sb_{0.02}O_{2-σ} (Fe5Sb2) and Sn_{0.93}Fe_{0.05}Mg_{0.02}O_{2-σ} (Fe5Mg2) were prepared from stoichiometric SnO₂, Fe₂O₃, Sb₂O₅ and MgO powders via solid-state reaction method described in

Section 6.1. Three thin film samples, labeled as TF:Fe5, TF:Fe5Sb2, and TF:Fe5Mg2 were fabricated on (10 $\bar{1}$ 2) sapphire by LMBE, using Fe5, Fe5Sb2, and Fe5Mg2 bulk samples as target, respectively. The deposition parameters were the same for all three thin film samples: Substrate temperature ($T_{\text{Sub}} = 900\text{ }^{\circ}\text{C}$), Oxygen pressure ($P_{\text{Oxy}} = 0.1\text{ Pa}$), Laser Energy ($E_{\text{Laser}} = 1.5\text{ J/cm}^2$). The thin film thickness is fixed at 500 nm. Their crystal structures were characterized by XRD. The phase structure of the bulk samples was investigated by powder XRD. HRTEM together with SAED and EDX mapping attachment were used to study the microstructure and doping homogeneity. Magnetic properties were measured by PPMS at 300 K. XPS spectra were obtained by a VG ESCALAB.

6.2.3 Results and discussions

Figure 6-7 shows the XRD results for all the samples, demonstrating pure rutile phase (JCPDS 21-1250). No trace of Fe metal, oxides or other phases was observed in any sample doped up to 5% Fe and 2% M, which is above the detection limit (1%) of our XRD. Lattice parameters (a , c , and cell volume V) were determined by Rietveld refinement and shown in Table 6-1. It can be seen that the a , c and V changed in different doping cases.

Figure 6-7. XRD patterns of the bulk polycrystalline samples of Fe₅Mg₂, Fe₅Sb₂ and Fe₅.

Table 6-1. Lattice parameters (a and c), cell volume (V), saturation magnetization (M_s), net contribution (Bohr magneton) per Fe atom and Fe³⁺ to Fe²⁺ ratio (Fe³⁺/Fe²⁺).

Sample	a (Å)	c (Å)	V (Å ³)	M_s (emu/g)	Fe ³⁺ /Fe ²⁺
Fe ₅	4.719(2)	3.166(2)	70.5(1)	0.08(1)	0.83(1)
Fe ₅ Sb ₂	4.711(2)	3.157(2)	70.0(1)	0.01(1)	0.53(1)
Fe ₅ Mg ₂	4.731(2)	3.181(2)	71.2(1)	0.14(1)	1.28(1)

The microstructure and doping homogeneity of sample Fe₅Mg₂ and Fe₅Sb₂ were investigated by TEM, and the results are shown in Figure 6-8. Figure 6-8 (b), (c) and (d) give the typical Sn, Fe and Mg maps, respectively, corresponding to the low-

magnification TEM image shown in Figure 6-8 (a). These elements mapping results provide the evidence that Fe and Mg have been homogenously distributed in the SnO₂ matrix. The low-magnification TEM image and element mapping results of sample Fe₅Sb₂ shown in Figure 6-8 (e) to (h), also demonstrate that the Fe and Sb have been uniformly distributed in the SnO₂ matrix.

Figure 6-8. (a), (b), (c) and (d) show the low-magnification TEM image and its corresponding element mappings of sample Fe₅Mg₂. (e), (f), (g) and (h) show the low-magnification TEM image and its corresponding element mappings of sample Fe₅Sb₂. (i) and (j) are the typical HRTEM images of Fe₅Sb₂ and Fe₅Mg₂. (k) and (l) are the SAED patterns corresponding to Fe₅Sb₂ and Fe₅Mg₂.

