ABSTRACT

MOLAEI, ROYA. Semiconductor to Metal Transition Characteristics of VO\textsubscript{2}/NiO Epitaxial Heterostructures Integrated with Si(100). (Under the direction of Prof. Jagdish Narayan).

The novel functionalities of Vanadium dioxide (VO\textsubscript{2}), such as, several orders of magnitude transition in resistivity and IR transmittance, provide the exciting opportunity for the development of next generation memory, sensor, and field-effect based devices. A critical issue in the development of practical devices based on metal oxides is the integration of high quality epitaxial oxide thin films with the existing silicon technology which is based on silicon (100) substrates. However, silicon is not suitable for epitaxial growth of oxides owing to its tendency to readily form an amorphous oxide layer or silicide at the film-substrate interface. The oxide films deposited directly on silicon exhibit poor crystallinity and are not suitable for device applications. To overcome this challenge, appropriate substrate templates must be developed for the growth of oxide thin films on silicon substrates.

The primary objective of this dissertation was to develop an integration methodology of VO\textsubscript{2} with Si (100) substrates so they could be used in “smart” sensor type of devices along with other multifunctional devices on the same silicon chip. This was achieved by using a NiO/c-YSZ template layer deposited in situ. It will be shown that if the deposition conditions are controlled properly. This approach was used to integrate VO\textsubscript{2} thin films with Si (100) substrates using pulsed laser deposition (PLD) technique. The deposition methodology of integrating VO\textsubscript{2} thin films on silicon using various other template layers will also be discussed. Detailed epitaxial relationship of NiO/c-YSZ/Si(100) heterostructures as a template to growth of VO\textsubscript{2} as well as were studied. We also were able to create a p-n junction
within a single NiO epilayer through subsequent nanosecond laser annealing, as well as established a structure-property correlation in NiO/c-YSZ/Si(100) thin film epitaxial heterostructures with especial emphasis on the stoichiometry and crystallographic characteristics. NiO/c-YSZ/Si(100) heterostructures were used as template to grow fully relaxed VO₂ thin films. The detailed x-ray diffraction, transmission electron microscopy (TEM), electrical characterization results for the deposited films will be presented. In the framework on domain matching epitaxy, epitaxial growth of VO₂ (tetragonal crystal structure at growth temperature) on NiO has been explained. Our detailed phi-scan X-ray diffraction measurements corroborate our understanding of the epitaxial growth and in-plane atomic arrangements at the interface. It was observed that the transition characteristics (sharpness, over which electrical property changes are completed, amplitude, transition temperature, and hysteresis) are a strong function of microstructure, strain, and stoichiometry. We have shown that by the choosing the right template layer, strain in the VO₂ thin films can be fully relaxed and near-bulk VO₂ transition temperatures can be achieved.

Finally, I will present my research work on modification of semiconductor-to-metal transition characteristics and effect on room temperature magnetic properties of VO₂ thin films upon laser annealing. While the microstructure (epitaxy, crystalline quality etc.) and phase were preserved, we envisage these changes to occur as a result of introduction of oxygen vacancies upon laser treatment.
Semiconductor to Metal Transition Characteristics of VO$_2$/NiO Epitaxial Heterostructures Integrated with Si(100)

by
Roya Molaei

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

Materials Science and Engineering

Raleigh, North Carolina

2014

APPROVED BY:

Prof. Jay Narayan
Committee Chair

Prof. John T. Prater

Prof. Mike Rigsbee

Prof. Roger Narayan
DEDICATION

I lovingly dedicate this thesis to my husband, Reza, who supported me each step the way, and has always been there through the hard times.
BIOGRAPHY

Roya Molaei was born in Tehran, Iran. After completing her schooling, she went to study Materials and Metallurgical Engineering at Iran University of Science and Technology in Tehran for her Bachelor of Science degree. She earned a M.Sc. degree in Material Science and Engineering at Iran University of Science and Technology. She joined Department of Materials Science and Engineering of NC State University in the spring of 2012 for her doctoral research, which involved integration of epitaxial VO$_2$ thin films on Silicon substrates, under the guidance of Prof. Jagdish Narayan.
ACKNOWLEDGMENTS

I would like to thank my supervisor Dr. Jay Narayan for his advice, guidance, patience, and tremendous help during the project. I wish to thank my committee members who were more than generous with their expertise and precious time. Thank you Dr. Roger Narayan, Dr. Mike Rigsbee, and Dr. John Prater for agreeing to serve on my committee.

I want to give special thanks to my colleagues and friends: Dr. Sudhakar Nori, Yee Fang Lee, Fan Wu, Sandhyarani Punugupati, Namik Temizer, Ranjan Singhal, and their support throughout my doctoral research at NC State has been invaluable and has made my stay a really enjoyable experience. A special thank goes to Edna Deas for her prompt help with the administrative work. Mentioning everyone who has in one way or the other helped and supported me during my stay here would make the list really very long, so I will not take specific names just in case I miss out someone. But, I want to thank from the bottom of my heart all my friends, on and off-campus, who have made my stay at NC State worthwhile.

And last, but not least, thanks to my husband, Dr. Reza Bayati, for his kindness, love, and for always being there with me throughout the process.

I also thank National Science Foundation for providing the funding for my work.
TABLE OF CONTENTS

LIST OF TABLES........................................................................................................vii

LIST OF FIGURES ......................................................................................................viii

Chapter 1. Introduction .............................................................................................. 1
  1.1 References ........................................................................................................ 6

Chapter 2. Background knowledge ........................................................................... 8
  2.1 Vanadium dioxide (VO₂) .................................................................................. 8
    2.1.1 Structural characteristics of VO₂ ............................................................... 11
    2.1.2 The nature of the insulating state ............................................................... 13
    2.1.3 Thermodynamic model for phase transition in VO₂ .................................. 17
    2.1.4 Applications of VO₂ thin films ................................................................. 20
  2.2 Thin Film Epitaxy ............................................................................................. 21
    2.2.1 Lattice Matching Epitaxy ......................................................................... 22
  2.3 Domain Matching Epitaxy ................................................................................ 24
  2.4 Substrate and buffer layer materials ................................................................. 28
    2.4.1 Silicon ....................................................................................................... 28
2.4.2 Yttria stabilized zirconia (YSZ)................................................................. 29

2.4.3 Nickel oxide (NiO) ......................................................................................... 30

2.5 References ........................................................................................................ 32

Chapter 3. Experimental techniques .................................................................... 35

3.1 Substrate preparation ...................................................................................... 36

3.2 Pulsed laser deposition (PLD) ......................................................................... 36

3.2.1 Physics of the laser-solid interaction ............................................................... 39

3.2.2 Advantages and disadvantages of PLD ............................................................ 47

3.3 X-Ray diffraction .............................................................................................. 49

3.4 Transmission electron microscopy ..................................................................... 53

3.5 Four-point probe resistivity measurement .......................................................... 57

3.6 X-Ray Photoelectron Spectroscopy ................................................................... 59

3.7 References ........................................................................................................ 61

Chapter 4. Enhanced photocatalytic efficiency in zirconia buffered n-NiO/p-NiO single crystalline heterostructures by nanosecond laser treatment ........................................................................... 63

4.1 Introduction ....................................................................................................... 64

4.2 Experimental .................................................................................................... 67

4.3 Results and discussion ..................................................................................... 69

4.3.1 Photocatalytic efficiency ................................................................................ 81
6.3.3 Semiconductor to metal transition ................................................................. 129
6.4 Conclusion ........................................................................................................... 132
6.5 References ......................................................................................................... 133

Chapter 7. Diamagnetic to ferromagnetic switching in VO₂ epitaxial thin films by nanosecond excimer laser treatment ................................................................. 136

7.1 Introduction ........................................................................................................ 136
7.2 Experimental ...................................................................................................... 139
7.3 Results and discussion ....................................................................................... 141
7.4 Conclusion ......................................................................................................... 148
7.5 References ........................................................................................................ 149

Chapter 8. A microstructural approach toward the effect of thickness on semiconductor-to-metal transition characteristics of VO₂ epilayers .................................................. 151

8.1 Introduction ........................................................................................................ 152
8.2 Experimental ...................................................................................................... 155
8.3 Results and discussion ....................................................................................... 157
8.4 Conclusions ....................................................................................................... 167
8.5 References ........................................................................................................ 169

Chapter 9. Semiconductor to metal transition characteristics of VO₂(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) epitaxial heterostructures ......................... 173

9.1 Introduction ........................................................................................................ 174
9.2 Experimental ............................................................................................................. 176
9.3 Results and discussion............................................................................................. 177
9.4 Conclusions ............................................................................................................. 188
9.5 References ............................................................................................................. 191

Chapter 10. Conclusions and suggestions for further work......................................... 195

10.1 Conclusions ........................................................................................................... 195
10.2 Future Work .......................................................................................................... 197
LIST OF TABLES

Tab. 3.1 Operating wavelengths of various excimer lasers .................................................. 39

Tab. 8.1 Thickness of the VO₂ epitaxial layers as a function of number of laser pulses...... 162

Tab. 9.1 Crystallographic parameters used to collect φ-patterns from (200) reflection of monoclinic VO₂ crystal and (220) reflections of NiO, MgO, TiN, and Si crystals. .......... 180
LIST OF FIGURES

Fig. 2.1 Hysteresis curves showing change in resistance (left) and reflection (right) as a function of temperature during phase transition in VO$_2$. ................................................................. 9

Fig. 2.2 Phase diagram of the V-O system. .................................................................................. 10

Fig. 2.3 Schematic delineation of electron band structure of: (a) tetragonal and (b) monoclinic VO$_2$. ................................................................................................................................. 12

Fig. 2.4 d-electron band splitting by crystal fields and their orbitals. ........................................... 13

Fig. 2.5. Schematic representation of lattices of the two structural phases of VO$_2$. Left: Monoclinic (M$_1$) VO$_2$. Right: Tetragonal or rutile (R) VO$_2$. ................................................................. 15

Fig. 2.6 Schematic representation of lattice matching epitaxy, $d_c$ denoted the critical thickness................................................................................................................................. 23

Fig. 2.7 Schematic illustration of domain matching epitaxy (DME), in which four lattice planes of film match with five lattice planes of substrate......................................................... 25

Fig. 2.8 (a) ZnO/Sapphire interface (b) Fourier filtered image showing DME (c) selected area electron diffraction pattern of ZnO/Sapphire interface (d) schematic plan view of the epitaxy. ................................................................................................................................. 27

Fig. 2.9 Diamond cubic crystal structure of Silicon .......................................................................... 28
Fig. 2.10 Crystal structure of tetragonal (left) and cubic (right) YSZ. Oxygen atoms are shown in red color while (Zr, Y) atoms are shown in green color.

Fig. 2.11 Crystal structure of NiO. Oxygen (bigger) atoms are shown in red color while Ni (smaller) atoms are shown in black color.

Fig. 3.1 Schematic diagram of a typical pulsed laser deposition chamber.

Fig. 3.2 Schematic illustration showing different regimes during laser irradiation of the target: (a) Bulk target that remains unaffected, (b) Thickness of the target that evaporates, (c) region in which the plasma absorbs the laser and (d) the expanding plasma region.

Fig. 3.3 (a) Schematic illustration showing the initial elliptical shape of the plasma just after the laser pulse is terminated, (b) Final shape of the plasma when it hits the substrate, (c) Shape of a YBCO film deposited on a Si substrate.

Fig. 3.4 A schematic diagram of Rigaku D-MAX/A diffractometer used for θ-2θ scans. DS: Divergence slit, ASS: Anti scatter slit, RS: Receiving slit, MRS: Monochromator receiving slit.

Fig. 3.5 A schematic diagram of the Philips X’Pert diffractometer used for φ-scans. IBO: Incident beam optics, DBO: Diffracted beam optics.

Fig. 3.6 A schematic diagram of the beam alignment in the two TEM modes (a) diffraction and (b) imaging mode.
Fig. 3.7 Schematic presenting a typical four point probe resistivity measurement setup...... 58

Fig. 4.1 θ-2θ patterns of the NiO/cYSZ/Si heterostructures: (a) pristine sample, (b) laser annealed sample, and (c) high resolution θ-2θ scan of the pristine and laser treated samples. ........................................................................................................................................................................... 70

Fig. 4.2 φ-patterns acquired from NiO(200) reflection (2θ = 43.31°, ψ = 54.24°), cYSZ(202) reflection (2θ=50.37°, ψ=45.00°), and Si(202) reflection (2θ=47.57°, ψ=45.00°)................. 71

Fig. 4.3 High resolution TEM micrographs showing a crystallographically continuous domain boundary in the NiO epilayer................................................................. 73

Fig. 4.4 Schematic illustration of the epitaxial relationship across the NiO/cYSZ interface. NiO and cYSZ lattices are represented in red and blue, respectively........................................ 74

Fig. 4.5 High resolution TEM image of the interface between the NiO epilayer and the cYSZ buffer.................................................................................................................... 75

Fig. 4.6 (a) Cross section bright field image and the SAED pattern taken from the laser annealed sample and (b) interface between the pristine and the laser treated regions. The SAED pattern belongs to Si[110], cYSZ[110], and NiO[413] zones......................................................... 76

Fig. 4.7 O (1s) core level binding energy in: (a) as-deposited and (b) laser annealed samples. ...................................................................................................................................................................................................... 79
Fig. 4.8 Ni(2p_{3/2}) core level binding energy in: (a) as-deposited and (b) laser annealed samples................................. 80

Fig. 4.9 The effect of nanosecond laser annealing on the photocatalytic activity of NiO(111)/cYSZ(001)/Si(001) heterostructures. ................................................................. 82

Fig. 5.1 θ-2θ XRD patterns of the NiO/c-YSZ/Si heterostructures grown under the pressures of: (a) 7×10^{-6}, (b) 5×10^{-4}, (c) 5×10^{-3}, and (d) 5×10^{-2} Torr. ............................................. 99

Fig. 5.2 Schematic arrangement of: (a) anion terminated NiO(111) and (b) cation terminated NiO(100) faces................................................................. 100

Fig. 5.3 φ-patterns acquired from NiO(111)/c-YSZ(001)/Si(001) epitaxial heterostructure. ................................................................. 102

Fig. 5.4 φ-patterns taken from NiO(100)/c-YSZ(001)/Si(001) epitaxial heterostructure..... 103

Fig. 5.5 (a) Cross-section low magnification TEM image from the NiO(100)/c-YSZ(001)/Si(001) heterostructure where the inset depicts the indexed SAED pattern, (b) High magnification TEM micrograph showing the NiO(100)/c-YSZ(100) interface, and (c) Arrangement of misfit dislocation and alternation of 6/5 and 5/4 matching domains across the NiO/c-YSZ interface......................................................... 104

Fig. 5.6 High resolution TEM image taken from the NiO(111)/c-YSZ(100) interface....... 106

Fig. 5.7 Dependence of the electrical properties on the oxygen partial pressure. ............... 107
Fig. 5.8 XPS O(1s) core level binding energy of the NiO epilayers grown under pressures of:
(a) 7×10^{-6}, (b) 5×10^{-4}, (c) 5×10^{-3} Torr, and (d) 5×10^{-2} Torr. ....................................................... 108

Fig. 5.9 Effect of the oxygen pressure on the content of -OH and NiO_2 compounds. ....... 109

Fig. 5.10 XPS Ni(2p) core level binding energy of the NiO epilayers grown under pressures
of: (a) 7×10^{-6}, (b) 5×10^{-4}, (c) 5×10^{-3} Torr, and (d) 5×10^{-2} Torr. ....................................................... 112

Fig. 6.1 θ/2θ XRD pattern of the VO_2/NiO/YSZ/Si(001) thin film heterostructure......... 123

Fig. 6.2 φ-scan XRD pattern acquired from: (a) YSZ(202) and Si(202), (b) NiO(200), and (c) VO_2(011) reflections. ..................................................................................................................... 125

Fig. 6.3 Atomic arrangement at the: (a) Si(001) surface, (b) YSZ(001) surface, and (c) YSZ/Si interface................................................................................................................................. 126

Fig. 6.4 Atomic arrangement at the: (a) Zr-terminated YSZ(001) surface, (b) O-terminated NiO(111) surface, and (c) NiO/YSZ interface................................................................. 127

Fig. 6.5 Atomic arrangement at the: (a) O-terminated NiO(111) surface, (b) V-terminated VO_2(010) surface, and (c) VO_2/NiO interface............................................................. 128

Fig. 6.6 TEM cross section bright field image of the VO_2/NiO/YSZ/Si(001) heterostructure and the selected area electron diffraction pattern (Si[110], YSZ[110], NiO [110], and VO_2[201] zones) ......................................................................................................................... 130
Fig. 6.7 Resistance as a function of the temperature for the VO$_2$/NiO/YSZ heterostructure.

Fig. 7.1 XRD 0-20 scans from: (a) pristine and (b) laser annealed VO$_2$ thin films. The inset shows high resolution scans of the VO$_2$(020) reflection.

Fig. 7.2 Low magnification cross-section TEM micrograph taken from the laser annealed VO$_2$/NiO/c-YSZ/Si heterostructure. In the SAED pattern, shown in the inset, the Si(004), c-YSZ(004), NiO(111), and VO$_2$(020) reflections are denoted by S, Y, N, and V letters.

Fig. 7.3 V(2p$_{3/2}$) core level binding energy in pristine and laser annealed samples.

Fig. 7.4 The isothermal field dependence of magnetic moment curves of laser annealed VO$_2$/NiO/c-YSZ films deposited on Si(100) substrates measured at 10, 100 and 300 K. Plotted in the bottom inset are the low field M-H hysteresis loops between ± 500 Oe deciphering clearly the coercivity. The diamagnetic contribution due to the Si substrate has been subtracted. The coercivity increases from ~60 Oe at RT to 250 Oe at 10K. The top inset plot shows the diamagnetic behavior of the pristine VO$_2$/NiO/c-YSZ/Si(100) sample.

Fig. 7.5 XPS survey scan acquired from the pristine and the laser annealed VO$_2$ epilayers.