HRTEM images and SAED patterns of these two samples were carried out to verify whether Fe clusters or other impurity phases exist, which are suspected to exhibit ferromagnetic ordering. Several arbitrary regions of samples Fe₅Sb₂ and Fe₅Mg₂

were investigated by HRTEM. Figure 6-8 (i) and (j) show the typical HRTEM results of samples Fe5Sb2 and Fe5Mg2, respectively, in which there is no nanocluster or other impurity phase observed. The SAED patterns corresponding to Fe5Sb2 and Fe5Mg2 are shown in Figure 6-8 (k) and (l), in which pure rutile SnO₂ phase is demonstrated. The microstructure and doping homogeneity of sample Fe5 (Sn_{0.95}Fe_{0.05}O_{2-σ}) have also been observed by TEM, with results presented in Figure 6-2. According to the TEM results in Figure 6-2, the Fe ions are found to be homogeneously distributed in the SnO₂ matrix, and there is no impurity phase or nanocluster can be observed in sample Fe5.

On the other hand, the ionic radii relationship in our samples is: Mg²⁺ (0.72 Å) > Sn⁴⁺ (0.69 Å) > Sb⁵⁺ (0.60 Å). Therefore, the Mg²⁺ substitution of Sn⁴⁺ will increase the lattice volume and Sb⁵⁺ substitution of Sn⁴⁺ will decrease the lattice volume. According to the lattice parameters obtained from XRD results (Table 6-1), the cell volume indeed increased when doped with Mg and decreased in the case of Sb doping. Based on the above analyses, the Mg and Sb ions most probably substituted the Sn in the lattice of SnO₂ instead of forming secondary impurity phase.

Figure 6-9 (a) presents the room-temperature magnetization (M , emu/g) versus magnetic field (H , Oe) data of the samples Fe5, Fe5Mg2 and Fe5Sb2, in which a linear component superimposed on a saturating ferromagnetic magnetization is observed. This co-existence of paramagnetic response and ferromagnetic behavior in Fe doped SnO₂ DMS samples has been reported, and the paramagnetic response was attributed to the Fe atoms which are not participating in the ordered magnetic state

[239,248]. According to the discussion of J.M.D. Coey *et al.* [7,16], and A. Punnoose *et al.* [239], these irons do not participate in an ordered magnetic phase, due to: a) the lack of Fe³⁺ neighbors and/or oxygen vacancies, b) the antiferromagnetic exchange interaction of Fe³⁺-O²⁻-Fe³⁺. By subtracting the linear component, the saturation of M expected for a ferromagnetic phase can be extracted, as shown in Figure 6-9 (b). The M_s of the three samples are summarized in Table 6-1. Compared with sample Fe5, the ferromagnetism is found to be strongly suppressed in the electron-doped Fe5Sb2. On the contrary, a significant M_s enhancement is observed in the hole-doped Fe5Mg2.

Figure 6-9. (a) M vs H data of Sample Fe5Mg2, Fe5Sb2 and Fe5 measured at 300 K. (b) M vs H curve after subtracting the paramagnetic response for the sample Fe5Mg2, Fe5Sb2 and Fe5 measured at 300 K.

Besides the bulk samples, the carrier doping effects on the ferromagnetism of Sn_{0.93}Fe_{0.05}M_{0.02}O_{2- σ} thin films have also been investigated. Figure 6-10 shows XRD patterns of all the thin film samples, TF:Fe5, TF:Fe5Sb2 and TF:Fe5Mg2. Pure SnO₂ rutile phase with no detectable secondary phase was observed in all the three thin

films. According to the SnO₂ (101) peak shift denoted by dash line in Figure 6-10, Sb doping reduced the lattice distance and Mg doping caused the increase of lattice distance. This doping induced lattice variation is consistent with the result obtained in bulk samples (shown in Table 6-1). Based on the previous analyses of the doping induced lattice variation in bulk samples, the similar phenomenon observed in thin film samples also implies that the Mg and Sb ions most probably substituted the Sn in the lattice of SnO₂ instead of forming secondary impurity phase in the thin film samples.