Fig. 8.1 XRD 0-20 patterns acquired from the VO$_2$/NiO/c-YSZ/Si thin film heterostructures for different number of VO$_2$ pulses: (a) 500, (b) 1000, (c) 2000, (d) 3000, (e) 4500, and (f) 6000 pulses.
Fig. 8.2 AFM 2D images of VO\(_2\)/NiO/c-YSZ/Si heterostructures for different VO\(_2\) thicknesses: (a) 200, (b) 100, (c) 30 nm................................................................. 159

Fig. 8.3 High resolution θ-2θ scans through VO\(_2\)(020) signal acquired from the VO\(_2\) epilayers with different thicknesses. ................................................................. 160

Fig. 8.4 Cross-section TEM images and corresponding selected area electron diffraction patterns obtained from the VO\(_2\)/NiO/c-YSZ/Si heterostructures for different VO\(_2\) thicknesses: (a) 10, (b) 30, (c) 70, (d) 100, (e) 150, and (f) 200 nm................................................................. 161

Fig. 8.5: Schematic delineation of: (a) VO\(_2\),monoclinic/NiO and (b) VO\(_2\),tetragonal/NiO interfaces. .............................................................................................................................................................................................................................................. 163

Fig. 8.6: Changes of resistance versus temperature for VO\(_2\) epilayers at different thicknesses. A semiconductor to metal transition (SMT) is clearly observed. ........................................ 165

Fig. 8.7 A summary of SMT parameters of VO\(_2\) epitaxial films with several thicknesses. . 167

Fig. 9.1 A θ-2θ XRD pattern acquired form VO\(_2\)(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) thin film heterostructure......................... 178

Fig. 9.2 XRD φ-patterns taken from VO\(_2\)(011), NiO(220), MgO(220), TiN(220), and Si(220) reflections................................................................. 179

Fig. 9.3 Schematic delineation of: (a) monoclinic and (b) Tetragonal VO\(_2\) unit cells. The (011) and (110) planes in monoclinic and tetragonal VO\(_2\) unit cells are highlighted in pink
and blue, respectively. The crystallographic relationship between two crystals are based on the Goodenough’s model. ................................................................. 181

Fig. 9.4 A cross-section TEM micrograph acquired from VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) thin film heterostructure. .......................... 182

Fig. 9.5 A 2D schematic illustration of (110) and (100) planes of tetragonal VO$_2$ and NiO at the VO$_2$/NiO interface at the temperature of growth. ................................................. 184

Fig. 9.6 High resolution θ-2θ scans through (110) and (011) reflections of tetragonal and monoclinic VO$_2$ at different temperatures during: (a) heating and (b) cooling cycles. The insets show the change of peak intensities as a function of temperature. ................................. 186

Fig. 9.7 The temperature dependence of inter-planar spacing for (110) and (011) planes of tetragonal and monoclinic (M$_1$) VO$_2$. ................................................................. 187

Fig. 9.8 Change of electrical resistivity of epitaxial VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) thin film heterostructure as a function temperature. ................................................................. 189
Chapter 1. Introduction

Vanadium dioxide (VO₂) has been one of the most extensively investigated correlated electron systems that exhibit a distinct semiconductor-to-metal transition.\(^1\)\(^2\) VO₂ has attracted this immense research and technological interest because of its ability to reversibly transform from monoclinic (semiconducting and infrared transparent) to tetragonal (metallic and infrared blocking) phase upon heating across 68 °C. Of all the transition metal oxides that exhibit any semiconductor-to-metal transition, VO₂ is distinguished by its thermal switching at 68 °C (near room temperature), the transition temperature that is modifiable by doping or stress, its ultrafast (~ 10\(^2\) femtoseconds) transition when excited by a laser and its metallic behavior under application of high electric-field (~10\(^6\) V/cm).\(^3\)\(^-\)\(^5\) This first-order semiconductor-to-metal transition (SMT) near room temperature has been well-studied over the last fifty years but the physics behind this intriguing phenomenon is less than well understood. The characteristics associated with SMT in VO₂ are fascinating scientifically and are of immense technological importance for potential applications in sensor- and memory-type applications.\(^6\)\(^-\)\(^9\)

Semiconductor-to-metal transition in VO₂ involves small lattice distortion along c-axis direction, which results in pairing of vanadium atoms and a distinct band structure in each phase. These distortions result in failure of VO₂ bulk single crystals when subjected to repeated heating and cooling cycles.\(^10\) Therefore, thin films and nanoparticles of VO₂, which are able to withstand these distortions and dissipate heat through the substrate, are critical to
a variety of technological applications. Recent advances in expertise of thin films growth techniques have allowed us to explore the huge technological potential that the multifunctional strongly-correlated materials, such as VO$_2$, have to offer. To date, most of the research on VO$_2$ thin films has focused on growth of epitaxial films with controlled properties on Al$_2$O$_3$ and TiO$_2$ substrates,$^{11-14}$ however, implementation of VO$_2$-based devices is restricted by the limited use of Al$_2$O$_3$ and TiO$_2$ substrates in the microelectronic industry. One of the essential prerequisites to the development of optoelectronic devices based on thermal switching is the development of methods that enable integration of VO$_2$ films with Si (001), which is the mainstay substrate material in the microelectronics industry. Though the epitaxial growth of VO$_2$ on Si (001) can be anticipated via domain matching epitaxy (DME),$^{15}$ in which integral multiples of planes match across the film-substrate interface, direct deposition of VO$_2$ on Si (001) remains a technological challenge. One challenge associated with direct deposition of VO$_2$ on Si (001) is the formation of silicides or native amorphous silicon dioxide layers, which can lead to growth of polycrystalline VO$_2$ thin films that show a diffused transition and provide limited control over transition characteristics.$^{16,17}$

Semiconductor to metal transition in VO$_2$ is characterized by sharpness $\Delta T$, over which electrical and optical property changes are completed, amplitude $\Delta A$, and width of thermal hysteresis $\Delta H$. These characteristics of VO$_2$ thin films have been known to be a strong function of microstructure (grain size distribution and grain boundary characteristics) and chemistry (stoichiometry, dopant and/or other defects). However, the individual effect of these factors on the SMT parameters is not well understood as films studied in most of these
cases were either polycrystalline or had other oxide phases (e.g. V$_2$O$_5$ or V$_2$O$_3$) or dopants present in the films which is likely to produce a combined effect of all these parameters in modification of SMT characteristics. Therefore, there is a major challenge in producing VO$_2$ thin films of correct structure, stoichiometry and controlled microstructures, especially high-quality single crystal films, which can be used to establish comprehensive structure-property correlations. In this dissertation we have addressed the integration of high quality epitaxial VO$_2$ thin films with Si (001) substrates by using epitaxial NiO/c-YSZ and NiO/MgO/TiN buffer layers. We anticipate that these high-quality epitaxial VO$_2$ thin films grown on Si (001) substrates could find potential use in a variety of electronic and optical devices.

The typical deposition temperature for the growth of high-quality VO$_2$ thin films with good SMT properties definitely exceeds the transition temperature which is close to 68 °C. Following the deposition at elevated temperatures, when films are cooled to ambient temperature, VO$_2$ crystal structure transforms from tetragonal (P4$_2$/mnm) to monoclinic (P2$_1$/c). It is important, therefore, to understand as to how the tetragonal unit cell arranges itself on the underlying template of substrate or buffer layer material. Understanding the details of epitaxy is important from the point of view of fundamental understanding and to develop methodology to tailor the thin film strain/stress and as a result, SMT characteristics suited to a particular application. In this dissertation, the epitaxial growth of VO$_2$ NiO/c-YSZ and NiO/MgO/TiN buffer layers were studied. We have been able to achieve semiconductor-
to-metal transition (SMT) temperature in VO$_2$ thin films close to the values reported for bulk VO$_2$ single crystals. This was achieved by complete relaxation of misfit strain, which leads to a negligible tension/compression along VO$_2$ [001], upon introduction of NiO buffer layer on silicon substrate. It was also found that introduction of NiO buffer layer led to improved SMT characteristics such as, $\Delta T$, $\Delta H$, and $\Delta A$. We have discussed the mechanism behind complete relaxation of misfit strain which occurs under the paradigm of domain-matching epitaxy, where integral multiples of planes match across the interface. NiO buffer layers were grown in situ, prior to the VO$_2$ deposition parameters related to SMT, such as hysteresis and transition width were extracted from the Gaussian fit of temperature dependence of electrical resistance. These parameters have also been discussed in correlation with the strain along c-axis of VO$_2$, in-plane orientation, and microstructure. Completely relaxed VO$_2$/NiO/c-YSZ/Si(100) and VO$_2$/NiO/MgO/TiN/Si(100) thin film heterostructure hold significant technological importance since robust devices that can withstand multiple thermal cycling, can be fabricated. Also, potential applications of NiO as an epitaxial electrode or gate oxide layer can open up exciting possibilities in devices based on SMT properties of strain-free VO$_2$ thin films.

To establish a correlation between nature of grain boundaries and relative orientation, grain size, and defects with SMT of VO$_2$ thin films grown on an NiO/c-YSZ buffer platform, films were deposited for different deposition times resulting in different thicknesses. It was shown that thickness of the films play a critical role in determining the characteristics of the hysteresis and the nature of the SMT. Electrical properties of VO$_2$ thin films were studied
systematically to correlate SMT characteristics with microstructural properties of the films using the theoretical predictions of thermodynamic model given by Narayan et. al.\textsuperscript{22}

Rest of the thesis is organized into following chapters:

Chapter 2: Background knowledge pertinent to this dissertation is presented.

Chapter 3: A brief description of experimental techniques used for the present work is given.

Chapter 4: Enhanced Photocatalytic Efficiency in zirconia buffered n-NiO/p-NiO Single Crystalline Heterostructures by Nanosecond Laser Treatment are presented.

Chapter 5: Results from study of crystallographic characteristics and p-Type to n-Type transition in epitaxial NiO thin film are presented and correlated.

Chapter 6: Results from thin film epitaxy and near bulk semiconductor to metal transition in VO\textsubscript{2}/NiO/YSZ/Si(001) heterostructures are presented and discussed.

Chapter 7: Results from study of diamagnetic to ferromagnetic switching in VO\textsubscript{2} epitaxial thin films by nanosecond excimer laser treatment are presented.

Chapter 8: Results are discussed from a microstructural approach toward the effect of thickness on semiconductor-to-metal transition characteristics of VO\textsubscript{2} epilayer.

Chapter 9: Results from study of semiconductor to metal transition characteristics of VO\textsubscript{2}(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) epitaxial heterostructures are presented.
1.1 References


Chapter 2. Background knowledge

2.1 Vanadium dioxide (VO$_2$)

As one of the focus areas of research in condensed matter physics, strongly correlated electron system exhibit some fascinating phenomena such as, high-temperature superconductivity, colossal magneto-resistance, exotic magnetic, charge and orbital ordering, and semiconductor-to-metal phase transition.$^1$ Vanadium dioxide (VO$_2$) is one of the most studied correlated electron systems that exhibits a highly useful semiconductor-to-metal transition (SMT). In 1959, Morin$^1$ observed that bulk vanadium dioxide crystals exhibit a reversible semiconductor-to-metal transition (SMT) at a critical temperature of about 68°C with change in resistivity and near-infrared transmission spanning several orders of magnitude. Being a transition-metal oxide with narrow $d$-electron bands, this strongly correlated electron system is extremely sensitive to small changes in extrinsic parameters such as temperature, pressure, or doping. In bulk crystals, the change in resistivity is of order $\sim 10^3$-$10^5$, with a hysteresis width of $\sim 1^\circ$C, as seen in Fig. 2.1. Being a transition-metal oxide with narrow $d$-electron bands, SMT in VO$_2$ is extremely sensitive to small changes in extrinsic parameters such as pressure, or doping.$^2$ In bulk single crystals, the change in resistivity is of order $\sim 10^3$-$10^5$, with a hysteresis width of $\sim 1^\circ$C.$^1$ On the other hand, hysteresis widths in thin films and in nanostructures may be in the range of $3^0$-$10^0$C and $30^\circ$-$35^\circ$C, respectively.$^4$-6
Thin films and nanoparticles tend to better withstand the repeated thermal cycling and also their transition temperature can be lowered to near room temperature by doping. Recent advances in thin film growth techniques and device fabrication methods have triggered numerous recommendations for technological applications of VO$_2$, such as, thermally activated optical switching and limiting,$^7,^8$ thermal relays and energy management devices,$^9,^{10}$ sensors and actuators,$^{11}$ micro-bolometers,$^{12,13}$ electrochromic and photochromic memory and optical devices.$^{14,15}$ Two and three terminal devices utilizing the electric field induced switching of VO$_2$ is also an active area of research.$^{16}$ A recent study$^{17}$ has found that, materials synthesis, especially the VO$_2$/gate dielectric interface, plays an immensely important role in the response to the gate voltage, and thus controls the functioning of such electrically controlled devices.

Fig. 2.1 Hysteresis curves showing change in resistance (left) and reflection (right) as a function of temperature during phase transition in VO$_2$.\textsuperscript{6}
Fig. 2.2 shows the phase diagram for the vanadium-oxygen system. It can be seen that there are as many as 15 to 20 other stable vanadium oxide phases, such as, $\text{V}_6\text{O}_9$, $\text{V}_6\text{O}_{13}$, $\text{V}_7\text{O}_{13}$ and others that exhibit no semiconductor-to-metal transitions. The existence of these stable competing oxides presents a particular challenge to the growth of VO$_2$ in both, bulk and thin film form. Therefore, to achieve optimum SMT characteristics, an elaborate synthesis procedure is required to ensure the formation of VO$_2$ and to avoid other undesirable vanadium oxide phases.

![Fig. 2.2 Phase diagram of the V-O system.](image)
2.1.1 Structural characteristics of VO$_2$

The subtle interplay between atomic structure, charge, spin and orbital dynamics is responsible for the phase transition observed in VO$_2$. A delicate balance of cooperative interactions of the crystal structure and electronic degrees of freedom drives it into a critical regime where it undergoes a first-order transition from a low-temperature semiconducting phase to a high temperature metallic phase at $T_c = 340K$. In this case, changes in the electronic band structure are associated with atomic rearrangement between a high-T, more symmetric tetragonal/rutile (P42/mnm) phase to low-T less symmetric monoclinic (P21/c) phase due to dimerization of the V atoms.\textsuperscript{2} The characteristic feature of this monoclinic phase is the presence of the cation-cation pairs along the $a_m = 2c_r$ axis, leading to the doubling of the unit cell, alternate V-V separations being 2.65Å and 3.12Å rather than the regular 2.87Å spacing in the tetragonal phase. This is accompanied by a slight tilting with respect to the $c_r$-axis to give one shortest vanadium-oxygen separation $R_{VO} = 1.76Å$ perpendicular to the $c_r$ axis, the other cation-anion distances being $\sim 2Å$. The displacement of a cation toward one or more anions is characteristic of a ferroelectric distortion. Thus the driving mechanism responsible for this transition is an anti-ferroelectric one.

The electronic structure of VO$_2$ was explained qualitatively long ago by Goodenough. In the rutile structure (space group P4$_2$/mmn), the V atoms are surrounded by O octahedral forming an edge-sharing chain along the $c$ axis. The d-levels of the V ions are split into lower lying $t_{2g}$ states and $e_g$ states (Fig. 2.3 and 2.4). The latter lie higher in energy and are empty.
The tetragonal crystal field splits the $t_{2g}$ multiplet into an $a_{1g}$ (dII) state and an $e_{g}^{\pi*}$ ($\pi^*$) doublet. The $a_{1g}$ orbitals are directed along the c axis, with strong bonding of the V-V pair along this direction. In the monoclinic phase (space group P2$_1$/c), the dimerization and tilting of the V-V pairs result in two important effects. First, the $a_{1g}$ band is split into a lower-energy bonding combination and a higher-energy antibonding one. Second, the V$_d$-O$_p$ antibonding $e_{g}^{\pi}$ states are pushed higher in energy, due to the tilting of the pairs increasing the overlap of these states with O states. Thus, in this picture, the single d electron occupies the $a_{1g}$-bonding combination, resulting in a (Peierls-like) band gap.

---

Fig. 2.3 Schematic delineation of electron band structure of tetragonal and monoclinic VO$_2$.\(^6\)
2.1.2 The nature of the insulating state

The origin of the SMT in VO$_2$ is a subject of a debate. Two main mechanisms of the MIT have been suggested in literature. In the Peierls model, the lattice transformation at the structural phase transition temperature ($T_{SPT} \sim 66$ °C) is accompanied by the band structure changes that result in the opening of the band gap and, consequently, the SMT. In this scenario the material is referred to as band insulator. In the Mott transition model, electron correlations alone cause the transition to the insulating state, while the ion arrangement and lattice-electron interactions are of secondary importance to the SMT. If electron-electron correlations are considered to be primarily responsible for the insulating state of VO$_2$, the material is often referred to as Mott or Mott-Hubbard insulator, even though current models go generally beyond the standard Mott-Hubbard picture.
The understanding of the electronic ground state was considerably improved after the studies of Cr-doped VO$_2$ alloys. Cr enters the V sites as 3C ions. The resulting alloy, V$_{1-x}$Cr$_x$O$_2$, also exhibits a metal-insulator transition close to the T$_{SMT}$ of pure VO$_2$ with Cr doping in the range $x = 0$-0.045. However the V$_{1-x}$Cr$_x$O$_2$ alloy has three different lattice structures, labeled as M$_1$, T, and M$_2$, in the insulating phase depending on the temperature and Cr doping level. M$_1$ lattice corresponds to the pure VO$_2$ lattice in the insulating state. T and M$_2$ are two new insulating phases. M$_2$ is a monoclinic lattice which is different from M$_1$ in that only half of the vertical (along c-axis) V-V chains are dimerized, i.e., V ions are displaced in the lateral (perpendicular to c-axis) direction so that the resulting vertical V chains have a zigzag pattern (Fig. 2.5). The other half of vertical V chains in M$_2$ remain straight (undistorted) as it is in the metallic tetragonal phase. T is believed to be a triclinic lattice and is a transitional phase between M$_1$ and M$_2$. Uniaxial pressure applied to pure VO$_2$ can also give rise to M$_2$ and T phases and leads to the phase diagram similar to the V$_{1-x}$Cr$_x$O$_2$ alloys. The study of electrical properties of M$_2$ and T showed that the conductivity changes only by 25% between the phases and both phases exhibit the same activation energy of 0.4 eV that is close to the activation energy in pure VO$_2$, 0.45 eV. Since the three phases, M$_1$, T, and M$_2$, have very different lattice structures, the similarity of electrical properties of the three phases (the existence of SMT, similar activation energies and conductivity values) indicates strongly that the lattice transformation at the phase transition is not the primary cause of the SMT. This conclusion led to substantiating the electron correlation models, such a Mott-Hubbard model, as the appropriate description of the SMT in VO$_2$. 
However the dispute on the primary mechanism of the SMT remained unresolved. Convincing evidence in favor of the band-like character (Peierls insulator) of VO$_2$ was given by LDA calculations of Wentzcovitch et al. showing that band theory can account for the low temperature monoclinic distorted state. First principles calculations of Wentzcovitch et al. employed an ab initio molecular dynamics scheme with variable cell shape to perform
unconstrained structural searches for the ground state within the 13-dimensional parameter space of the low-T phase. The result was the stable monoclinic $M_1$ phase with lattice parameters in good agreement with experimental data. The fact that the calculation failed to reproduce the band gap opening was not considered to be discouraging, since local density approximation was notorious for underestimation of the measured optical band gaps.

Support to the band-like character of insulating VO$_2$ came also from experimental studies. Cavalleri et al. applied ultrafast spectroscopy to establish time domain hierarchy between structural and electronic effects in VO$_2$. In the pump-probe reflectivity experiments conducted by Cavalleri et al. the MIT in thin films of VO$_2$ was induced by short optical pulses and the dynamics of the reflectivity change due to SMT was measured with femtosecond resolution. It was shown that the transition time can be brought down to 80 fs but not less (“structural bottleneck”), even though much shorter time, 15 fs, was expected if the SMT were due to pure electronic effects. The femtosecond time scale of the transition excluded the lattice temperature effects. The existence of the structural bottleneck was explained by the arguments that the collapse of the band gap was due to the structural motion brought about by optical phonons. Thus the atomic arrangement of the high-T unit cell was believed to be necessary for the formation of the metallic phase of VO$_2$. 