Figure 6-10. XRD patterns of TF:Fe5, TF:Fe5Sb2 and TF:Fe5Mg2. The dashed line is a reference for viewing the shift of diffraction peaks.

Figure 6-11 shows the room-temperature *M-H* data of thin film samples TF:Fe5, TF:Fe5Sb2 and TF:Fe5Mg2, in which prominent RTFM can be observed. In addition, it is evident that the ferromagnetism is strongly suppressed in the electron-doped

sample TF:Fe5Sb2, compared with sample TF:Fe5. On the contrary, a significant M_s enhancement is observed in the hole-doped sample TF:Fe5Mg2. This carrier doping tuned ferromagnetism in Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} thin films is in good agreement with the ferromagnetic behavior discovered in the Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} bulk samples.

Figure 6-11. Room-temperature M vs H data of thin film samples TF:Fe5, TF:Fe5Sb2 and TF:Fe5Mg2.

Based on the above characterizations, it is evident that the ferromagnetism in SnO₂:Fe based DMS samples (both bulk and thin film samples) can be tuned by different carrier doping (electron- and hole-doping). Considering that the ferromagnetism in Fe-doped SnO₂ originates from the spin of Fe atoms and their exchange interactions, the oxidation state of Fe should be directly related to the magnetic properties of Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} samples [16,258]. In order to investigate the oxidation state of Fe, high-resolution Fe 2p core level spectra of the samples Fe5, Fe5Sb2 and Fe5Mg2

were recorded and shown in Figure 6-12 (a). Fitting of the asymmetric core lines into four Voigt components together with Shirley background gives a good description of the overall core line shape. The peaks located around 711.1 eV and 713.7 eV are assigned to the Fe²⁺ and Fe³⁺, respectively. The Sn 3p peak (716.5 eV) is also observed since its binding energy is very close to the Fe 2p. The peak with highest binding energy in the spectra corresponds to the Fe 2p satellite. From these XPS results, we can see that both Fe³⁺ and Fe²⁺ co-exist in all three samples. By calculating the peak area ratio of Fe³⁺ to Fe²⁺, the relative concentration of Fe³⁺ and Fe²⁺ was estimated and the results are shown in Table 6-1.

Figure 6-12. (a) Core-level Fe 2p XPS spectra of bulk Sample Fe₅Mg₂, Fe₅Sb₂ and Fe₅. The spectra were fitted to a Shirley background (green dot line) together with the Voigt profiles for Fe²⁺ (dash line), Fe³⁺ (dash dot line), Sn 3p (dash line) and Fe 2p satellite (short dot line). The fitting curves (solid line) are seen to match well with the experimental data points. (b) VB spectra of the Samples Fe₅Mg₂, Fe₅Sb₂ and Fe₅.

It is interesting to note that, compared with sample Fe₅, the sample Fe₅Sb₂ has lower Fe³⁺ intensity and Mg doping leads to more Fe³⁺ in sample Fe₅Mg₂. This oxidation state variation of Fe can be understood in terms of the compensation effect to the

charge imbalance arising from the substitution of Sn⁴⁺ by Mg²⁺ and Sb⁵⁺. Since the spin state of Fe³⁺ is higher than Fe²⁺, the enhancement of M_s in Fe₅Mg₂ and decrease in Fe₅Sb₂ which were revealed in $M-H$ measurements, can be attributed to this doping induced oxidation state variation of Fe.