2.1.3 Thermodynamic model for phase transition in VO$_2$

Following details are after the phenomenological thermodynamic model given by Narayan et al. The change in Gibbs free energy associated with phase transition, $\Delta G_r$, can be derived to be equal to $\Delta G_r = \Delta T_r \Delta S_0$, where $\Delta T_r$ is the deviation from the equilibrium transition temperature, and $\Delta S_0$ is change in entropy between the two phases. On the basis of the nucleation model, the critical size ($r_c$) of stable nuclei was be derived as $r_c = 2\gamma / (\Delta T_r \Delta S_0)$, where $\gamma$ is the interfacial energy.$^4$ It is known that tetragonal to monoclinic phase transformation in VO$_2$ is reversible and is ultrafast with time scale on the order of picoseconds. To model the phase transition, it was envisaged that a single coordinated atomic jump can accomplish monoclinic to tetragonal (M↔T) and reverse structural phase transition. Using these concepts, the rate or velocity of phase transition was derived as $(V) = \lambda \nu_D (\Delta T_r \Delta S_0 / kT_r) \exp(-\Phi / kT)$, where, $\lambda$ is jump distance, $\nu_D$ is Debye frequency, and $\Phi$ is the activation barrier. The activation barrier is about $kT_r$, where $k$ is the Boltzmann constant and $T_r$ is the transition temperature. Assuming $\lambda \approx 1\text{Å}$, $\nu_D \approx 10^{12}\text{s}^{-1}$, and $\Phi \approx kT_r$, transformation velocity $V$ was estimated to be about $40\text{ ms}^{-1}(2)$. Using time-resolved, near-edge x-ray absorption measurements of the SMT (M↔T) transition, Cavalleri et al estimated these velocities in thin films, which were found to be in a good agreement with the model.$^2$ In addition, the experimental results of others$^{3,20}$ were found to be consistent with the projections of the model.
Based upon this model, $\Delta T$, $\Delta A$ and $\Delta H$ were predicted for different microstructures under the following four film microstructures:

1. Single-crystal films: (a) for high-quality films (large-grains separated by low-angle less than 1 degree), the model predicts sharp transition (small $\Delta T$) with a large amplitude ($\Delta A$) and negligible hysteresis (very small $\Delta H$); (b) for poor-quality films (small grains with high defect content, but still separated by low-angle less than 1 degree), the model predicts larger transition width without much hysteresis. The transition width can be controlled by defect content, and hysteresis width ($\Delta H$) can be kept to a minimum by having low-angle boundaries. For sensor applications, this is the most desirable microstructure.

2. Textured polycrystalline films: (a) small-angle boundary textured - This will be similar to 1(a) but with a finite $\Delta T$, and $\Delta H$ will increase with the misorientation of small-angle boundaries.; (b) large-angle boundary textured - As the boundary misorientation increases, $\Delta H$ will continue to increase.

3. Random polycrystalline films (formed on amorphous substrate or nucleated from amorphous phase): large-angle random boundaries (a) small grains - Small random grain materials will exhibit larger $\Delta T$ and $\Delta H$ with a smaller amplitude ($\Delta A$); (b) large grains - As the grain size increases, the $\Delta T$ decreases as the bulk defect density decreases, however, $\Delta H$ will stay constant or even increase with increasing grain
boundary misorientation. This microstructure will be suitable for memory device applications.

4. Amorphous films - We can predict the properties of amorphous films through the equation: \( \Delta T_r = 2\gamma/(r_c \Delta S_0) \). In amorphous films, \( \gamma \), \( r_c \) and \( \Delta S_0 \) all tend to zero, which makes \( \Delta T_r \) or hysteresis to approach to zero. Thus, for those devices where reliability is critical, amorphous films can be used although it means sacrificing sensitivity and efficiency. In the case of amorphous films, the SMT transition is predicted to be large with a minimum of hysteresis, i.e., large \( \Delta T \) and very small \( \Delta H \). The amplitude of transition will be smaller due to higher defect content. The absence of grain boundaries in amorphous films reduces \( \Delta H \) because the propagation of transition phase boundary upon heating and cooling remains symmetric. This transition in amorphous films is of second order and is less of a structural nature, i.e., pairing of V atoms, unit cell doubling, and charge ordering are of less relevance. Amorphous characteristics emphasize the importance of Coulomb effects as the electrons diffuse more slowly and interact more strongly.

For sensor applications, high efficiency and high sensitivity require films with large \( \Delta T \) and \( \Delta A \), and a negligible \( \Delta H \), therefore, microstructures similar to 1(a) or 2(a) are suited. This can be accomplished on single-crystal substrates via domain matching epitaxy or by inducing textured growth on polycrystalline substrates. The key considerations are related to control of overall defect content and characteristics of grain boundaries. Amorphous films, on the other
hand, provide high reliability (negligible $\Delta H$), but reduced efficiency and sensitivity. For memory applications, which require large $\Delta H$, microstructure similar to 3(b) would be suitable.

2.1.4 Applications of VO$_2$ thin films

VO$_2$ belongs to the class of “smart materials”, which generally react to temperature variations, electric or magnetic fields and/or pressure variations and have capabilities of sensing, actuating and switching, relying on an intrinsic property of the material. Thin films and nanoparticles of VO$_2$ tend to survive the stress generated during repeated cycles of phase transition better than bulk crystals and are therefore suited for many device applications. The large change in resistivity and transmittance/reflectivity during the semiconductor-to-metal (SMT) transition for VO$_2$ occurs closer to room temperature than any other commonly-known compound and can also be conveniently depressed to about room temperature by doping. The metal-insulator transition in VO$_2$ has triggered numerous suggestions and their subsequent realizations for technological applications. These include thermally activated VO$_2$ thin films and nanoparticles for optical switching and beam limiting, resistive switching, thermal relays and energy management devices such as solar cells and smart window coatings; and sensors and actuators. It is also being used in optical computing, variable reflectivity mirrors, light modulators, holographic recording media, high-speed solid-state optical displays and in a variety of other modulation, polarization and control
functions such as real-time coherent optical data processors and fast, random access scan laser. VO₂ has also been used as the channel layer in field-effect transistors in effort to produce Mott transisitors. VO₂ thin films also have potential applications in the millimeter-wave and microwave portions of the electromagnetic spectrum. Applications for VO₂ nanoparticles, with their plasmonic response in the vicinity of the near-infrared communications wavelengths, ferroelasticity and negative mechanical stiffness, have an even greater range of potential applications that are only beginning to be explored. VO₂ single-crystalline nanobeams have lately opened up a whole new possibility of using switching nanowires with enhanced mechanical strength and stress-resistance. A gas sensor application utilizing the metal-insulator transition in VO₂ has also been realized recently.

2.2 Thin Film Epitaxy

Epitaxy, which represents an important concept observed in thin films, has its roots in two ancient Greek words ε π ι (epi - placed or resting upon) and τ α ξ ι ξ (taxis - arrangement). In the context of thin films, epitaxy refers to the formation of an extended single-crystalline film on top of a crystalline substrate. The actual word epitaxy was introduced into the literature by the French mineralogist L. Royer in 1928, although it was probably observed in alkali ihalide crystal over a century ago. Epitaxy can largely be categorized in two forms: homoepitaxy and heteroepitaxy. In homeepitaxy, the films and the substrate are the same material. Epitaxial Si (or epi-Si) deposited on Si wafers using vapor-phase epitaxy (VPE) is the most
common example of homoepitaxy. The second type of epitaxy is known as heteroepitaxy in which films and substrates are different materials, e.g. Germanium on Silicon or Zinc oxide (or Gallium nitride) on Sapphire (Al\(_2\)O\(_3\)) substrates. It is heteroepitaxy which is technologically of utmost importance since it allows the growth of novel materials and devices in form of epitaxial thin films on commonly available substrate systems. For example, compound semiconductor heteroepitaxial film structures have application in optoelectronic devices such as light-emitting diodes and lasers. Since the film and the substrate materials are different in heteroepitaxy, the properties of heteroepitaxial films are influenced by the crystallographic properties of the substrate and the film, difference in film and substrate chemistry, and the difference in film and substrate thermal expansion coefficients. The lattice misfit between substrate and film is the key parameters which controls growth, morphology, and the properties of the film. The lattice misfit is defined as:

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

(2-1)

2.2.1 Lattice Matching Epitaxy

In lattice matching epitaxy, one-to-one matching of the lattice parameters (matching of unit cells) of the film and substrate occurs across the interface. This matching of lattice parameters takes place by means of strain in the films as the films grows pseudomorphically,
initially. The pseudomorphic growth of the film continues until a “critical thickness” is reached. At this point, strain energy becomes large enough to trigger the nucleation of dislocation to relax the strain. These dislocations are nucleated at the film surface and must glide to the interface to relieve the strain in the film. A schematic illustration of lattice matching epitaxy is presented in Fig. 2.6. The critical thickness at which dislocation nucleation occurs is directly related to the misfit. In low misfit systems the critical thickness for dislocation nucleation may be quite large and dislocation nucleation and therefore, strain relaxation may not be possible. Also, the obstacles to the glide of dislocations often results in a high threading dislocation density in the films, which is detrimental to the devices as these dislocations act as charge carrier trap or recombination centers.

Fig. 2.6 Schematic representation of lattice matching epitaxy, $d_c$ denoted the critical thickness.
2.3 Domain Matching Epitaxy

Conventional lattice matching epitaxy during thin film growth is possible as long as the lattice misfit, defined as $f$ earlier, between the film and the substrate is less than 7-8%. Above this misfit, it was expected that the films can grow only as textures or largely polycrystalline. However, it was observed that the epitaxial growth can occur in large misfit systems, such as TiN/Si etc., as well. Since the strain relaxation occurs by dislocations which are essentially an extra plane or a missing plane, the epitaxial growth in large misfit systems can be explained by considering the matching of lattice planes in the concept domain matching epitaxy (DME), proposed by Narayan et.al.\textsuperscript{5} In the domain matching epitaxy, we consider the matching of lattice planes, which could be different in different direction of the film-substrate interface. This is in contrast to the lattice matching epitaxy where one-to-one matching of lattice constants occurs, across the film-substrate interface. An important feature of the domain matching epitaxy is that the most of the strain is relieved quickly within a couple of monolayers, so that the misfit strain and dislocations can be engineered and confined near the film-substrate interface. Nucleation of the dislocations in first couple of monolayers makes it possible for the rest of the film to be grown free of defects and lattice strains. In DME misfit is accommodated by matching of integral multiple of lattice plane, and there is an extra half plane (dislocation) corresponding to each domain (Fig. 2.7). If the misfit falls in between the perfect matching ratios of planes, then the size of the domain can vary in a systematic way to accommodate the additional misfit.

24
The matching of m planes of the film with n planes of substrate will lead to a residual strain of \( \varepsilon_r = \frac{md_f}{nd_s} - 1 \), where m and n are simple integers and \( d_f \) and \( d_s \) are the interplanar spacing of the film and the substrate, respectively. In case of perfect matching, residual strain is zero and \( md_f = nd_s \). If \( \varepsilon_r \) is finite, then two domains may alternate with a certain frequency to provide for a perfect matching according to:

\[
(m+\alpha) d_f = (n+\alpha) d_s
\]  

(2-2)

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

Fig. 2.7 Schematic illustration of domain matching epitaxy (DME), in which four lattice planes of film match with five lattice planes of substrate.
Since the concept of DME was first proposed, it has been shown to be important for growing thin heterostructures with large lattice misfit. Some typical examples for the DME growth are TiN/Si (100) heterostructures, III-nitride epitaxy on Si (111), and ZnO and III-nitrides on sapphire (0001). The growth of high quality ZnO (having wurtzite hexagonal structure, \(a = 3.252 \text{ Å}, \ c = 5.213 \text{ Å}\)) on a practical substrate such as sapphire \((a = 4.758 \text{ Å}, \ c = 12.991 \text{ Å})\) presents a major challenge. However, the epitaxial growth of high quality of ZnO has been accomplished by DME. Fig. 2.8 (a) shows a HRTEM image of the ZnO/Sapphire interface grown by pulsed laser deposition. It is taken in the Sapphire [2\(\overline{2}\)0] zone axis. Fig. 2.8 (b) shows a Fourier-filtered image from which it is seen that, 5 or 6 [2\(\overline{2}\)0] planes of ZnO match with 6 or 7 [0\(\overline{1}\)0] planes of sapphire. The epitaxial relations derived from a corresponding diffraction pattern shown in Fig. 2.8 (c) are ZnO [0\(\overline{1}\)0] \(\parallel\) Sapphire [2\(\overline{2}\)0] and ZnO (0001) \(\parallel\) Sapphire (0001). From these epitaxial relations it is also deduced that, the c-plane of ZnO is rotated by 30° or 90° with respect to basal plane of Sapphire as shown in Fig. 2.8 (d). The misfit between the films and the substrate can be analyzed as follows: \(a_{\text{ZnO}}\) planes of ZnO match with the \((a/\sqrt{3})\) planes of sapphire. We can see that \(5.5.a (\text{ZnO}) \approx 6.5 \text{ a (Al}_2\text{O}_3)\) for \(\alpha = 0.5\). From this analysis, we get a planar misfit of about 15.4% which can be relaxed by 5/6 and 6/7 plane matching. Thus with DME, it is possible to grow thin films of material system that have small as well as large misfit with substrates. When the misfits are not perfectly accommodated, there is a periodic variation of the domain sizes to accommodate for the residual misfit. Also, as the domain size changes, the nature of the dislocations remains the same. Typically in systems like ZnO/sapphire, the critical thickness is only a couple of
monolayers. Beyond that thickness the subsequent monolayers continue to grow fully relaxed. Thus DME can be utilized to grow films with very low concentration of defects in the active device region.

Fig. 2.8 (a) ZnO/Sapphire interface (b) Fourier filtered image showing DME (c) selected area electron diffraction pattern of ZnO/Sapphire interface (d) schematic plan view of the epitaxy. \(^{28}\)
2.4 Substrate and buffer layer materials

2.4.1 Silicon

Silicon is a group VI elemental semiconductor. Most of the commercial electronic devices are currently based on silicon. Owing to the natural abundance and large scale industrial use, silicon substrates are widely and cheaply available. Hence the integration of new functional materials with silicon substrate offers unique technological advantage. Silicon has a diamond-cubic crystal structure with lattice constant of 5.431 Å (Fig. 2.9). The thermal expansion coefficient of Silicon is \( \sim 2.6 \times 10^{-6} \text{ K}^{-1} \). The band gap of silicon is \( \sim 1.12 \text{ eV} \) at room temperature.

![Diamond cubic crystal structure of Silicon](image-url)
Silicon substrates are available in large sizes (up to 400 mm diameter). Both n-type and p-type silicon substrates with different doping concentration are available. One of the biggest challenges in integrating oxide materials with silicon is the tendency of silicon to readily form an amorphous silicon dioxide oxide (SiO$_2$) layer.

2.4.2 Yttria stabilized zirconia (YSZ)

Yttria-stabilized zirconia (YSZ) is an attractive buffer layer for the subsequent growth of numerous oxide materials on non-oxide substrates. YSZ has a high dielectric constant (~25) and large bandgap (7.8 eV). YSZ has excellent chemical stability on silicon. The free energy of formation of ZrO$_2$ ($\Delta G$ (800 K) = −941.6 kJ kmol$^{-1}$) is smaller than that of SiO$_2$ ($\Delta G$ (800 K) = −734.2 kJ kmol$^{-1}$). The thermal expansion coefficient of YSZ is ~ 11.4 x 10$^{-6}$ K$^{-1}$.

Crystal structure of YSZ is dependent on the yttria content. Pure zirconia (ZrO$_2$) is monoclinic. When doped with 3-5 mol % yttria, the tetragonal phase of zirconia is stabilized at room temperature. Lattice parameters of tetragonal YSZ (space group P4$_2$/nmc) are a = 3.6067 Å, c= 5.1758 Å (for 3 mol % Y$_2$O$_3$ doped ZrO$_2$). A unit cell of tetragonal YSZ is shown in Fig. 2.10 (left). Yttria content of 8 mol % or higher makes cubic phase of zirconia stable at room temperature. Cubic YSZ crystallizes in a fluorite-type structure (space group Fm$\bar{3}$m) with a lattice parameter ~5.1289 Å (for 15 mol % Y$_2$O$_3$ doped ZrO$_2$). A unit cell of tetragonal YSZ is shown in Fig. 2.10 right).
**Fig. 2.10** Crystal structure of tetragonal (left) and cubic (right) YSZ. Oxygen atoms are shown in red color while (Zr, Y) atoms are shown in green color.

### 2.4.3 Nickel oxide (NiO)

Nickel oxide has a cubic rock salt (NaCl) structure (Fig. 2.11). This structure belongs to the space group Fm\̅3m. The lattice constants of NiO cubic unit cell is \(a = 4.178\ \text{Å}\). NiO is an insulator with an optically measured band gap of 4 eV.\(^6\) The thermal expansion coefficient of NiO is \(2.1 \times 10^{-5}\ \text{K}^{-1}\).

The use of NiO as a buffer also holds significant technological importance as NiO is a p-type semiconductor whose conductivity can be controlled by varying the deposition conditions,
such as oxygen partial pressure during growth or by doping with monovalent cations, such as Li$^+$. While NiO, in its undoped stoichiometric form, exhibits a very high electrical resistivity of $\sim 10^{13}$ ohm-cm, values as low as $\sim 0.15$ ohm-cm can be achieved by doping with monovalent cations, such as Li$^+$ or by introducing non-stoichiometry (NiO$_x$).\textsuperscript{22,27}

Fig. 2.11 Crystal structure of NiO. Oxygen (bigger) atoms are shown in red color while Ni (smaller) atoms are shown in black color.
2.5 References


Chapter 3. Experimental techniques

In this chapter, experimental methods employed to fabricate VO$_2$ thin film heterostructures and to modify and characterize these heterostructures have been discussed. All the thin films in the present study were fabricated using pulsed laser deposition technique. The structural characterization of the thin film heterostructures was performed by X-ray diffraction (out-of-plane and in-plane) and transmission electron microscopy. To investigate the semiconductor-to-metal transition characteristics electrical resistance measurements were performed as a function of temperature where samples was glued to a evacuated copper stage with controlled heating. To further support our results from electrical measurements, infra-red transmission spectroscopy was performed. Detailed chemical studies using X-ray photoelectron spectroscopy were performed to establish the role of non-stoichiometric defects in SMT characteristics of VO$_2$ based thin film heterostructures. Also, to further illustrate the role of non-stoichiometry on structural properties of the VO$_2$ thin films Raman spectroscopy studies were done. Only brief description of the relevant experimental techniques is given in this chapter. Further details on these techniques are available in the references provided at the end of the chapter.
3.1 Substrate preparation

In the present study Si (100) was used for thin film growth. Substrates were 300-500 μm thick. Over the time of storage, organic impurities and dust particles that stick on the substrate surface may hamper nucleation and epitaxial growth of the thin films on these substrates. Hence cleaning of the substrates was necessary prior to their loading into thin film deposition chamber. The substrates were degreased and agitated for 10 minutes to remove dust particles in an ultrasonic bath using acetone. Subsequently, substrates were rinsed and vapors cleaned in acetone and then with methanol to further remove the organic impurities. Finally, substrates were dried by blowing high purity nitrogen. After cleaning, substrates were immediately loaded into the pulsed laser deposition chamber. The substrates were mounted on the substrate heater using a fast drying silver paste for a good thermal contact.

3.2 Pulsed laser deposition (PLD)

In the research work reported in this dissertation, all the thin film heterostructures were deposited using Pulsed laser deposition (PLD) technique. PLD has been widely used to synthesize a variety of high quality thin films of metals, oxides and nitrides. PLD is a versatile non-equilibrium thin film growth technique based on physical vapor deposition. In this technique, a high-powered laser is focused to vaporize the material to be deposited, referred to as the target. The interaction of the target material with the laser leads to localized evaporation of the material and the formation of a highly energetic plasma. This phenomenon is frequently referred to
as laser ablation. The ablated material is ejected in a direction normal to the target surface in the form of a plume. The material in this plume is deposited on the substrate which is usually heated.

The PLD system consists of three main components; the laser, the vacuum chamber and the optics that control the laser. The schematic diagram of the PLD system used in the present study is shown in Fig. 3.1. The peak power of most commercial lasers is inversely correlated with the duration of the laser pulse. Since ablation of most materials requires very high energy densities, typically nanosecond, and sometimes femtosecond, lasers are used for pulsed laser deposition. The term LASER stands for light amplification by stimulated emission of radiation. A laser emits coherent light, with a well-defined wavelength, in a narrow low divergent beam. Hence, lasers can be focused and directed effectively to be used for material processing. The most important lasers used for PLD are the Nd:YAG and the excimer laser. Nd:YAG is a solid state neodymium doped yttrium aluminum garnet laser. The fundamental frequency for this laser is 1064 nm. But these lasers can be doubled, tripled or quadrupled to produce 532 nm, 355 nm and 262 nm wavelengths. Excimer lasers are most commonly used for pulsed laser deposition due to the fact that these lasers can deliver high energy densities with high energy photons. The emission wavelength of excimer lasers depends on the composition of the gas that is used in the laser cavity. ArF (193 nm) and KrF (248 nm) excimer lasers are most commonly used for pulsed laser deposition. Various excimer lasers with their corresponding wavelengths are listed in Tab. 3.1. The term excimer is a short form of excited dimer. In these systems lasing action is possible due the population
inversion that develops between a bound excited state and a repulsive ground state. The excited state is formed from the inert gas (Kr) that forms temporarily bound molecules either with themselves or the halide (KrF). The excited state is usually induced by an electric discharge. The excited state then gives up its energy via stimulated emission to form the dissociated ground state molecules. This happens very rapidly (within picoseconds), resulting in a population inversion between the excited and ground state molecules. The lasing equations for a KrF excimer laser are shown below.
\[ 2\text{Kr}_\text{(g)} + F_2\text{(g)} \rightarrow 2\text{KrF}_\text{(g)} \quad \text{(excited state)} \quad (3-1) \]

\[ 2\text{KrF}_\text{(g)} \rightarrow 2\text{Kr}_\text{(g)} + F_2\text{(g)} + \text{energy} \quad \text{(dissociated state)} \quad (3-2) \]

Tab. 3.1 Operating wavelengths of various excimer lasers

<table>
<thead>
<tr>
<th>Excimer Laser</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(_2)</td>
<td>157</td>
</tr>
<tr>
<td>ArF</td>
<td>193</td>
</tr>
<tr>
<td>KrCl</td>
<td>222</td>
</tr>
<tr>
<td>KrF</td>
<td>248</td>
</tr>
<tr>
<td>Cl(_2)</td>
<td>259</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
</tr>
<tr>
<td>XeF</td>
<td>351</td>
</tr>
</tbody>
</table>

3.2.1 Physics of the laser-solid interaction

Although the start-up cost for a PLD system is low and it is easy to build and operate, the underlying physics involving the laser-solid interaction and creation/expansion of the plasma is a complicated process. At energy densities above the threshold for vaporization the laser-solid interaction was analyzed and modeled by Singh et. al.\(^2\,^3\) Depending upon the interaction
of the laser with the target material, Singh et. al. divided the laser ablation process into three importance regimes.\textsuperscript{3,9}

1. In the evaporation regime, interaction of the laser beam with the target material results in evaporation of the surface layers.

2. When the laser beam interacts with the evaporated material, it results in the formation of a high-temperature isothermal expanding plasma plume. This process regime starts when the target starts to evaporate and continues until the end of the pulse.

3. At the termination of the laser pulse, another regime starts in which the anisotropic three-dimensional adiabatic expansion of the plume takes place giving rise to the characteristics forward nature of the deposition.

Each of these regimes is discussed below in brief.

3.2.1.1 Laser target interaction

When a laser beam strikes the target, the electromagnetic energy is used to excite free electrons in the target material. The thermal energy generated by the electron-phonon coupling then evaporates the target material. It is important to realize that the reaction time for this process to occur is on the order of picoseconds.\textsuperscript{1,3} In order to have better laser-solid coupling the target must be suitably prepared. A target with high roughness, low reflectivity
(R) and high absorption coefficient ($\alpha_t$) allows for efficient laser-solid coupling and thus provides low threshold energy for vaporization. Depending on the laser wavelength and the porosity and surface roughness of the target, typical values of threshold energy vary from 0.11 to 0.40 J/cm$^2$. It is important to realize that the energy deposited by the laser beam comprises, the energy required to evaporate the target material, conduction heat loss in the target and energy loss due to laser absorption by the expanding plasma. Using these concepts of energy balance, the thickness of the target for which evaporation ($\Delta X_t$) takes place can be calculated as,$^{10-15}$

$$\Delta X_t = (1-R) \left( E - E_{th} \right) / \left( \Delta H + C_v \Delta T \right)$$  (3-3)

Where R is the reflectivity, $E_{th}$ is the threshold energy, $\Delta H$ is the latent heat, $C_v$ is the volume heat capacity and $\Delta T$ is the maximum rise in temperature. It is important to realize that this equation is valid when the thermal diffusion length $(2Dt)^{0.5}$ is larger than the light penetration depth $(L = 1/\alpha_t)$. Here D is the thermal diffusion constant and t is the pulse duration of the laser. This validation is true for most metallic and semiconducting targets. However, for low thermal diffusivity materials (non-metallic targets), i.e. $(2Dt)^{0.5} < 1/\alpha_t$ a second regime is
relevant. Here, thermal diffusivity does not play an important role and evaporation depth mainly depends on the attenuation distance of the laser beam.\textsuperscript{1,9}

3.2.1.2 Plasma formation and initial isothermal expansion:

The laser interaction with the target material yields surface temperatures in the range of 2000-3200 K.\textsuperscript{3,9} This results in the emission of positive ions and electrons from the free surface. Generally, the ablation of the target is accompanied by the formation of a plasma (bright glow) extending normal to the target surface. The plasma contains charged and neutral species of atoms and molecules. The plasma also interacts with the incoming laser; this produces temperatures higher than the vaporization temperature in the plasma. The absorption of laser energy by the plasma occurs due to electron-ion collisions. This absorption primarily occurs by an inverse Bremsstrahlung process that involves absorption of a photon by a free electron.\textsuperscript{2} The absorption coefficient ($\alpha_p$) of the plasma is given as,\textsuperscript{3}

$$\alpha_p = 3.69 \times 10^{8} \left( \frac{Z}{n_i} \right)^2 \frac{2}{T^{0.5}} \nu^3 \left[ 1 - \exp(-h\nu/KT) \right] \quad (3-4)$$

Where, $Z$ is the average charge, $n_i$ is the ion density, $T$ is the temperature of the plasma, $h$ is Plank's constant, $K$ is the Boltzmann constant and $\nu$ is the free energy of the laser light. Since
the absorption coefficient \( (\alpha_p) \) is proportional to \( n_i^2 \), the laser light is heavily absorbed close to the target surface, where the density of the ionized species is high. In comparison the leading edge of the plume, is associated with high expansion velocities and low electron and ion densities. Hence, the outer edge of the plasma is transparent to the laser beam. The \([1 - \exp(-\hbar \nu / KT)]\) term takes into account the losses that occur due to stimulated emission depending upon the plasma temperature and laser wavelength.\(^3\) A variety of processes such as impact ionization, photo ionization, thermal ionization and electronic ionization effect the extent of ionization of the laser generated species.

Fig. 3.2 is a schematic that shows the different regimes that are present during the laser-solid interaction.\(^3\) Region A is the unaffected bulk target and B is the thickness of the target material that is evaporated. Region C is the plasma region close to the target that absorbs the laser heavily. In this region, evaporated particles are continuously injected into the plasma. Region D depicts the outer region of the plasma that expands rapidly. In the region near the target surface, a dynamic self-regulating equilibrium exists between the plasma absorption coefficient and the rapid transfer of thermal energy into kinetic energy (due to injection of evaporated particles of the target into the plume). These compensating mechanisms govern the isothermal temperature attained by the plasma near the target surface.

Singh et. al. have come up with expressions that determine the variation of density, pressure and velocity along the direction perpendicular to the target surface. It should be noted that the direction perpendicular to the target surface is the x direction. It is clear from the figure that
the density of particles is a maximum in the near-target regions, where as the velocity is minimum. The particle density in the plasma in the near surface regions can be approximated as a Gaussian. It has also been observed that the initial dimensions of the plasma are larger in the transverse direction when compared to the longitudinal direction. During the initial stages the velocity is low and acceleration is relatively high. After a while, when the expansion velocity increases, the acceleration decreases and eventually reaches zero. This aspect governs the elongated shape of the plasma.

Fig. 3.2 Schematic illustration showing different regimes during laser irradiation of the target: (A) Bulk target that remains unaffected, (B) Thickness of the target that evaporates, (C) region in which the plasma absorbs the laser and (D) the expanding plasma region that is transparent to the laser.
3.2.1.3 Adiabatic expansion of the plasma:

After the plasma formation and isothermal regime, the plasma plume expands adiabatically into the vacuum. The adiabatic expansion regime initiates after the termination of the laser pulse.\(^3\) It is important to realize that in this regime, there is no injection of particles from the target into the plume and also the laser is no longer being absorbed by the plume. Singh et. al. have developed equations that explain the adiabatic expansion in relation to the dimensions of the plume.\(^3,9\) They have come up with the following inferences. In this regime, the expanding plasma is associated with very high velocities arising from the thermal energy being converted to kinetic energy. The loss in thermal energy leads to a drop in temperature determined by a balance between cooling due to expansion and energy gain due to recombination of ions in the plasma shows a schematic of the developing shape of the plume in the adiabatic regime. The initial dimensions of the plasma are larger in the transverse directions, i.e. in the y and z direction. In the longitudinal x direction the expansion is minimal. The transverse dimensions are in the order of a few millimeters as opposed to 20-100 microns in the longitudinal direction. It is also important to note that the plasma is elliptically shaped with y axis being the major axis (a). During the adiabatic expansion regime, the longitudinal x dimension expands rapidly resulting in the characteristic PLD plume. The plasma pressure drops rapidly until most of the thermal energy is converted to kinetic energy. Then the plume has no more energy for expansion and the plasma elongates in the shorter dimension. Eventually, elliptical shapes are retained but with the z dimension
being the major axis (see Fig 3.3 (b)). This theory was confirmed from the shape of the deposited YBCO film on Si, as shown in Fig 3.3 (c).

Fig. 3.3 (a) Schematic illustration showing the initial elliptical shape of the plasma just after the laser pulse is terminated, (b) Final shape of the plasma when it hits the substrate, (c) Shape of a YBCO film deposited on a Si substrate.
3.2.2 Advantages and disadvantages of PLD

There are several advantages associated with PLD that make it a popular thin film deposition technique. Most advantages arise due to the high energy of the ablated species. The energy of the ablated species can be as high as 10 to 100 eV (i.e. about 100-1000 kT). In comparison, the energy of the ejected species in an evaporation technique (thermal or e-beam) is about 0.1 eV at 1200 K. Listed below are some advantages and salient features of the PLD technique.

1. PLD is a highly non-equilibrium processing technique due to high energy of the plume. Using PLD, complex metastable phases could be formed that would otherwise be difficult to form by typical equilibrium synthesizing routes. For example, L1₀ ordered FePt (superlattice structure) can be synthesized using PLD at a low processing temperature of 500 °C.

2. In case of a multi-component system (like YBCO) the high energy and forward directed nature of the plume helps to reproduce the stoichiometry of the target in the film. Due to the high energy density of the laser, the material removal from the target is so fast that vapor pressures of the individual components do not play a role.

3. The high energy of the plume helps reduce the required processing temperatures to achieve high quality epitaxial films. For example, epitaxial TiN can be grown on Si (100) at 600 °C by PLD. On the other hand CVD growth of TiN requires temperatures as high as 900 °C.
4. Multi-layered heterostructure thin films can easily be synthesized using PLD. The target carousel can be suitably manipulated to hold multiple targets (4 to 6 targets). This means multi-layered films can be deposited without breaking the vacuum.

5. Conceptually, any material can be ablated to form a thin film as long as it has a large enough absorption coefficient for the laser used.¹

6. Depending on the repetition rate of the laser the deposition rate of the film can be controlled. In fact, in PLD the number of nucleation sites can be controlled such that they are much higher than those formed in MBE or sputter deposition. By controlling the impingement rate and increasing nucleation site density the smoothness of the film can be improved.³

7. It is important to realize that in the PLD system the energy source, which is the laser, is placed externally. The vacuum chamber in itself is devoid of filaments and other sources of contamination, thereby resulting in a clean process environment. The interaction between the laser and gas in the vacuum chamber is minimal. This means that the dynamic range of deposition pressures could be high, resulting in less stringent requirements. Also, the spatial confinement of laser-solid interaction and the subsequent plume render PLD a clean process.

8. On the other hand, PLD also suffers from some disadvantages. The area of deposited material obtained by PLD is relatively low (typically 1 cm x 1 cm). In the case of large
substrates, non-uniformity in film thickness is observed due to the forward directed nature \((\cos^n\theta\) type of thickness dependence, where \(n \sim 8-12\)) of the plume. Deposition on larger substrates and uniformity of film thickness can be achieved to some extent by rastering the laser beam over a large target and/or rotation and translation of the substrate. The other drawback of PLD is the formation of chunks during ablation, which can prove to be detrimental to the quality of the film. Chunks are nothing but large (few microns) particulates or globules of molten material. These undesirable chunks are formed due to improper ablation that involves various mechanisms such as subsurface boiling, expulsion of the liquid layer by shock wave recoil and exfoliation.\(^1,3,14\) Chunk control is also possible by increasing the absorption coefficient and thermal conductivity of the target material. A compact target with better cohesion of the grains also reduces the emission of chunks. By careful manipulation of the laser parameters, the size and number of chunks can be minimized to some extent.\(^1,14\)

3.3 X-Ray diffraction

X-ray diffraction (XRD) was used to study the crystal structure and orientation of our samples. This technique also provides information about the phase composition, lattice parameter, grain size and lattice strain. The XRD technique is based on diffraction governed by the Bragg’s law.\(^4\) Diffraction typically occurs when waves interact with a periodic structure. It is important to realize that the wavelength of the wave should be about the same
as the repeat distance of the periodic structure for diffraction to occur.\textsuperscript{15} Inter-atomic distances are of the order of a few angstroms. X-rays have wavelengths of the same order and hence they are used to investigate the crystals. When an X-ray beam is incident on a crystal it interacts with the parallel plane of atoms either constructively or destructively depending upon the path difference. Bragg’s law is satisfied when the waves interfere constructively and the following condition is met.\textsuperscript{15}

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (3-5)

Where \( n \) is an integer indicating the order of reflection, \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the inter-planar spacing and \( \theta \) is the incident angle. In the present work \( \theta \)-2\( \theta \) scans were performed using Rigaku D-MAX/A diffractometer with Cu K\( \alpha \) radiation. This instrument is a two-circle diffractometer in which the sample can be rotated along one of the axis (\( \theta \)-axis) and also the detector can be rotated independently (2\( \theta \)-axis). A schematic diagram for this diffractometer is shown in Fig. 3.4.\textsuperscript{4} This diffractometer is based on Bragg-Brentano parafocusing diffraction geometry. In this geometry, the detector is at 2\( \theta \) and the sample surface is at \( \theta \) angle to the incident beam. The incident beam, normal to sample surface and detector are in the same plane. Since the diffracted beam always lies in the plane containing the incident beam and plane normal, and due to the restricted rotation of the sample only along \( \theta \)-axis, this diffractometer can be used to access diffraction information only from the planes which are parallel to surface of the sample.
Though two-circle diffractometer gives information about the growth orientation, it does not give any information on in-plane orientation of thin film. Knowing in-plane orientation is important to establish epitaxy. The in-plane orientation of thin films can be accessed by four-circle diffractometer. In addition to rotation along θ-axis and 2θ-axis, in four-circle diffractometer the sample can be tilted with respect to the incident beam (ψ-axis) and also rotated 360 degrees around the surface normal (φ-axis). A schematic diagram of four-circle diffractometer is shown in Fig. 3.5. The in-plane epitaxial details can be established by φ-scans. To perform a φ-scan an appropriate crystallographic plane (hkl), which is inclined to
the growth plane (sample surface) is identified. The $\theta$ and $2\theta$ angles are set to corresponding to Bragg angle for the identified plane. The sample tilt, $\psi$ is set equal to the crystallographic angle between the growth plane (sample surface) and the (hkl) plane identified for the $\varphi$-scan. The diffraction intensity is then recorded as a function of sample rotation along $\varphi$-axis.

If the film is epitaxial, the $\varphi$-scan exhibits sharp peaks at certain $\varphi$-angles. On the other hand if the in-plane orientation of the film is random, there is no appreciable variation in the diffraction intensity in the $\varphi$-scan. Another way to assess and represent texture in materials is through pole figures. Pole figures are constructed by combining the data of $\varphi$-scans recorded
at different sample tilts (in the range \( \psi = 0 \) to \( \psi = 90 \) degrees). In the present study the Philips expert system was used to perform \( \phi \)-scans and pole figure measurements. Stereographic projections are very useful in analyzing \( \phi \)-scan data. Stereographic projections can be used to calculate the \( \psi \) and \( \phi \) angles, and also to know the relative position and number of peaks expected in the \( \phi \)-scan for single crystalline materials.

3.4 Transmission electron microscopy

Transmission electron microscope (TEM) utilizes electrons to image materials. Owing to very small de Broglie wavelength of electrons (e.g., \( \lambda = 0.0251 \text{ Å} \) for electrons accelerated through 200 keV), resolutions of the order of 1 Å can be achieved, which makes possible imaging with atomic resolution. Transmission electron microscopes can be operated in two basic modes: imaging and diffraction. In the present study TEM characterization was done to get atomic scale details of interfaces, crystalline defects, grain boundaries and other microstructural features in the deposited films. Selected area electron diffraction (SAED) patterns were also acquired to establish the epitaxial details. Unlike \( \theta-2\theta \) x-ray diffraction scans, SAED patterns can give information about in-plane crystallographic orientation of textured thin films. In-plane orientation of the deposited thin films was established by indexing SAED patterns.
In TEM there are two important systems: (i) the illumination system that controls the electron source (intensity) and (ii) the imaging system that collects the electrons scattered and transmitted from the sample. Depending on the operation mode the electrons collected by the imaging system can either form a diffraction pattern or an image. The corresponding alignment of the electron beam in the two modes is shown in Fig. 3.6. In diffraction mode, the electrons that form the SAED pattern are elastically scattered by the sample. Thus, if the atomic arrangement in the sample is periodic the diffraction pattern consists of well-defined spots, whereas; in case of polycrystalline sample with less atomic order the diffraction results in diffused spots, arcs or even rings. This particular TEM feature is very important and reveals information about the microstructure of the films.

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

Fig. 3.6 A schematic diagram of the beam alignment in the two TEM modes (a) diffraction and (b) imaging mode.\textsuperscript{17}
High resolution TEM (HRTEM) imaging is based on phase contrast and relies on the difference in phase among the electron waves scattered through a thin sample. In contrast to BF or DF imaging, in which a single electron beam is used to form the image, phase-contrast image requires the selection of more than one beam. In HRTEM the objective astigmatism has to be minimized to achieve atomic resolution. Other main requirement for a HRTEM is highly coherent and monochromatic electron beam. The interpretation of contrast in HRTEM images is not easy as it is sensitive to many factors: the appearance of the image varies with small changes in the thickness, orientation, or scattering factor of the specimen, and variations in the focus or astigmatism of the objective lens.