On the other hand, the carriers are found to play a critical role in the ferromagnetic exchange of DMS [257,259,260]. According to the equations (6-1) and (6-2), the roles of Mg and Sb in SnO₂ are acceptor and donor, respectively. To experimentally determine the carrier type for the Mg and Sb doping, we further carried out the XPS VB measurement. Figure 6-12 (b) presents the VB spectra for all three bulk samples. In semiconductor materials, the position of Fermi level (E_f) is a function of the doping type and doping concentration. For an n -type doped semiconductor, its E_f is near to CBM, i.e. far from the VBM. In the case of p -type doping, the E_f is near to VBM. As shown in the Figure 6-13, with respect to the VBM, the E_f of a semiconductor will shift up (away from VBM) in energy due to the n -type (donor) doping and shift down (towards VBM) in the case of p -type (acceptor) doping. Accordingly, by studying the shift of Fermi level, we can determine the doping type.

Figure 6-13. Schematic diagrams of band structure of semiconductors in different doping cases.

The XPS VB spectrum is an effective method to measure the relative position between the E_f and VBM. In a typical XPS VB spectrum (shown in the Figure 6-14), the E_f is located at 0 eV and the relative position of the VBM with respect to the E_f can be determined by extrapolating the leading edge of the VB to its intersection with the background.

Figure 6-14. The schematic diagram of the band alignment in XPS VB measurements for a semiconductor.

Obviously, from a XPS VB spectrum, we can study the shift of E_f and further determine the doping type. Actually, this technique has already been employed in determining the doping type by other research groups [261-263]. In our case, according to VB spectra shown in Figure 6-12, the E_f of sample Fe5Sb2 shifts away from the VBM, compared with sample Fe5. In the case of Mg doping (sample Fe5Mg2), the E_f moves toward the VBM. As a result, electron-doping of Sb and hole-doping of Mg in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ are confirmed. Corresponding to the $M-H$ results, the ferromagnetism in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ is found to be enhanced by hole-doping and destroyed by electron-doping.

6.2.4 Summary

In summary, the doping effects of Sb and Mg on the ferromagnetic properties of $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ were investigated in the forms of both polycrystalline bulk and epitaxial thin film. XPS results demonstrate that the concentration of high spin state Fe ions (Fe^{3+}) increased in the hole- (Mg) doped sample and decreased in the case of electron- (Sb) doping. The doping type of Mg and Sb in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$ was confirmed by XPS VB results. The oxidation state transition of Fe and carrier type variation are believed to be responsible for the co-doping tuned ferromagnetism behavior in $\text{Sn}_{0.93}\text{Fe}_{0.05}\text{M}_{0.02}\text{O}_{2-\sigma}$.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

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

7.1 Conclusions

In this dissertation, SnO_2 thin film and SnO_2 -based multifunctional materials have been fabricated on various substrates by LMBE technology. Using differently orientated sapphire substrates, crystal orientation controlled SnO_2 thin film epitaxy was realized. The epitaxial growth of thin film on perovskite substrate has also been investigated. Based on these SnO_2 thin film deposition technologies, the electrical transport property of SnO_2 thin films was studied, in which the effects of crystal

orientation, thickness and thermal annealing temperature were specifically investigated. On the other hand, the ferromagnetism in SnO₂:Fe based DMS has been explored in the form of both polycrystalline bulk and single crystal thin films. The main conclusions can be summarized as follows:

1. Epitaxial growth of SnO₂ thin films on sapphire substrates by LMBE has been extensively studied. Using differently orientated sapphire substrate, i.e. the (10 $\bar{1}2$), (0001), and (10 $\bar{1}0$) sapphire substrates, the crystal controlled epitaxial growth of SnO₂ thin films was realized. *In-situ* RHEED observations and *ex-situ* XRD results confirmed the single crystallinity of our SnO₂ thin films. According to the comprehensive XRD characterizations, the out-plane epitaxy relationships were determined as (101)_{SnO₂} // (10 $\bar{1}2$)_{sapphire} ∴, (200)_{SnO₂} // (0001)_{sapphire}, and (002)_{SnO₂} // (10 $\bar{1}0$)_{sapphire}. The in-plane epitaxy relationships can be determined as: (a) [010]_{SnO₂} // [$\bar{1}2\bar{1}0$]_{sapphire} and [$\bar{1}01$]_{SnO₂} // [$\bar{1}011$]_{sapphire} for the (101) SnO₂ thin film on (10 $\bar{1}2$) sapphire; (b) [001]_{SnO₂} // $\langle\bar{1}010\rangle$ _{sapphire} [010]_{SnO₂} // $\langle 1\bar{2}10\rangle$ _{sapphire} for the (200) SnO₂ thin film on (0001) sapphire. A six-fold rotation for the SnO₂ grains was observed in the (200) SnO₂ thin film on (0001) sapphire substrate, due to the six equivalent nucleation directions in the surface of (0001) sapphire substrate; (c) [010]_{SnO₂} // [0001]_{sapphire} and [100]_{SnO₂} // [$\bar{1}010$]_{sapphire} for the (002) SnO₂ thin film on (10 $\bar{1}0$) sapphire substrate. The surface morphology was investigated by AFM, from which smooth surface was observed in all the three differently orientated SnO₂ thin films.

2. Besides the conventionally used substrate for SnO₂ epitaxy (sapphire), the epitaxial growth of SnO₂ thin film on perovskite substrate [STO (111)] was explored. Detailed analysis with *in-situ* RHEED, *ex-situ* XRD, AFM and TEM confirmed the possibility of epitaxial growth of SnO₂ on perovskite substrate under a wide range of deposition conditions, despite of the large lattice mismatch and hetero structure between the films and substrate. The optimum deposition parameters for SnO₂ thin film on STO was found to be T_{Sub} = 700 °C and P_{Oxy} = 10⁻² Pa. The epitaxy relationship of SnO₂ on STO was determined as:

Out of plane: SnO₂ (100) // SrTiO₃ (111),

$$\text{In plane: } \begin{cases} \text{SnO}_2 [010] // \text{SrTiO}_3 [\bar{1}\bar{2}1], \text{SnO}_2 (001) // \text{SrTiO}_3 [\bar{1}01] \\ \text{SnO}_2 [010] // \text{SrTiO}_3 [11\bar{2}], \text{SnO}_2 (001) // \text{SrTiO}_3 [1\bar{1}0] \\ \text{SnO}_2 [010] // \text{SrTiO}_3 [\bar{2}11], \text{SnO}_2 (001) // \text{SrTiO}_3 [01\bar{1}] \end{cases}$$

The dielectric function for SnO₂ epilayer on STO was investigated in the UV-Vis-NIR region by ellipsometry. A TL-Drude model was developed to fit the measured ellipsometry data. The best-fit result shows an energy band gap of 3.65 eV and the trace of intraband transitions induced by the free electrons. This successful growth of epitaxial SnO₂ thin film on STO also opens a way for combining SnO₂ thin films with many other materials which are compatible with STO, and consequently offers the feasibility of new hybrid device design.

3. As a determining parameter for the optoelectronic properties, dictating the degree of charge carrier separation and localization of the interface, the band alignment between SnO₂ epilayer and STO substrate in SnO₂/STO sample was

quantitatively determined by comprehensive XPS measurements. Based on the XPS CL and VB spectra, the energy band diagram is deduced and presented in Figure 4-21 (showing in the following), from which a type-II band alignment is revealed for the SnO_2/STO heterostructure.

Figure 4-21. Schematic energy band diagram of the SnO_2/STO heterostructure, in which a type-II alignment is indicated.

4. Using the orientation controlled growth technique developed in Chapter 4, (002)- and (200)-orientated SnO_2 thin films were epitaxially deposited on sapphire and STO substrates by LMBE. Temperature dependent electrical transport properties of these SnO_2 films have been investigated from 400 K to 90 K. The electrical transport properties, including resistivity, activation energy and density of localized states at the Fermi level, were found to show a strong dependence on film orientation. This orientation controlled electrical conduction behavior can be understood on the basis of the anisotropic crystal structure of rutile SnO_2 .