In the present study, a JEOL 2000 FX TEM was used for bright/dark field imaging and electron diffraction. This microscope is equipped with a LaB$_6$ filament and was operated at
200 kV. The high resolution TEM characterization was done using a JEOL 2010 F microscope operated at 200 kV. This microscope is equipped with a field emission gun which provides highly coherent electron beam. This microscope can also be operated in STEM, STEM-Z contrast and EELS spectroscopy modes. Most of the TEM samples were cross section samples. A few plan view samples were also investigated. The electron transparent TEM samples were prepared by mechanical grinding, dimpling and ion milling.

In the present study, a JEOL 2000 FX TEM was used for bright/dark field imaging and electron diffraction. This microscope is equipped with a LaB$_6$ filament and was operated at 200 kV. The high resolution TEM characterization was done using a JEOL 2010 F microscope operated at 200 kV. This microscope is equipped with a field emission gun which provides highly coherent electron beam. This microscope can also be operated in STEM, STEM-Z contrast and EELS spectroscopy modes. Most of the TEM samples were cross section samples. A few plan view samples were also investigated. The electron transparent TEM samples were prepared by mechanical grinding, dimpling and ion milling.

3.5 Four-point probe resistivity measurement

Four-point probe technique has been the preferred method to measure electrical resistivity of both bulk and thin film samples. A schematic of this method is shown in Fig. 3.7. In this method, four probes are made to contact the specimen with known distances between them,
two of which are used to pass a current and the other two are used to measure the voltage drop. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and the specimen material. The sheet resistivity ($\rho$) of the thin films can be calculated using the equation $\rho=(\pi t/\ln2)(V/I)$, where $t$ is the thickness of the film.$^5$

![Fig. 3.7 Schematic presenting a typical four point probe resistivity measurement setup](image)

In the present study the ohmic contacts to the VO$_2$ thin films were made using gold wires attached to the film by freshly cleaved indium pads. The measurements were performed using a self-made labview program employing a Keithley 2400 sourcemeter. The measurements were done typically in a temperature range of 50-370K. The samples were cooled using closed cycle helium cryostat.
3.6 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a quantitative spectroscopic surface chemical analysis technique also known as Electron Spectroscopy for Chemical Analysis (ESCA). It can be used to perform the following surface (up to 10 nm) analysis:

1. Detection of elements (except H and He) with concentrations > 0.1 – 1 %
2. Quantitative analysis of sample composition within a few % (error < 10%)
3. The chemical or oxidation state identification of one or more of the elements in the sample.
4. Measure the uniformity of elemental composition as a function of ion beam etching (depth profiling) – a) non-destructive < 10 nm, b) destructive ~ several hundred nanometers by Ar+ ion sputtering.
5. Measure the uniformity of elemental composition across the top surface (line profiling or mapping) with a lateral resolution of few μm – mm.

In XPS, X-Ray irradiation of a material under ultra-high vacuum (UHV) leads to the emission of electrons from the core orbitals of the surface elements present in the top 10 nm of the material being analyzed. The binding energy of the emitted photoelectron can be determined from the following equation:

\[ h\nu = KE + BE + \Phi_s \]  

(3-5)
where, $h\nu$ is the energy of the incident radiation, $KE$ is the kinetic energy of the photoelectron as measured by the instrument, $BE$ is the binding energy of the orbital from which the electron is ejected, and $\Phi_s$ is the work function of the instrument. The binding energy of the electrons reflects the local environment of the specific surface elements from which they are ejected. Thus, any shift observed in the peak position can be correlated with a change in the oxidation state. The number of electrons reflects the proportion of the specific elements at the surface and in the near surface regions. To count the number of electrons at each $KE$ value, with the minimum error, XPS must be and detected by a complex energy analyzer. In this research, a PHOIBOS 150 analyzer with a resolution better than 1 eV was employed. The photoelectrons passing through the energy analyzer are deflected by the electrostatic field and leave the analyzer at a specific position depending on its energy. XPS analysis was carried out by a SPEC X-ray photoelectron spectrometer using Mg/Al Kα X-ray source. The obtained data were interpreted by using the SDP ver.4.1 software where the C(1s) core level binding energy was set at 285.0 eV, as the reference point.
3.7 References


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


Chapter 4. Enhanced photocatalytic efficiency in zirconia buffered n-NiO/p-NiO single crystalline heterostructures by nanosecond laser treatment

In this chapter, the formation of NiO based single crystalline p-n junctions with enhanced photocatalytic activity induced by pulsed laser irradiation is reported. The NiO epilayers were grown on Si(001) substrates buffered with cubic yttria-stabilized zirconia (c-YSZ) by using pulsed laser deposition. The NiO/c-YSZ/Si heterostructures were subsequently laser treated by 5 pulses of KrF excimer laser (pulse duration = 25×10^{-9} sec.) at lower energies. Microstructural studies, conducted by X-ray diffraction (θ-2θ and φ techniques) and high resolution TEM, showed a cube-on-cube epitaxial relationship at the c-YSZ/Si interface; the epitaxial relationship across the NiO/c-YSZ interface was established as NiO[111]||c-YSZ[001] and in-plane NiO[110]||c-YSZ[100]. Electron microscopy studies showed that the interface between the laser annealed and the pristine region as well as the NiO/c-YSZ interface was atomically sharp and crystallographically continuous. The formation of point defects, namely oxygen vacancies and Ni^0, due to the coupling of the laser photons with the NiO epilayers was confirmed by XPS. The p-type electrical characteristics of the pristine NiO epilayers turned to an n-type behavior and the electrical conductivity was increased by one order of magnitude after laser treatment. Photocatalytic activity of the pristine (p-NiO/c-YSZ/Si) and the laser-annealed (n-NiO/p-NiO/c-YSZ/Si) heterostructures were assessed by
measuring the decomposition rate of 4-chlorophenol under UV light. The photocatalytic reaction rate constants were determined to be 0.0059 and 0.0092 min$^{-1}$ for the as-deposited and the laser-treated samples, respectively. The enhanced photocatalytic efficiency was attributed to the suppressed charge carrier recombination in the NiO based p-n junctions and higher electrical conductivity. Besides, the oxygen vacancies ease the adsorption of 4-chlorophenol, hydroxyl, and water molecules to the surface. Thus, n-NiO/p-NiO single crystalline catalysts can be introduced as a potent candidate to remediate the environmental pollution.

4.1 Introduction

Higher energy consumption, which is a result of increasing world population, gives rise to a decrease in fossil fuel reservoirs and creates of environmental pollution. Arguably, semiconductor mediated photodecomposition of pollutants to non-harmful compounds can be considered as the most promising technique for remediation of environmental pollutants, the mechanism behind which is based on the creation of e$^{-}$-h$^{+}$ pairs upon light-excitation phenomenon.$^{1-3}$ Metal oxides such as TiO$_2$, Ta$_2$O$_3$, WO$_3$, and NiO$^{12-15}$ have exhibited promising photocatalytic characteristics.

Photocatalytic characteristics of nickel oxide (NiO) have not been studied in detail in spite of its interesting properties. NiO crystallizes in a rock salt structure (a=4.176 Å) and exhibits
characteristics of a p-type wide band gap semiconductor ($E_g = 3.6$–$4.0$ eV). Stoichiometric NiO is modeled as a charge transfer insulating material with a resistivity of about $10^{+13}$ $\Omega$.Cm at room temperature. Nickel defects, as core-hole states at nickel sites, lead to extra valence holes and settle primarily at oxygen orbitals near Ni sites. These holes are responsible for the inherent p-type electrical conductivity in pure NiO.\textsuperscript{16–19} The valence and conductance bands of NiO are made up of 3d orbitals and are pH insensitive. With a chemical stability over a wide pH range (5–14), NiO is an attractive material for the solar-chemical energy conversion.\textsuperscript{20,21} The d–d transitions leads to a strong absorption tail in the visible spectrum and gives the oxide a pale green color.\textsuperscript{21} NiO exhibits excellent chemical stability and due to its desirable optical, electrical, and magnetic properties, it has immense potential in a number of applications such as transparent conductive films,\textsuperscript{22} spin-valve giant magneto (GMR) sensors,\textsuperscript{23} gas sensors,\textsuperscript{24} chemical sensors,\textsuperscript{25} and electrochromic display devices.\textsuperscript{26} NiO has been also used as a co-catalyst loaded on different photocatalysts. The photocatalysts grafted with NiO exhibit improved photocatalytic efficiencies, particularly for water splitting.\textsuperscript{27–30}

The efficiency of semiconductor based photochemical systems is dictated by the light absorption capacity, which determines the number of electrons and holes, and separation of the charge carriers. Electron-hole recombination is an important competing process decreasing the carrier mobility and preventing them from reaching to the surface. Different methods have been proposed to suppress the charge recombination phenomenon including defect mediation,\textsuperscript{31,32} doping,\textsuperscript{33} and fabrication of p-n junctions.\textsuperscript{34–36} When a p–n junction is
formed, the electrons and holes diffuse toward the p-type and n-type semiconductors, respectively. The inner electric field is established at the equilibrium of electron and hole diffusion process, which acts as a potential barrier against the combination of electron and hole. Therefore, the photogenerated electron–hole pairs excited by UV irradiation are efficiently separated by the inner electric field to minimize the recombination. In order to have an efficient charge separation, the interface between p- and n-type semiconductors has to be crystallographically continuous, defect free, and atomically sharp. Any discontinuity as well as defects may lead to charge scattering and deep energy states within the band gap of the material acting as charge recombination centers.

In this research, we integrated single crystalline NiO thin films with Si(100) substrates using cubic yttria-stabilized-zirconia (cYSZ) buffer. The epitaxial relationship and the crystallographic arrangement across the interfaces were studied. We were able to create a p-n junction within a single NiO epilayer through subsequent nanosecond laser annealing. We show that the interface between the p-NiO and n-NiO is atomically sharp leading to an enhanced charge transfer and, therefore, prominent photocatalytic efficiency. Considering our results, the p-NiO/n-NiO single crystalline heterostructures can be considered for an efficient and promising photoanode for hydrogen production and environmental remediation.
4.2 Experimental

Epitaxial NiO(111)/cYSZ(100) heterostructures were deposited on Si(100) substrates by pulsed laser deposition technique where a Lambda Physik LPX200 KrF excimer laser was employed to ablate high purity NiO and cYSZ (8-10 wt% Y₂O₃) targets. The cYSZ buffer was deposited for 500 pulses under vacuum of 10⁻⁶ Torr and 1000 pulses under the oxygen partial pressure of 5×10⁻⁴ Torr at 750 °C. Then, the NiO top layer was grown onto the cYSZ/Si(100) platform for 4500 pulses under the oxygen pressure of 5×10⁻⁴ Torr at 500 °C, followed by cooling down to room temperature under the pressure of about 1 Torr. The energy density and repetition rate were the same for both layers as 3.0-3.5 J.cm⁻² and 5 Hz, respectively. Laser annealing was performed by 5 shots of the excimer laser at the energy density of about 0.35 J.cm⁻² in the air.

Microstructural studies were conducted by using of θ-2θ and φ scan X-ray diffraction where a Philips X-Pert Pro X-ray diffractometer equipped with a Cu-Kα X-ray source (λ=0.154 nm) was employed. A nickel filter and a hybrid monochromator were utilized to condition the incident X-ray beam. A JEOL 2010F transmission electron microscope, operated at 200 KV, with a point-to-point resolution of 1.8 Å was employed for cross section imaging and acquiring selected area electron diffraction (SAED) patterns. A SPECS X-ray photoelectron spectrophotometer with an Mg-Kα excitation of 1254 eV and a PHOIBIS 150 hemispherical analyzer was used to study the stoichiometry of the films. The peak fitting and data interpretation were performed by the SDP software, considering the C(1s) core level binding
energy at 285.0 eV as the reference point.

We also performed Hall measurement to study the electrical characteristics of both pristine and laser treated samples where the electrical contacts to the samples were made by cold pressing fresh cut indium dots on the sample surface followed by pressing indium glazed gold wires to the indium contacts. In order to minimize any interfacial reaction between the contact metal indium and the NiO/cYSZ/Si(001) heterostructures, the contacts were tried to have small dimensions (~ 1 mm$^2$). The measurements were conducted at room temperature under a magnetic field of 0.55 T (5500 G).

Photocatalytic activity of the pristine and the laser annealed samples was evaluated by measuring the degradation rate of aqueous 4-chlorophenol (4CP) solution at room temperature. 50 milliliters of the 4CP solution (2×10$^{-4}$ M) and a 1 cm × 1 cm sample, as a photocatalyst, were placed in a beaker. A UV lamp ($\lambda = 365$ nm) was used to excite the samples during experiments. Prior to UV irradiation, in each experiment, the solution and the catalyst were left in the dark for 30 minutes (considered as a reference point) until adsorption/desorption equilibrium was reached. The solution was then irradiated by UV light. A UV-Vis spectrophotometer (Hitachi, U3010) was used to measure the change in concentration, based on the Beer-Lambert equation stating $A = \varepsilon \times b \times C$ where $A$, $\varepsilon$, $b$, and $C$ are absorbance of the solution, molar absorptivity, path length, and solution concentration, respectively. Using a quartz cell, a fixed quantity of the solution was removed every 20 minutes to measure the absorption and, then, the concentration at a wavelength of 23 nm.
4.3 Results and discussion

Fig. 4.1 shows the θ-2θ scan of the pristine and the laser annealed NiO(111)/cYSZ(001)/Si(001) heterostructures. Since θ-2θ scan provides information on the alignment along the films normal only, we can conclude a growth of highly textured or epitaxial NiO thin film along its [111] axis and absence of other out-of-plane orientations are evident. The inter-planar spacing of NiO(111) family of planes was calculated to be 2.40 Å and the lattice constant was obtained as 4.17 Å which shows the formation of a fully relaxed NiO film. Fig. 4.1b reveals that no new phase and no new out-of-plane orientation formed after laser annealing and the cubic structure of the NiO[111] thin films was preserved after the laser treatment. Considering the high resolution θ-2θ pattern in the inset of Fig. 4.1c, it was found that laser treatment leads to a larger full width at half maximum (FWHM) of the NiO(111) peak. In addition, a small peak shift toward lower 2θ values was observed. The change of the lattice constant after laser annealing is attributed to the formation of lattice defects due to the interaction of a high energy laser beam with the material. Such defects introduce residual strain to the crystallographic lattice and alter the inter-planar spacing. Intensity of the NiO(111) characteristic line was suppressed after laser treatment. This change is attributed to the formation of point defects and, hence, decrease in the structure factor.

The epitaxial growth of NiO(111)/cYSZ(001) epitaxial heterostructure on Si(001) substrate was confirmed by φ-scan technique of XRD, results of which are presented in Fig. 4.2. These
Fig. 4.1 0-20 patterns of the NiO/YSZ/Si heterostructures: (a) pristine sample, (b) laser annealed sample, and (c) high resolution 0-20 scan of the pristine and laser treated samples.
Fig. 4.2 φ-patterns acquired from NiO(200) reflection (2θ = 43.31°, ψ = 54.24°), cYSZ(202) reflection (2θ=50.37°, ψ=45.00°), and Si(202) reflection (2θ=47.57°, ψ=45.00°).
data were acquired from NiO(200) reflection (2θ = 43.31°, ψ = 54.24°), cYSZ(202) reflection (2θ=50.37°, ψ=45.00°), and Si(202) reflection (2θ=47.57°, ψ=45.00°). The results show a cube-on-cube growth across the cYSZ/Si interface; therefore, the epitaxial relationship is expressed as (100)$_{cYSZ}$$||$(100)$_{Si}$ and [100]$_{cYSZ}$$||$[100]$_{Si}$. Considering this epitaxial relationship and the lattice parameters of two crystals (a$_{cYSZ}$=5.14 Å and a$_{Si}$=5.43 Å), the misfit strain is calculated to be about 5.3%. More details on the cYSZ/Si interface can be found in our previous works.$^{40,41}$ Appearance of 12 sharp NiO(200) φ-peaks, with an azimuthal separation of 30°, confirm growth of highly epitaxial NiO thin film on the cYSZ/Si platform. The question why 12 φ-peaks are seen from the NiO crystal can be answered by the equation $N_{RD}=\text{lcm}(n,m)÷m$ where $N_{RD}$ is the number of domains in the epilayer and $C_n$ and $C_m$ are the symmetries of the substrate and the epilayer along the normal direction to the surface. Possible values for n and m are 1, 2, 3, 4, and 6.$^{42}$ In the NiO(111)/cYSZ(001) system, n=4 and m=3, so $N_{RD}$ is obtained to be 4 showing that there are 4 domains in the NiO epilayer separated by low energy and crystallographically continuous twin boundaries.

Fig. 4.3 shows a high resolution TEM micrograph of a typical domain boundary which is highlighted by a square and arrows in the inset image. The corresponding inverse FFT image shown in the inset of Fig 4.3 confirms the continuity of the domain boundaries. Due to the number of domains ($N_{RD}=4$) and the 3-fold symmetry along the [111] direction of the NiO epilayer and number of domains, 12 φ-peaks are observed. Taking the angular positions of NiO(200) and cYSZ(202) φ-peaks into consideration, the epitaxial relationship at the NiO/cYSZ interface is established as [110]$_{NiO}$$\parallel$[010]$_{cYSZ}$, and (111)$_{NiO}$$\parallel$[001]$_{cYSZ}$. Here, any
[\bar{1}0], [0\bar{1}1], and [\bar{1}0] directions of NiO can get aligned with any [100] orientations of cYSZ, as is schematically delineated in Fig. 4.4. According the domain matching epitaxy paradigm,\textsuperscript{43} to fully relax the -14.6% misfit strain ($\varepsilon = 1 - 5.89/5.14$) along the cYSZ[100] orientation, 6/7 and 7/8 domains should alternate with a frequency factor of about 0.85. A high resolution TEM image from the NiO/cYSZ interface is presented in Fig. 4.5 where an atomically sharp interface is observed. This image also indicates that no interfacial reaction has taken place between the NiO and the cYSZ films.

Fig. 4.3 High resolution TEM micrographs showing a crystallographically continuous domain boundary in the NiO epilayer.
Fig. 4.4 Schematic illustration of the epitaxial relationship across the NiO/cYSZ interface. NiO and cYSZ lattices are represented in red and blue, respectively.

Low magnification cross section image of the laser annealed NiO(111)/cYSZ(001)/Si(001) heterostructure is displayed in Fig. 4.6a. The inset shows indexed selected area diffraction (SAED) pattern which further ascertains the established epitaxial relationship. Furthermore, this pattern indicates that the initial crystalline structure as well as the single crystalline nature of the NiO film has been preserved after laser treatment. It is observed that the interface between the laser irradiated and pristine regions is parallel to the free surface of the sample. The reason is that the thermal gradient parallel to the interface is much smaller than
the gradient perpendicular to the interface to many orders of magnitude, due to the short thermal diffusion distance and the large dimensions of the laser beam compared to the melt depth, in nanosecond laser processing. Hence, one-dimensional heat flow conditions are essentially prevailing. High resolution TEM image and the corresponding inverse FFT displayed in Fig. 4.6b, reveals a crystallographically continuous interface. The charge carriers are envisaged to undergo minimum scattering when passing such an interface. Moreover, they are not trapped or recombined at this interface, since the interface is free of dislocations.

Fig. 4.5 High resolution TEM image of the interface between the NiO epilayer and the cYSZ buffer.
The change in electrical conductivity from p-type to n-type in NiO(111)/cYSZ(001)/Si(001) epitaxial heterostructures due to the interaction of the laser beam with the sample was studied by Hall measurements. The Hall coefficient was measured to be \( R_h = +40633.33 \, \Omega \cdot \text{cm} \cdot \text{G}^{-1} \) for the pristine sample, confirming the growth of a p-type NiO epilayer. It was interesting to find that the Hall coefficient changed to \( R_h = -29051.48 \, \Omega \cdot \text{cm} \cdot \text{G}^{-1} \) after laser treatment, revealing transition from the initial p-type behavior to an n-type conductivity. The electrical conductivity was observed to increase from \( 4.93 \times 10^{-3} \) to \( 5.67 \times 10^{-2} \, \Omega \cdot \text{cm} \) after laser annealing. As it was already shown in Fig. 4.6a, only a thin region from the surface was
affected by the laser beam; therefore, it is concluded that an n-type NiO layer formed onto the p-type NiO. Electrical conductivity of NiO is correlated to the valence state of nickel which, in turn, depends on the microstructural defects and stoichiometry. The effect of excimer laser treatment on stoichiometry of the NiO(111) epitaxial thin films was investigated by using XPS technique. Fig. 4.7 depicts the O(1s) core level binding energy of the pristine and the laser annealed samples which was deconvoluted into 5 distinct peaks. This indicates that oxygen is present in 5 different compounds in the NiO epilayers. The peaks A and B with binding energies of 533.4 and 532.5 eV are assigned to oxygen anions in H₂O and –OH compounds which are almost always present onto the free surface of oxides exposed to the atmosphere. Since the hydroxyl groups are attached to the defect sites (oxygen vacancies) on the surface, concentration of surface oxygen vacancies can be surmised from the portion of the peak B. The peak C at the binding energy of 531.6 eV is attributed to oxygen in the Ni₂O₃ compound.⁴⁵,⁴⁶ The oxygen in NiO compound is represented by the peak D at the binding energy of about 529.9 eV. Peak E is attributed to the nonstoichiometric nickel oxides. We found that the portion of the peak B increases from 3.2% to 6.9% after laser treatment showing that the concentration of surface oxygen vacancies increased due to the coupling of the high energy laser beam with the NiO epilayer. In our previous work,⁴⁷ we showed that conductivity of the NiO films converts from p-type to n-type, while maintaining the cubic crystal structure and the epitaxial nature. We attribute this change to formation of Ni⁹ species due to the laser treatment. The pristine NiO crystal has a general formula of NiO₁₊ₓ. Basically, what happens through laser treatment is removing the excess
oxygen anions from the lattice and creating oxygen vacancies. The following mechanism is proposed for the formation of n-type NiO via laser treatment:

\[
\text{NiO} + \text{h} \nu \text{(from the laser photons)} \rightarrow \text{NiO} (e^{-}_{cb} + h^{+}_{vb}) \quad (4-1)
\]

\[
O^{2-} + 2h^{+} \rightarrow \frac{1}{2}O_{2} + \text{Oxygen Vacancy} \quad (4-2)
\]

To preserve the charge neutrality of the material, \( \text{Ni}^{2+} \) cations have to convert into \( \text{Ni}^{0} \) states through trapping the photogenerated electrons.

\[
\text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni}^{0} \quad (4-3)
\]

Formation of \( \text{Ni}^{0} \) species after laser annealing was confirmed by XPS. Fig. 4.8a and Fig. 4.8b display \( \text{Ni}(2p_{3/2}) \) core level binding energy in the pristine and the laser treated samples, respectively. Peak A and B with the binding energies of about 856.3 and 855.0 eV represent nickel cations in the 3+ and 2+ states. Peak C at the binding energy of 853.0 eV is assigned to \( \text{Ni}^{0} \). Results show that the relative portion of the peaks A and particularly C increased and
that of the peak B decreased after the laser treatment. Actually, the portion of peak C increased by a factor of about 6; thus, the formation of Ni$^{3+}$ states is confirmed. The Ni$^{3+}$ ionic
sites are not energetically favorable charge compensating states in NiO. The observed Ni$^{3+}$ XPS signals have different origins in the pristine and the annealed samples. In the as-deposited sample, the reason behind formation of Ni$^{3+}$ is nonlocal site charge transfer screening effects.\textsuperscript{47-49} However, the reason behind the formation of Ni$^{3+}$ state in the annealed sample is exposure of the samples to the atmosphere. Under normal conditions in the air, an Ni$_2$O$_3$ oxide layer forms on the metallic nickel (Ni$^{0}$)\textsuperscript{50} formed through interaction of the laser beam with the NiO epilayer.

Fig. 4.8 Ni(2p$_{3/2}$) core level binding energy in: (a) as-deposited and (b) laser annealed samples.
4.3.1 Photocatalytic efficiency

Formation of p-NiO/n-NiO single crystalline structures having crystallographically continuous interfaces via nanosecond laser annealing is extremely important for fabrication of high efficiency photochemical devices where the efficiency is dictated by initial number of the photogenerated charge carriers and, of course, their separation. Using a p-n junction, the electrons and holes get separated due to the electric field between the p-type and n-type semiconductors.

Fig. 4.9 delineates results of photocatalytic degradation of 4CP by pristine and laser annealed NiO/cYSZ/Si(001) heterostructures under UV illumination. Fig. 4.9a shows that the concentration of 4CP decreases over time confirming the decomposition of 4CP. As is seen, the concentration of 4CP decreases faster when the annealed NiO/cYSZ/Si(001) heterostructure was used as catalyst. To confirm that the 4CP is degraded by the catalyst and not the UV light, an experiment was performed without any sample inside the cell. The curve “No catalyst” represents the results of this experiment where no noticeable change was observed in the 4CP concentration over the measurement period. Hence, it is deduced that, in other experiments, 4CP is degraded photocatalytically. It is well-established that the photocatalytic degradation of 4CP by metal oxides follows a first-order kinetics. Therefore, the photocatalytic reaction rate constant (k) can be calculated through the equation \( \ln(C/C_0) = -kt \) (\( C_0 \) is the initial concentration of 4CP at \( t=0 \) and \( C \) represents the concentration of 4CP at...
Fig. 4.9 The effect of nanosecond laser annealing on the photocatalytic activity of NiO(111)/cYSZ(001)/Si(001) heterostructures.
time t). Fig. 4.9b displays changes of ln(Co/C) as a function of the irradiation time. The photocatalytic reaction rate constant (k) is represented by the slope of the straight lines. This constant was determined to be 0.0059 and 0.0092 min$^{-1}$ for the pristine and the laser treated samples, respectively. Thus, it is deduced that the photocatalytic activity increased significantly after excimer laser annealing. We already showed that a n-NiO/p-NiO junction separated by atomically sharp and continuous boundary formed by laser irradiation. The mechanism behind semiconductor mediated photocatalysis is based on the creation of e$^-\cdot$h$^+$ pairs upon light-excitation phenomenon where the efficiency is dictated by the light absorption capacity, which determines the number of electrons and holes, and separation of the charge carriers. Electron-hole recombination is an important competing process suppressing the carrier mobility and preventing them from reaching to the surface of the catalysts and participating in the following reactions:

$$\text{Semiconductor} + h\nu \rightarrow h^+ + e^- \quad (4-4)$$

$$O_2(\text{ads}) + e^- \rightarrow O_2^{\cdot-} \quad (4-5)$$

$$H_2O + h^+ \rightarrow H^+ + OH^\cdot \quad (4-6)$$

$$O_2^{\cdot-} + H^+ \rightarrow HO_2^{\cdot-} \quad (4-7)$$

$$2HO_2^{\cdot-} \rightarrow H_2O_2 + O_2 \quad (4-8)$$
\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2\text{OH}^- \quad (4-9) \]

\[ 2\text{C}_6\text{H}_5\text{OCl} + 13\text{O}_2 \rightarrow 12\text{CO}_2 + 4\text{H}_2\text{O} + 2\text{HCl} \quad (4-10) \]

One way to enhance the charge separation is juxtaposing a p-type semiconductor to an n-type semiconductor. When a p–n junction is formed, the electrons and holes diffuse to p-type and n-type semiconductors, respectively. The inner electric field is established at the equilibrium of electron and hole diffusion, which acts as a potential barrier to prevent the combination of electrons and holes. Therefore, the photogenerated electron–hole pairs generated by the UV irradiation are efficiently separated by the inner electric field. Due to the enhanced charge separation, the positive holes which are prerequisite for photocatalytic decomposition of 4CP (reactions 6 and 10) can approach toward the surface to participate in the chemical reactions without recombination with electrons. The formation of metallic Ni in the layers enhances the electrical conductivity; thus, the carriers can reach the surface more easily. Meanwhile, as we discussed earlier, oxygen vacancies are created by laser treatment. They promote the adsorption of 4CP molecules. It has been demonstrated that the surface of reduced oxide layers is more acidic. The increased acidity can generate a higher affinity for species with unpaired electrons; therefore, these films can absorb more \( \text{OH}^- \) or \( \text{H}_2\text{O} \), and create more hydroxyl radical necessary for photo-oxidation reactions\(^{51}\). Enhanced charge separation, higher electrical conductivity, and formation of a more acidic surface along with the better
adsorption of 4CP molecules to the catalysts surface lead to a noticeable increase in photocatalytic efficiency of the NiO thin films after the laser annealing treatments.

4.4 Conclusions

Single crystalline p-type NiO(111) thin films were grown epitaxially on cYSZ buffered Si(001) substrates. The p-NiO/cYSZ/Si heterostructures were subsequently laser treated by 5 pulses of KrF excimer laser to create an n-type NiO layer at the top of the as-deposited p-type NiO layer and form an n-NiO(111)/p-NiO(111) heterojunction. The formation of these oxide p-n junctions showed enhanced photocatalytic characteristics. The formation of point defects, i.e. oxygen vacancies and Ni\(^{\circ}\), is responsible for the observed change in the electrical conductivity. HRTEM studies revealed an atomically sharp and crystallographically continuous interface between the laser annealed and the pristine regions. The laser-treated (n-NiO/p-NiO) heterostructure exhibited a higher photocatalytic efficiency as compared to the pristine sample where the enhanced photocatalytic efficiency was mainly attributed to the improved charge carrier separation in the NiO based p-n junctions.
4.5 References


Chapter 5. Achieving crystallographic characteristics and p-type to n-type transition in epitaxial NiO thin film

In this chapter systematically control crystallographic characteristics and electrical properties of nickel oxide epitaxial thin films integrated with cubic yttria-stabilized zirconia (c-YSZ) buffered silicon(001) substrates is reported. The NiO epilayers were grown under several oxygen partial pressures by pulsed laser deposition. The out-of-plane orientation of the NiO layers showed an interesting behavior where it changed from [111] at lower pressures (7×10^{-6} Torr) to [100] at higher pressures (5×10^{-2} Torr). This observation was attributed to the nature of surface termination and templating effect of the c-YSZ(100) platform at different pressures. Using θ-2θ and φ scans of X-ray diffraction, the epitaxial alignment across the NiO/c-YSZ interface was determined to be (111)NiO||(100)c-YSZ and [110]NiO||(100)c-YSZ for the heterostructure grown under a low pressure and (100)NiO||(100)c-YSZ and [100]NiO||(100)c-YSZ for the heterostructure grown under a high oxygen pressure. Our high resolution TEM studies revealed formation of atomically sharp interfaces with no evident of interfacial reaction and confirmed the established epitaxial relationships. An n-type electrical conductivity was observed in the NiO epilayers grown under lower pressures which was turned p-type in the films deposited under higher oxygen partial pressures. Besides, the electrical resistivity increased with the growth pressure. These observations were correlated to the nature of point defects in the NiO crystal. The formation of oxygen vacancies and metallic nickel at lower pressures and excess oxygen and trivalent nickel at higher pressures
was revealed by XPS. We established a structure-property correlation in NiO/c-YSZ(100)/Si(100) thin film epitaxial heterostructures with especial emphasis on the stoichiometry and crystallographic characteristics.

5.1 Introduction

Nickel oxide (NiO) is a transparent p-type semiconductor (hole-type conductivity) with a wide band gap of 3.6–3.8 eV. NiO has a cubic (Rock salt type) structure with a lattice parameter of 4.17 Å. It is an antiferromagnetic transition metal oxide semiconductor with excellent electrochemical stability as well as desirable optical, electrical, and magnetic properties, and low material cost which make it an attractive material for variety of applications such as smart windows, p-type transparent conducting films, chemical gas sensors, catalyst in fuel cell electrodes, electrochromic devices, and solar thermal absorbers. Nickel oxide thin films are one of the important components for the forthcoming nanoscale optoelectronic devices. Many techniques such as sol–gel, chemical deposition, sputtering, and vacuum evaporation, have been used for the preparation of NiO thin films. Pulsed laser deposition (PLD) has been shown to be a very successful method for the growth of materials in thin film form. However, little is known about the dependence of the film properties on the deposition process parameters. In fact, there is no comprehensive report on the manipulation of structure and, properties of NiO thin films via changing the PLD variables.
As it was already mentioned, NiO is a p-type semiconductor with cation vacancies, electrically compensated by electronic holes, as the primary defects which leads to the formation of Ni$^{3+}$ states. The conductivity scales with the concentration of Ni$^{3+}$ ions in the lattice.\(^{16,17}\) Deviation from stoichiometry, which determines the electrical conductivity of nickel oxide, depends on temperature and the partial pressure of oxygen in equilibrium with the NiO. According to Kroger-Vink notation, the following equilibria are considered in NiO:\(^{18,19}\)

\[
\frac{1}{2}O_2 \rightleftharpoons O_O + V_{\text{Ni}}^{\alpha}\tag{5-1}
\]

\[
V_{\text{Ni}}^{\alpha} \rightleftharpoons V_{\text{Ni}}^\alpha + \alpha^e \tag{5-2}
\]

\[
V_{\text{Ni}}^{\alpha^\prime} \rightleftharpoons V_{\text{Ni}}^\alpha + \alpha^e \tag{5-3}
\]

where $O_O$, $V_{\text{Ni}}^\alpha$, and $^e$ denote an oxygen atom on its normal lattice site, an $\alpha$ times ionized nickel vacancy, and an electron hole. Since $V_{\text{Ni}}^\alpha$ is the predominant defect in the lattice, the following condition must be satisfied for electrical neutrality:

\[
p = \alpha[V_{\text{Ni}}^\alpha] \tag{5-4}
\]
where $p$ is the molar fraction of electron holes $\hat{h}$, and $[\nu_{Ni}^\alpha]$ the molar fraction molar fraction of nickel vacancies, which is equal to the deviation from stoichiometry. Considering the above discussion and reactions, the electrical properties of NiO is dictated by the ionization degree, nature, and the population of the point defects. Taking the electroneutrality condition (6-4) into account, the equilibrium constant for the formation of nickel vacancies is expressed by the following equation:

$$K_\alpha = \frac{1}{\alpha} \frac{p^{\alpha+1}}{p_{O_2}^{1/\alpha}}$$

(5-5)

As a consequence, the concentration of charge carriers can be obtained by the below relation:

$$p = A \exp\left[-\frac{\Delta H_\alpha^O}{(\alpha+1)RT}\right] p_{O_2}^{1/2(\alpha+1)}$$

(5-6)

in which $\Delta H_\alpha^O$ is the enthalpy of formation of the point defect of consideration. Eq. (5-6) tells that the carrier concentration is a function of temperature and oxygen partial pressure ($P_{O_2}$). The electrical characteristics of NiO have been studied over a wide range of temperature and
oxygen partial pressures. It has been shown that the p-type conduction is enhanced at higher oxygen pressures and the formation temperature via increased Ni vacancies and the resultant holes.\textsuperscript{20-31}

Even though growth of epitaxial nickel oxide,\textsuperscript{32-34} and the dependence of NiO film properties on deposition conditions have been studied, the influence of the process parameters on the film out-of-plane orientation and the electrical characteristics has not been well demonstrated. In this study, epitaxial NiO thin films are integrated with silicon(001) substrates via buffering with cubic yttria-stabilized zirconia (c-YSZ). Special emphasis is placed on epitaxial growth and controlling the crystallographic alignment in NiO/c-YSZ(001)/Si(001) heterostructures in the light of the domain matching epitaxy (DME) paradigm where integral multiples of planes match across the interfaces.\textsuperscript{35} We are able to precisely tune the out-of-plane orientation of NiO epilayers from [111] to [100] by adjusting the growth pressure. This observation is attributed to the nature of the surface termination and bonding characteristics of c-YSZ(100) face. Interestingly, we show that the p-type electrical conductivity of the NiO thin films grown under medium and high oxygen partial pressures turns n-type at lower pressures where we envisage that nature of the point defects plays a critical role in determining the electrical conductivity. This study is important for practical applications of NiO based devices where different and controlled crystallographic and electrical characteristics are required.
5.2 Experimental

Epitaxial NiO thin films were integrated with Si(001) substrates by using c-YSZ as buffer. All thin films were grown by pulsed laser deposition where a Lambda Physik (LPX200) KrF excimer laser ($\lambda = 248$ nm, $\tau = 25$ ns) was employed to ablate high purity NiO and c-YSZ targets. The c-YSZ target contained $8-10$ wt% yttria to stabilize cubic polymorph of zirconia at room temperature. During the deposition, the targets were constantly rotated to avoid pitting on the target surfaces. The Si(001) substrates were cleaned by degreasing in hot acetone for 5 min., ultrasonic cleaning in acetone for 5 min., and ultrasonic cleaning in methanol for 5 min. at room temperature. The substrates were then etched in diluted HF solution to remove the SiO$_x$ amorphous layer and prepare a hydrogen-terminated surface. After loading the substrate and the targets, the deposition chamber was pumped down to a background pressure of $8 \times 10^{-7}$ Torr using a turbomolecular pump backed by a rotary pump. The c-YSZ and NiO thin films were deposited at 750 and 500 °C, respectively. Energy density and repetition rate were set at 3-3.5 J.cm$^{-2}$ and 5 Hz for both layers. The c-YSZ buffer was deposited for 1000 pulses under vacuum and 1000 pulses under the oxygen partial pressure of $5 \times 10^{-4}$ Torr. Without breaking the vacuum and employing a target carousel, NiO thin films were deposited for 4500 pulses onto the buffer layers under several oxygen partial pressures. The samples were eventually cooled down to room temperature inside the deposition chamber under an oxygen partial pressure similar to the deposition pressure.
A Rigaku diffractometer was used to evaluate the out-of-plane orientation of the heterostructures. The in-plane orientation and the epitaxial relationship across the interfaces were studied employing a Philips X’Pert Pro diffractometer. Both diffractometers were equipped with a Cu-Kα radiation source (λ_{ave}=0.154 nm). A JEOL 2010 field emission transmission electron microscope, with a Gatan image filter (GIF) attachment and a point-to-point resolution of 1.8 Å, was used to study the atomic and crystallographic arrangements at the interfaces and to confirm the epitaxial growth. The microscope was operated at 200 kV. Defect structure and stoichiometry of the samples were studied by X-ray photoelectron spectrometry where an SPECS instrument equipped with an Mg-Kα source (λ=1254 eV) and a PHOIBIS 150 hemispherical analyzer was used. The results were interpreted by SDP software ver. 4.1. Peak fitting procedure and all data interpretations were performed considering the C(1s) core level binding energy at 285.0 eV. Hall measurement was performed to study the effect of oxygen partial pressure on electrical conductivity (p-type or n-type), carrier concentration, and resistivity of the samples. The electrical contacts to the samples were made by cold pressing of indium dots on the sample surface followed by pressing indium glazed gold wires to the indium contacts. The contacts were tried to be as small as 1 mm² to minimize any interfacial reaction between the indium contacts and the surface of samples. The Hall measurements were performed at room temperature under a magnetic field of 0.55 T (5500 G).
5.3 Results and discussion

5.3.1 Microstructure and crystallographic characteristics

Fig. 5.1 depicts log-scale θ-2θ patterns acquired from the NiO/c-YSZ/Si(001) heterostructures grown under varying oxygen partial pressures. As is seen, NiO assumes a [111] out-of-plane orientation when grown under lower pressures, namely $7 \times 10^{-6}$ Torr. For the NiO layer deposited under high oxygen pressures ($5 \times 10^{-2}$ Torr), however, the out-of-plane direction turns into [100]. A combination of these growth orientations is observed in the thin layers grown at intermediate pressures. This behavior was attributed to the surface termination nature and atomic arrangement on the c-YSZ(100) face under different oxygen pressures. As it was explained in the experimental section, all zirconia buffers were grown under the same conditions ($P_{\text{O}_2} = 5 \times 10^{-4}$ Torr, $T_{\text{substrate}} = 750 \, ^{\circ}\text{C}$); hence, it can be assumed that they initially have more or less similar defect content onto their surface. However, when the oxygen pressure is decreased to $7 \times 10^{-6}$ Torr prior to the deposition of the NiO top layer, oxygen vacancies form on the surface and a zirconium-terminated c-YSZ platform is obtained. In contrast, an oxygen-terminated surface forms, when the oxygen partial pressure is raised to $5 \times 10^{-2}$ Torr prior to depositing the NiO thin film. The cation terminated (100) face of c-YSZ is atomically jagged, while its anion terminated surface is smooth in the atomic scale. When we have a jagged cation terminated platform, a jagged anion terminated NiO is favored. This condition is satisfied by the (111) face of nickel oxide which is atomically rough and contains deeper holes among the oxygen anions (Fig. 5.2a). In contrast, the cation
terminated (100) face of NiO is atomically smooth (Fig. 5.2b) and is the preferred plane when a smooth anion terminated c-YSZ platform has already formed.