5. The thickness effect on the electrical transport property of $\text{SnO}_2\text{:Sb}$ based conductive oxide thin films was studied. According to the electrical and spectroscopic studies, the $\text{SnO}_2\text{:Sb}$ thin film evolved from metal-like behavior to insulating nature. The critical thickness for this metal to insulator transition in $\text{SnO}_2\text{:Sb}$ thin films was found to be ~ 7.9 to 3.1 nm. This approach allows one to examine the size scaling limitation for conducting oxide applications for $\text{SnO}_2\text{:Sb}$. High resolution XPS core level spectra of Sb indicate that the thickness induced metal to insulator transition in $\text{SnO}_2\text{:Sb}$ thin films should be directly related to the oxidation states variation of Sb from +5 to +3. In addition, a prominent quantum confinement effect was observed in our $\text{SnO}_2\text{:Sb}$ thin films. Based on the first principles calculation results reported by other groups, this quantum confinement is believed to be responsible for the oxidation states variation of Sb.
6. SnO_2 thin films were deposited on quartz substrates by LMBE and post-annealed at different temperatures in oxygen ambience. The influence of annealing temperature on the structure and electrical transport property of LMBE deposited SnO_2 thin films was investigated using XRD, Hall measurement and XPS. By varying the annealing temperature, an anomalous electrical transport behavior of the SnO_2 thin films was observed and explained by the crystal grain size growth and temperature-dependent oxygen vacancy density variation.
7. The ferromagnetism in $\text{SnO}_2\text{:Fe}$ based DMS was studied in both bulk and thin film samples. Based on the XRD results, the solid solubility of Fe in SnO_2 was

determined to be up to 10%. In 5% Fe doped SnO₂ bulk sample, robust RTFM was achieved, in which no secondary phase or small cluster was observed using XRD and HRTEM. Using orientation control technique, magnetic anisotropy was discovered in (200)- and (002)-orientated Sn_{0.95}Fe_{0.05}O_{2-σ} thin films deposited on sapphire (0001) and (10 $\bar{1}$ 0) substrates, respectively. This anisotropy suggests that the ferromagnetism in Sn_{0.95}Fe_{0.05}O_{2-σ} unlikely originates from Fe clusters or magnetic secondary phase.

8. To further study the ferromagnetism in SnO₂:Fe based DMS system, the electron- and hole-doping effect on the magnetic properties of Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} was investigated by varying the dopant M (Sb/Mg). In both bulk and thin film forms, prominent decrease of saturation magnetization (M_s) was observed in Sn_{0.93}Fe_{0.05}Sb_{0.02}O_{2-σ}. On the contrary, the M_s was significantly enhanced in the case of Mg doping. It clearly indicated a carrier doping tuned ferromagnetism in SnO₂:Fe based DMS system. Comprehensive XPS results demonstrated that the concentration of high spin state Fe ions (Fe³⁺) increased in the hole- (Mg) doped sample and decreased in the case of electron- (Sb) doping. The doping type of Mg and Sb in Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ} was confirmed by XPS VB measurements. The oxidation state transition of Fe and carrier type variation are believed to be responsible for the co-doping tuned ferromagnetism behavior in Sn_{0.93}Fe_{0.05}M_{0.02}O_{2-σ}.