Fig. 5.1 0-20 XRD patterns of the NiO/c-YSZ/Si heterostructures grown under the pressures of: (a) $7 \times 10^{-6}$, (b) $5 \times 10^{-4}$, (c) $5 \times 10^{-3}$, and (d) $5 \times 10^{-2}$ Torr.
Fig. 5.2 Schematic arrangement of: (a) anion terminated NiO(111) and (b) cation terminated NiO(100) faces.

The epitaxial growth as well as the crystallographic alignment across the NiO/c-YSZ interface was investigated employing φ-scan XRD. Fig. 5.3 shows the φ patterns taken from the NiO(200) and c-YSZ(202) reflections in the NiO(111)/c-YSZ(001)/Si(001) heterostructure. These patterns were obtained at 2θ=43.31°, and ψ=54.24° for NiO(200) and 2θ=50.37° and ψ=45.00° for c-YSZ(202) faces. Appearance of 12 sharp peaks from the NiO(200) reflection confirms formation of highly epitaxial NiO(111) thin film onto the zirconia buffer. Briefly, the epitaxial alignment was shown to be NiO(111)||c-YSZ(001) and NiO[110]||c-YSZ[100] in this heterostructure. Detailed discussion can be found in our previous work. The epitaxial relationship at the NiO/c-YSZ interface was studied in the NiO(100)/c-YSZ(001)/Si(001) heterostructure as well. For this case, NiO(202) at 2θ=63.2°
and $\psi=45^\circ$, and c-YSZ(202) reflections were selected. Results, displayed in Fig. 5.4, reveal a cube-on-cube growth; thus, the epitaxial alignment is written as NiO(100)||c-YSZ(001) and NiO[100]|c-YSZ[100]. Assuming that the distance between 2 subsequent oxygen anions on the (100) face of c-YSZ along the [100] direction equals 2.57 Å and distance between 2 subsequent nickel cations on the NiO(100) plane along the [100] direction equals 4.17 Å, the lattice misfit strain is calculated as 18.87% along the [100] direction ($\varepsilon = 1 - \frac{4.17}{2 \times 2.57}$). In accordance with the domain matching epitaxy paradigm, 5/4 and 6/5 domains alternate with a frequency factor of about 0.29 to accommodate the lattice misfit strain.\textsuperscript{35} The epitaxial relationship between the c-YSZ buffer layer and the Si(001) substrate was already studied in detail by our group.\textsuperscript{15,36,37-39} We showed that a cube-on-cube growth takes place at the c-YSZ/Si(001) interface.

Low magnification cross-section TEM image along with the indexed SAED pattern acquired from the NiO(100)/c-YSZ(100)/Si(100) heterostructure is shown in Fig. 5.5a. The SAED pattern further confirms the aforementioned epitaxial relationships. This pattern belongs to the Si[110], c-YSZ[110], and NiO[110] zones. High resolution TEM micrograph obtained from the NiO(100)/c-YSZ(100) interface is presented in Fig. 5.5b where a clean interface is observed. There is no evident of chemical reaction between the NiO film and the c-YSZ buffer. Arrangement of misfit dislocations across the NiO/c-YSZ interface and alternation of 5/4 and 6/5 matching domains can be observed in Fig. 5.5c. The misfit dislocations nucleate on the free surface of NiO epilayer after the film reaches a critical thickness. Then, the misfit
Fig. 5.3 \( \phi \)-patterns acquired from NiO(111)/c-YSZ(001)/Si(001) epitaxial heterostructure.
Fig. 5.4 $\varphi$-patterns taken from NiO(100)/c-YSZ(001)/Si(001) epitaxial heterostructure
dislocations glide toward the interface to relax the misfit strain. The critical thickness is the thickness at which the misfit strain energy stored in the system exceeds the energy of misfit dislocations; as a consequence, the system prefers to accommodate dislocations to minimize the free energy. It is worth mentioning that the stored strain energy is proportional with the thickness of the NiO layer. For the thicknesses below the critical thickness, the strain energy is smaller than the energy of misfit dislocations; therefore, the misfit dislocations are not

Fig. 5.5 (a) Cross-section low magnification TEM image from the NiO(100)/c-YSZ(001)/Si(001) heterostructure where the inset depicts the indexed SAED pattern, (b) High magnification TEM micrograph showing the NiO(100)/c-YSZ(100) interface, and (c) Arrangement of misfit dislocation and alternation of 6/5 and 5/4 matching domains across the NiO/c-YSZ interface.
generated and, hence, the system remains under strain. After the growing NiO epilayer reaches the critical thickness, the misfit dislocations are generated and the misfit strain relaxes. This misfit dislocations are generated within the first monolayer as the critical thickness for 18.87% planar misfit is less than a monolayer. These dislocations nucleate easily at the surface steps which are created during the initial stage of the film growth. The relaxation takes place in accordance with domain matching epitaxy paradigm through matching of integral multiples of crystallographic planes. Fig. 5.6 shows high resolution image of the NiO(111)/c-YSZ(100) interface which is atomically sharp. There is no evidence of any interfacial reactions along the interfaces in both heterostructures.

5.3.2 Electrical properties

The changes of electrical resistivity and concentration of charge carriers in the NiO epilayers grown at different oxygen partial pressures are depicted in Fig. 5.7. As is seen, the electrical resistivity increases as the oxygen pressure is raised from $7 \times 10^{-6}$ to $5 \times 10^{-4}$ Torr and, then, decreases with further increasing the pressure. Besides, the carrier concentration shows a minima at the pressure of $5 \times 10^{-4}$ Torr. Interestingly, a negative Hall coefficient was obtained for the sample grown under the pressure of $7 \times 10^{-6}$ Torr, while positive coefficients for the samples deposited under higher pressures. In other words, we were able to grow n-type NiO under lower pressures and p-type NiO under higher pressures and tune the electrical conductivity. The electrical resistivity of the c-YSZ/Si(100) sample was measured to be
7.4×10⁰ Ω.cm. The observed changes in electrical characteristics of the NiO epilayers were attributed to stoichiometry and defect structure of the samples, studied in detail by XPS technique in the following section.

Fig. 5.6 High resolution TEM image taken from the NiO(111)/c-YSZ(100) interface.
5.3.3 Stoichiometry and defect structure

Fig. 5.8 shows O(1s) core level binding energy in the NiO epilayers grown at different partial pressures. Peaks A and B, at binding energies of about 533.1 and 531.9 eV, are assigned to oxygen in H₂O and –OH compounds. Hydroxyl groups (-OH) couple with the oxygen vacancies onto the surface and, consequently, portion of peak B indirectly expresses the concentration of oxygen defects on the surface. Peak C, with a binding energy of 530.8 eV, represents oxygen in the Ni₂O₃ compound and, consequently, excess oxygen in the lattice.⁴⁰,⁴¹ Actually, this peak is an indication of the growth of a p-type NiO, which will be
Fig. 5.8 XPS O(1s) core level binding energy of the NiO epilayers grown under pressures of: (a) \(7 \times 10^{-6}\), (b) \(5 \times 10^{-4}\), (c) \(5 \times 10^{-3}\) Torr, and (d) \(5 \times 10^{-2}\) Torr.
discussed later on. Peak D at the binding energy of 529.9 eV is assigned to oxygen in NiO compound and represents a perfect and stoichiometric NiO. Finally, nonstoichiometric nickel oxides are represented by peak E. Quantitative studies were performed by the SDP software and the results are presented in Fig. 5.9. In this figure, the normalized portions of peaks B and C, i.e. portion of peak B(C)/portion of peak D, are shown for different oxygen partial pressures. The results reveal that the concentration of oxygen vacancies increases with decreasing the growth pressure and oxygen vacancies are the dominant point defects when

![Graph showing the effect of oxygen partial pressure on the content of -OH and Ni$_2$O$_3$ compounds.](image)

Fig. 5.9 Effect of the oxygen partial pressure on the content of -OH and Ni$_2$O$_3$ compounds.
the NiO epilayers were grown under the pressure of $7 \times 10^{-6}$ Torr. In contrast, the normalized portion of peak C, representing excess oxygen, increases when the NiO layers were grown under higher pressures. In summary, oxygen deficit NiO thin films ($\text{NiO}_{1-x}$) were obtained at lower pressures and NiO thin films with excess oxygen ($\text{Ni}_{1-x}\text{O}$) were obtained at higher oxygen pressures. The excess oxygen defects are responsible for the p-type conductivity in NiO. Oxygen vacancies, however, lead to an n-type electrical conductivity. Under the equilibrium conditions, defect chemistry in NiO is defined as excess oxygen accommodated by nickel vacancies. When a nickel vacancy forms, to preserve the overall charge neutrality in the crystal, some $\text{Ni}^{2+}$ cations must be converted to $\text{Ni}^{3+}$ cations via trapping the positive holes.\textsuperscript{42,43} Actually, the appearance of $\text{Ni}_2\text{O}_3$ signal in O(1s) core level binding energies in Fig. 5.8 is an indication of the growth of a p-type NiO. Oxygen vacancies form via the following reactions:

\[
\text{O}^2- \rightarrow \frac{1}{2}\text{O}_2 + \text{Oxygen Vacancy} + 2e^- \quad (5-7)
\]

The released electrons are trapped by $\text{Ni}^{2+}$ cations to preserve the charge neutrality of the sample:

\[
\text{Ni}^{2+} + e^- \rightarrow \text{Ni}^+ \quad (5-8)
\]
\[
\text{Ni}^+ + e^- \rightarrow \text{Ni}^0 \quad (5-9)
\]
The Ni\textsuperscript{0} defects move to the interstitial sites and, create nickel vacancy (V_{Ni}). Formation of Ni\textsuperscript{0} defects was confirmed by XPS investigations on Ni(2p) core level. Ni(2p) core level binding energies in the samples grown under different pressures are displayed in the insets of Fig. 5.10a to Fig. 5.10d. Peaks A and B, located at the binding energies of about 857.0 and 855.1 eV, represent Ni\textsuperscript{3+} and Ni\textsuperscript{2+} cations. Peak C at the binding energy of about 853.0 eV is attributed to the metallic nickel (Ni\textsuperscript{0}). As is seen, the relative portion of peak C is significantly larger in the grown under the pressure of 7\times10^{-6} Torr. Given our discussion on the formation of metallic nickel due to the formation of oxygen vacancies, appearance of the Ni\textsuperscript{0} signal is an indication of the growth of n-type NiO. The critical role of oxygen vacancies in many resistive switching oxides has been demonstrated by electrochemical phenomena because these defects result in the n-type conductivity in many transition metal oxides.

We showed that electrons and holes are the majority charge carriers at lower and higher pressures, respectively. Under n-type region, the concentration of oxygen vacancies and free electrons decreases with increasing oxygen pressure. Hence, conductivity as well as carrier concentration decreases as the pressure is increased from 7\times10^{-6} to 5\times10^{-4} Torr. Beyond this pressure, we enter into the p-type regime where the concentrations of nickel vacancies and holes increase with increasing oxygen pressure. As a result, p-type conductivity and carrier concentrations increase with the oxygen pressure from 5\times10^{-4} to 5\times10^{-2} Torr. These are the reasons behind the resistivity maxima and the minima in carrier concentration at the oxygen pressure of 5\times10^{-4} Torr in Fig. 5.7. The reason why the highest conductivity was achieved in
Fig. 5.10 XPS Ni(2p) core level binding energy of the NiO epilayers grown under pressures of: (a) $7 \times 10^{-6}$, (b) $5 \times 10^{-4}$, (c) $5 \times 10^{-3}$ Torr, and (d) $5 \times 10^{-2}$ Torr.
the sample grown under the pressure of $7 \times 10^{-6}$ Torr is that the metallic nickel (Ni$^0$) participate in conductivity, in addition to the majority charge carriers.

5.4 Conclusions

We were able to epitaxially grow nickel oxide thin films on c-YSZ/Si(001) platform and tune the out-of-plane orientation, in a controlled way by changing the growth pressure. The crystallographic alignment across the NiO/c-YSZ interface was found to be: (111)$_{\text{NiO}}$||(100)$_{c\text{-YSZ}}$ and [110]$_{\text{NiO}}$|[100]$_{c\text{-YSZ}}$ for the heterostructures grown under a low oxygen pressure and (100)$_{\text{NiO}}$||(100)$_{c\text{-YSZ}}$ and [100]$_{\text{NiO}}$|[100]$_{c\text{-YSZ}}$ for the heterostructures grown under a high pressure. This observation was attributed to the change of surface termination and atomic arrangement on the c-YSZ(100) face. In addition, electrical conductivity of the NiO epilayers was observed to change from n-type for the films grown under lower pressures to p-type for the films deposited under higher oxygen partial pressures. It was also found that the electrical resistivity increases as the growth pressure is raised and goes through a maximum. We correlated the electrical conductivity of NiO epilayers to the microstructural defects and stoichiometry.
5.5 References


Chapter 6. Thin film epitaxy and near bulk semiconductor to metal transition in VO$_2$/NiO/YSZ/Si(001) heterostructures

In this chapter the growth of VO$_2$/NiO epitaxial thin film heterostructures by pulsed laser deposition technique is reported where integration with Si(001) substrates was successfully achieved by cubic-yttria-stabilized zirconia (YSZ) buffer layer. The most interesting aspect of this work is that a complete relaxation of VO$_2$ is achieved in these large misfit systems through the paradigm of domain matching epitaxy, which is critical to controlling the SMT characteristics. The in-plane and out-of-plane orientations of the thin films were studied by $\theta/2\theta$ and $\phi$ scans, respectively. Using X-ray diffraction and cross-section TEM, the epitaxial relationship across the YSZ/Si(001) interface was shown to be (001)[100]$_{\text{YSZ}}$||(001)[100]$_{\text{Si}}$. In the case of YSZ/NiO interface, the epitaxial relationship was found to be (001)[010]$_{\text{YSZ}}$||(111)[$\overline{2}$]$_{\text{NiO}}$. Finally, the epitaxial relationship at the NiO/VO$_2$ interface was determined to be (010)[001]$_{\text{VO}_2}$||(111)[$\overline{2}$]$_{\text{NiO}}$. From X-ray and TEM studies, we deduced possible atomic arrangements across the interfaces. Since the VO$_2$ films in the heterostructure is fully relaxed along the c-axis of the rutile phase, the SMT characteristics were found to be close to those of the bulk. The SMT characteristics of these fully relaxed films were determined and a transition temperature of 341 K with amplitude over five orders of magnitude and the hysteresis of 3.4 K hysteresis were obtained, which are close to those of
the bulk high quality single crystals. These superior thin film characteristics of fully relaxed heterostructures open new opportunities for sensors integrated with Silicon electronics.

6.1 Introduction

Vanadium dioxide (VO$_2$) single crystals exhibit an extremely abrupt first-order phase transformation from a semiconducting monoclinic phase, with a P21/C space group, to a metallic tetragonal phase, with a P42/mnm space group, at about 68 °C.$^{1-5}$ This semiconductor to metal transition (SMT) affects the optical and electrical properties making VO$_2$ an attractive material for a variety of technological applications such as sensors,$^{6,7}$ optical switching,$^8$ energy management devices,$^9$ actuators,$^{10}$ and photochromic memories.$^{11}$ The SMT in VO$_2$ involves a small lattice distortion along the c-axis, which results in failure of VO$_2$ bulk single crystals when subjected to repeated heating and cooling cycles.$^{5,12,13}$ Therefore, VO$_2$ thin films and nanoparticles, which are able to sustain these distortions and dissipate heat through the substrate, are needed for a variety of technological applications. So far, most of the studies on VO$_2$ thin films have been focused on growth of epitaxial films with controlled properties on Al$_2$O$_3$ and TiO$_2$ substrates;$^{14,15}$ however, implementation of VO$_2$-based devices is restricted by the limited use of Al$_2$O$_3$ and TiO$_2$ substrates in the microelectronic industry. An essential prerequisite to the development of optoelectronic devices based on thermal switching is the integration of VO$_2$ films with Si(001), which is the mainstay substrate material in the microelectronics industry. This epitaxy on Si(100) also
allows integration of functionality on a computer chip for smart device functions.\textsuperscript{16} Though the epitaxial growth of VO\textsubscript{2} on Si(001) can be anticipated via domain matching epitaxy,\textsuperscript{17} where integral multiples of planes match across the film-substrate interface, direct deposition of VO\textsubscript{2} on Si(001) remains a technological challenge due to the formation of silicides or native amorphous silicon dioxide layers. In this research, we have addressed the integration of high quality epitaxial VO\textsubscript{2}/NiO thin film heterostructures with Si(001) substrates by cubic yttria-stabilized zirconia buffer system. Introduction of NiO platform provides a complete relaxation of misfit strain, which leads to a negligible tension/compression along the VO\textsubscript{2} [001] direction. The tensile strain in VO\textsubscript{2} [001] increases the SMT temperature, while the compressive strain decrease the SMT temperature, compared to the bulk value. Thus we can combine the positive characteristics of VO\textsubscript{2} and NiO and develop a new system with novel properties suitable for integrated and reliable device applications.