7.2 Recommendations for future work

In this dissertation, it is evident that SnO₂ thin films can be epitaxially deposited on various substrates, i.e., (10 $\bar{1}$ 2), (0001), and (10 $\bar{1}$ 0) sapphire and (111) STO by LMBE technique. However, compared with other metal oxides, e.g. ZnO [264], TiO₂ [265], and LaAlO₃ [266], the crystal quality of SnO₂ epitaxial thin films is still relatively low and no layer-by-layer growth model has been realized in the SnO₂ thin film growth. One of the most prominent difficulties of achieving high quality SnO₂ thin films is the large lattice mismatch between the film and substrate. For instance, the lattice mismatch between (101) SnO₂ and (10 $\bar{1}$ 2) sapphire is 12%, and it is 16% between (200) SnO₂ and (111) STO. Since the high quality epitaxial thin film will assist the understanding to the intrinsic properties of SnO₂ and be beneficial for its application explorations in the mean time, the improving of SnO₂ thin film epitaxy is still highly demanded. To get higher quality SnO₂ thin films, the most direct way is to search a new substrate, which has smaller lattice mismatch with SnO₂. However, it is still very difficult, since the commercially available single crystal substrates are limited. Another way to improve the thin film quality, which is more practical, should be using the buffer layer. The buffer layer technique has been widely used in the epitaxy growth of ZnO thin films [267,268]. It is evident that the thin film quality can be essentially improved by introducing a buffer layer between the film and substrate. As for the growth of SnO₂ on sapphire, the rutile TiO₂ should be a promising buffer material, since TiO₂ is known to possess appropriate lattice constants intervenient between those of SnO₂ and Al₂O₃. High-temperature-annealed self-buffer layer (HITAB) technique developed by A. Tsukazaki *et al.* may also be applicable for the

growth of SnO_2 , in which the layer-by-layer growth of high-optical-quality thin film was achieved on atomically smooth and lattice relaxed self buffer layer [269].

More systematical investigation on the structural, electrical, and optical properties for all growth regimes, laser ablation energy and substrate temperature would essentially expand the control of the SnO_2 properties by adjusting the epitaxial conditions. Future work should lead to a better analysis and understanding of the relationship between the thin film deposition conditions and its physical properties (structural, electrical, and optical). In Section 4.2 of this dissertation, the epitaxial growth of SnO_2 on (111) STO substrate was discussed. It makes the integration between SnO_2 and other multifunctional perovskite materials become possible and facilitates the study of novel layer structures and device design. The perovskite materials have a wide spectrum of physical properties, such as ferroelectricity, ferromagnetism, multiferroics, and superconductivity. The integration of semiconducting oxides and complex perovskite oxides has attracted much attention. Several prototype electronic devices based on this integration have been reported, such as current rectify effect [163], photovoltaics [164], colossal magnetoresistance [165], and resistive memory switching [166,167]. In this light, the integration of SnO_2 and multifunctional perovskite materials will offer an interesting opportunity to the design of new devices with novel functionalities, e.g. the $\text{SnO}_2/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ based p-n junction.

As one of the most promising applications developed recently, the SnO_2 based DMS materials are receiving a great deal of attention. In this dissertation, the ferromagnetism in $\text{SnO}_2\text{:Fe}$ based DMS bulk and thin film samples have been studied

and a carrier doping tuned ferromagnetism in $\text{SnO}_2\text{:Fe}$ was discovered. As an immediately continuous work, other magnetic dopants such as Ni or Co could also be introduced in SnO_2 as the host material in order to further study the potential of this particular DMS for spintronic applications. The carrier doping effect on the magnetic properties of $\text{SnO}_2\text{:Ni}$ or $\text{SnO}_2\text{:Co}$ is worthy to study, in order to get a more profound understanding to the ferromagnetism in SnO_2 based DMS. Furthermore, more sophisticated methods, such as point contact Andreev reflection measurements, could be adopted to directly determine the spin polarization of the SnO_2 based DMS [270].

AUTHOR'S PUBLICATION

Journal Papers

- 1). **C. Ke**, Z. Yang, J. S. Pan, W. Zhu, and Z. P. Li, "*Fabrication of $\text{SnO}_2/\text{SrTiO}_3$ Epitaxial Heterojunction and Its Band Alignment Measured by XPS*" Submitted.
- 2). **C. Ke**, J. S. Pan, W. Zhu, Z. Yang, and Z. P. Li, "*Thickness induced Metal-Insulator transition in $\text{SnO}_2:\text{Sb}$ thin films*" Submitted.
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