Nickel oxide (NiO) is a p-type semiconducting material with a band gap of 3.6-4.0 eV and has been introduced as a promising candidate for a wide range of applications such as solar cells,\textsuperscript{18} spin-valve giant magneto resistance sensor,\textsuperscript{19} transparent conducting electrodes,\textsuperscript{20} gas sensors,\textsuperscript{21} electrochemical display devices,\textsuperscript{22} and organic light emitting diodes.\textsuperscript{23} Moreover, NiO has been employed in the fabrication of oxide p-n junctions as the p-type layer.\textsuperscript{24} Potential applications of NiO as an epitaxial electrode or gate oxide layer can open up exciting possibilities in devices based on SMT properties of VO\textsubscript{2} thin films.\textsuperscript{25}
Epitaxial growth of VO$_2$/NiO on Si(001) represents a major milestone towards achieving VO$_2$-based smart sensor or memory based devices. Fully relaxed VO$_2$/NiO thin film heterostructures hold a significant technological importance, since the SMT characteristics can be influenced by the misfit strains. In this study, special emphasis is placed on the growth of high quality single crystalline thin film heterostructures and explaining the epitaxial relationships across the interfaces in accordance with the domain matching epitaxy (DME) paradigm$^{17}$ where integral multiples of planes match across the film-substrate interface. We could achieve a near bulk and sharp SMT in the VO$_2$/NiO/YSZ heteroepitaxy through engineering the interfaces and relaxing the strains.

6.2 Experimental

The VO$_2$/NiO/YSZ heterostructures were grown on Si(100) substrates by the pulsed laser deposition (PLD) technique. PLD is a versatile technique to deposit high quality thin films by optimizing the laser and substrate variables.$^{26-28}$ The silicon substrates were cleaned by boiling in acetone at 200 °C for 5 min, followed by ultrasonic cleaning in acetone (5 min.) and methanol (5 min.) at room temperature. The substrates were fully dried by purified nitrogen and loaded to the deposition chamber immediately. The chamber was evacuated to a background pressure of about 1×10$^{-6}$ Torr. During the deposition, oxygen partial pressure was controlled by leaking oxygen into the chamber. A Lambda Physik (LPX200) KrF excimer laser with a wavelength of 248 nm and pulse duration of 25 ns was employed to
ablate the high purity targets being rotated during the deposition to avoid pitting on the target. To fully eliminate the native SiO$_2$ amorphous layer, the YSZ buffer layer was deposited under vacuum for 500 pulsed and under an oxygen atmosphere at a pressure of 5×10$^{-4}$ Torr for 1500 pulses at 700 °C.$^{29}$ Without breaking the vacuum, the NiO films were grown at 700 °C under the pressure of 5×10$^{-4}$ Torr for 4500 pulses. Finally, the VO$_2$ films were deposited at 500 °C under the oxygen pressure of 1×10$^{-2}$ Torr for 4500 pulses. Repetition rate, laser energy density, and the target-substrate distance were the same for all films and maintained at 5 Hz, 3-3.5 J/cm$^2$, and 4.5 cm, respectively. The films were cooled down to the room temperature inside the PLD chamber under the growth pressure.

The phase structure and the out-of-plane orientation of the films were studied by θ/2θ scan X-ray diffraction using a Rigaku X-ray diffractometer with a CuKα radiation at λ=1.54 Å. Employing a Philips X’Pert Pro X-ray diffractometer (φ-scan), the in-plane alignment of the films was determined as well. A JEOL-2010F field emission TEM was used to study the atomic and crystallographic arrangements across the interfaces and to confirm the epitaxial growth of the films. A self-made labview program employing a Keithley 2400 sourcemeter was used to study the electrical properties and the SMT behavior of the heterostructures. The measurements were done in a temperature range of 325-355 K where the sample was cooled using a closed cycle helium cryostat.
6.3 Results and discussion

6.3.1 Out-of-plane orientation

The θ/2θ X-ray diffraction pattern of the VO$_2$/NiO/YSZ/Si(001) heterostructure is depicted in Fig. 6.1. The pattern shows that VO$_2$ only grows along its b-axis or c-axis and other orientations are absent. The VO$_2$ peak at 39.8°, which has shifted by ~0.1° from the Bragg's
angle of VO$_2$(020) reflection, may be attributed to either (002) or (020) orientations, since the inter-planar spacing of low temperature monoclinic phase of VO$_2$ along the [010] and [001] orientations are to some extent similar (a=5.743, b=4.517, and c=5.375 Å)$^2$. To distinguish the growth orientation of the VO$_2$ film, φ-scan measurement was conducted on the VO$_2$(010) reflection (2θ=33.39° and ψ=27.8°). This reflection has angular separations of 27.8° from (002) and 90° from (020) planes. No φ-peak was observed when the ψ-angle was set at 27.8° indicating that the XRD peak at 39.8° corresponds to VO$_2$(020) and not to VO$_2$(002). Meanwhile, the absence of any other peaks of vanadium oxide indicates that other phases of vanadium oxide have not been formed. The θ/2θ pattern also shows that the YSZ buffer layers and the NiO films grow along [001] and [111] orientations, respectively.

6.3.2 In-plane orientation

YSZ/Si(001) interface

To study the epitaxial relationship between the YSZ buffer layer and the silicon substrate, φ-scanning XRD was performed on the YSZ(202) reflection at 2θ=50.37° and ψ=45.00° and on the Si(202) reflection at 2θ=47.57° and ψ=45.00° (Fig. 6.2a). As is seen, the φ-peaks from(202) reflections of YSZ and Si appear at the same azimuthal positions due to the 4-fold symmetry in both crystals and their approximately similar lattice parameters (a$_{\text{Si}}$=5.43 and a$_{\text{YSZ}}$=5.14 Å). The epitaxial relationship between the YSZ film and the Si(001) substrate was
explained as a cube-on-cube growth: \( \{001\}_{\text{YSZ}} \parallel \{001\}_{\text{Si}} \) and \( <100>_{\text{YSZ}} <100>_{\text{Si}} \). The atomic arrangement across the YSZ/Si interface was modeled, as shown in Fig. 6.3. The misfit strain across the YSZ/Si interface was calculated as \(~5.3\%\) which is relaxed by alternating of 18/17 and 19/18 domains with a frequency factor of about 0.7, according to the domain matching epitaxy (DME) paradigm.

![XRD patterns](image)

Fig. 6.2 φ-scan XRD pattern acquired from: (a) YSZ(202) and Si(202), (b) NiO(200), and (c) VO₂(011) reflections.

NiO/YSZ interface

The φ-scan XRD was conducted on the (200) reflection of NiO (\(2\theta=43.31^\circ\) and \(\psi=54.24^\circ\)) to
investigate the epitaxial relationship at the YSZ/NiO interface and the results are depicted in Fig. 6.2.b. The appearance of six sharp peaks confirms the epitaxial growth of NiO on the YSZ buffer layer. The presence of these strong peaks with a $30^\circ$ angular separation is attributed to the three-fold symmetry of the NiO structure along the [111] direction and four crystallographically equivalent directions on the cubic YSZ structure which has a four-fold symmetry. Considering these results, the epitaxial relationship between the YSZ and NiO films was expressed to be $(001)_{YSZ}$$\parallel$$[111]_{NiO}$, $(010)_{YSZ}$$\parallel$$[\overline{1}12]_{NiO}$, and $(\overline{1}00)_{YSZ}$$\parallel$$[\overline{1}10]_{NiO}$. The atomic arrangement at the YSZ/NiO interface is modeled and the corresponding results are presented in Fig. 6.4. Because both YSZ buffer layer and NiO films were deposited under the

![Diagram of atomic arrangement](image)

**Fig. 6.3** Atomic arrangement at the: (a) Si(001) surface, (b) YSZ(001) surface, and (c) YSZ/Si interface.
pressure of $5 \times 10^{-4}$ Torr, surface of the YSZ layer would be Zr-terminated (Fig. 6.4a). As a consequence, an O-terminated surface of NiO film grows onto the cation terminated buffer layer. The O-terminated surface of NiO is schematically illustrated in Fig. 4b. The misfit strain at the interface along the a-axis of the YSZ buffer layer was determined as $\varepsilon_1 = 1 - \left( \frac{d_{(100)\text{NiO}}}{d_{(100)\text{YSZ}}} \right) = 42.6\%$ which is fully relaxed through alternating of 3/2 and 2/1 domains with a frequency factor of about 0.34. The misfit strain along the b-axis of the YSZ layer was calculated as $\varepsilon_2 = 1 - \left( \frac{d_{(020)\text{NiO}}}{d_{(020)\text{YSZ}}} \right) = 33.5\%$ which is accommodated by matching of 2 planes of NiO with 1 plane of YSZ or 3 planes of NiO with 2 planes of YSZ domains with a frequency factor of about 0.34. The misfit strain along the b-axis of the YSZ

![Fig. 6.4 Atomic arrangement at the: (a) Zr-terminated YSZ(001) surface, (b) O-terminated NiO(111) surface, and (c) NiO/YSZ interface.](image-url)
layer was calculated as $\varepsilon_2 = 1 - (d_{(112)\text{NiO}}/d_{(020)\text{YSZ}}) = 33.5\%$ which is accommodated by matching of 2 planes of NiO with 1 plane of YSZ or 3 planes of NiO with 2 planes of YSZ where the frequency factor is about 0.99. That is, a kind of a perfect 3/2 matching takes place at the YSZ/NiO interface along the [010] direction of YSZ. Fig. 6.4c shows the atomic arrangement at the YSZ/NiO interface.

**VO$_2$/NiO interface**

The in-plane alignment of the VO$_2$ film was studied by doing $\varphi$-scan XRD on the (011) reflection of VO$_2$ ($2\theta=27.80^\circ$ and $\psi=45.00^\circ$). In this case, six peaks with an azimuthal separation of 30$^\circ$, aligned with the (200) reflection of NiO, were observed (Fig. 6.2c). The
reasons why six φ-peaks were observed are that the VO₂ film has a two-fold symmetry along its b-direction and there are three equally probable variants of VO₂, rotated by 120° from each other, on the NiO(111) platform. Moreover, we already showed that there are four equivalent variants in the NiO film. Based on this information, the epitaxial relationship for the VO₂/NiO/c-YSZ/Si heterostructure is VO₂(010)||NiO(111)||c-YSZ(001)||Si(001) and VO₂[100]||NiO[110]||c-YSZ[100]||Si[100]. Because the oxygen partial pressure was increased from 5×10⁻⁴ Torr (oxygen pressure for NiO deposition) to 1×10⁻² Torr (oxygen pressure for VO₂ deposition), surface of the NiO inner layer gets O-terminated which is illustrated in Fig. 6.5a. Hence, a cation (vanadium) terminated surface of VO₂ (Fig 6.5b) grows onto the NiO film. The atomic arrangement between the NiO and the VO₂ thin films is depicted in Fig. 6.5c. NiO film indicates the in-plane rotation of the grains, as discussed earlier. Such a structure is not observed in the YSZ buffer layer because of the cube-on-cube epitaxial growth. The selected area electron diffraction (SAED) pattern (Inset of Fig. 6.6) shows the diffraction spots from Si[110] and YSZ[110] and NiO[1̅1₀] zones. These results are consistent with details of the epitaxial relationship between Si, YSZ, NiO, and VO₂ that were obtained from X-ray diffraction studies.

6.3.3 Semiconductor to metal transition

Fig. 6.7 shows the electrical resistance of the VO₂/NiO/YSZ/Si(001) heterostructure as a function of the temperature where a semiconductor to metal transition (SMT) is observed at
about 341 K which is close to the transition temperatures reported for the bulk VO$_2$. The SMT characteristics are excellent in terms of amplitude of the resistance change ($10^5$ Ω) and the sharpness of the transition region (~3.4 K hysteresis). Such a shift of transition towards that of the bulk VO$_2$ is attributed to strain relaxation along c-axis of VO$_2$. This was achieved by complete relaxation of misfit strain across the VO$_2$/NiO interface resulting in a negligible
tension or compression along the c-axis of VO$_2$. The small width of the transition hysteresis reveals growth of the high quality VO$_2$ films with negligible defect content.

Fig. 6.7 Resistance as a function of the temperature for the VO$_2$/NiO/YSZ heterostructure. Temperature for the VO$_2$/NiO/YSZ heterostructure.
6.4 Conclusion

The VO$_2$/NiO/YSZ epitaxial thin film heterostructures were grown on Si(001) substrates. The epitaxial relationship at the YSZ/Si(001) interface was determined as (001)[100]$_{YSZ}$//(001)[100]$_{Si}$. The epitaxial relationship between the YSZ buffer layer and the NiO thin film was written as (001)[010]$_{YSZ}$//(111)[$\bar{1}$1$\bar{2}$]$_{NiO}$. The epitaxial relationship across the NiO/VO$_2$ interface was expressed as (010)[001]$_{VO_2}$|(111)[$\bar{1}$$\bar{1}$2]$_{NiO}$. All of the proposed epitaxial relationships were confirmed by TEM diffraction pattern. A sharp and near bulk SMT was observed at about 341 K with amplitude over five order of magnitude and 3.4 K hysteresis. This is consistent with near complete relaxation of stress in thin films. Such epitaxial structure integrated with Si(100) can be used to enhance functionality and obtain smart devices that are quite reliable due to the absence of initial strains/stresses.
6.5 References


Chapter 7. Diamagnetic to ferromagnetic switching in VO$_2$
epitaxial thin films by nanosecond excimer laser treatment

In this chapter the integration of VO$_2$(010)/NiO(111) epitaxial heterostructures with Si(100) substrates using a cubic yttria-stabilized zirconia (c-YSZ) buffer was studied where the diamagnetic behavior of epitaxial VO$_2$ was changes to ferromagnetic behavior via nanosecond laser treatment. The epitaxial alignment across the interfaces was determined to be VO$_2$(010)||NiO(111)||c-YSZ(001)||Si(001) and VO$_2$(100)||NiO(110)||c-YSZ(100)||Si(100). The samples were subsequently treated by a single shot of a nanosecond KrF excimer laser. Pristine as-deposited film showed diamagnetic behavior, while laser annealed sample exhibited ferromagnetic behavior. The population of majority charge carriers (e$^-$) and electrical conductivity increased by about two orders of magnitude following laser annealing. These observations are attributed to the introduction of oxygen vacancies into the VO$_2$ thin films and the formation of V$^{3+}$ defects.

7.1 Introduction

Future progress in electronic and spintronic industries will require high performance multifunctional devices. This will necessitate precise control over electrical, magnetic, and
optical properties which can be achieved only by synthesis of high quality materials and complete understanding of the correlation between microstructure and properties. The fabrication of spintronics devices, where both charge and spin functionalities are utilized, could revolutionize the technology by providing improved efficiency, reduced power consumption, high boot-up speed, and data retention in the power-down state. One way of combining both spin and charge states of the carriers in a device is to incorporate magnetic semiconductors. To achieve this goal, different materials have been extensively studied. In this contest oxide semiconductors such as ZnO, TiO$_2$, Y$_2$O$_3$, and In$_2$O$_3$ have shown promising results at room temperature.

VO$_2$ is a strongly correlated electron system with a small band gap (~0.7 eV at room temperature). However, its magnetic properties have not been studied. VO$_2$ belongs to the class of smart materials, which generally react to temperature variations, electric or magnetic fields, and pressure variations. This material is well-known for its semiconductor-to-metal transition (SMT) at about 68 °C. The SMT observed in VO$_2$ originates from an ultrafast phase transformation from a high temperature tetragonal state to a low temperature monoclinic state. At the transition temperature, the material undergoes changes in the electronic band structure associated with atomic rearrangement from the more symmetric tetragonal (P4$_2$/mnm) phase to the less symmetric monoclinic (P2$_1$/c) phase.$^{6-8}$

Our group has been able to tune in a controlled way the electrical, optical, magnetic, and photochemical properties of TiO$_2$, ZnO, and NiO [11] epilayers via laser treatment. It has
been shown that coupling of high energy laser beam with these oxides gives rise to the introduction of point defects, particularly oxygen vacancies, which, in turn, introduces after defects and alters the physical and chemical characteristics of the material. We believe that the laser energy is absorbed by the electronic excitation in the oxides that leads to oxygen vacancies form cation through the following reactions:

\[ \text{MO}_x + h\nu \rightarrow e^- + h^+ \]  \hspace{1cm} (7-1)

\[ \text{O}^{2-} + 2h^+ \rightarrow \frac{1}{2}\text{O}_2 + \text{Oxygen Vacancy} \]  \hspace{1cm} (7-2)

Simultaneously, other point defects, such as interstitials, must form to preserve the charge neutrality. In addition to this athermal formation mechanism, oxygen vacancies might form by a thermal mechanism where the temperature of the surface is increased due to the coupling of the high energy laser beam leading to reduction of the oxide and formation of oxygen vacancies.

In chapter 6, the growth of fully relaxed VO\(_2\) epilayers with a near bulk SMT temperature on NiO platform by using cubic yttria-stabilized zirconia (c-YSZ) as a buffer layer on Si(100) substrate was reported. This study focuses on the generation of point defects into the VO\(_2\) lattice by nanosecond laser annealing. We show that the diamagnetic behavior of as-deposited sample changes to ferromagnetic behavior and the concentration of charge carrier
increases after laser treatment. These findings might introduce VO$_2$ as interesting candidate for spintronic applications where both semiconducting and ferromagnetic behavior are required, in addition SMT characteristics.

7.2 Experimental

Epitaxial VO$_2$/NiO/c-YSZ thin film heterostructures were grown on Si(100) substrates employing pulsed laser deposition (PLD). A Lambda Physik (LPX200) KrF excimer laser, with $\lambda = 248$ nm and $\tau = 25$ ns, was used to ablate the targets and, also, for subsequent laser annealing of the samples. The laser beam was incident at an angle of $45^\circ$ on the surface of the targets which were rotated during the deposition to provide uniform ablation characteristics of the target surface. The laser energy density and repetition rate were set at 3.0-3.5 J.cm$^{-2}$ and 5 Hz for all layers. The c-YSZ buffers were deposited at 750 $^\circ$C. The first 1000 pulses were prepared in vacuum followed by another 1000 pulses deposited under an oxygen pressure of 5×10$^{-4}$ Torr. The NiO layers were then deposited at 700 $^\circ$C under an oxygen partial pressure of 5×10$^{-4}$ Torr for 3000 pulses. Finally, VO$_2$ films were grown on the NiO/c-YSZ platforms under a pressure of 5×10$^{-2}$ Torr for 4000 pulses at 500 $^\circ$C. A single-spot Excimer laser treatment was performed at room temperature laser energy density of 0.35 J.cm$^{-2}$.

A Rigaku diffractometer with Cu-K$\alpha$ radiation ($\lambda=0.154$ nm) was used to study the out-of-plane orientation of the films. A JEOL 2010F transmission electron microscope with 0.18 nm
resolution and a Gatan image filter (GIF) attachment was used for microstructural studies and acquiring selected area electron diffraction patterns. The microscope was operated at 200 kV. Stoichiometry of the samples was investigated by X-ray photoelectron spectrometry using SPECS tool equipped with Mg-Kα source (λ=1254 eV) and a PHOIBIS 150 hemispherical analyzer. The results were interpreted by SDP 4.1 software where the C(1s) core level binding energy was set at 285.0 eV as a reference to compensate for surface charging effects. The influence of laser treatment on the concentration of charge carriers and electrical conductivity was studied by Hall measurement. The measurements were conducted at room temperature under a magnetic field of 0.55 T (5500 Oe). Magnetic-field dependent magnetization (M-H) measurements were carried out using a physical property measurement system (PPMS) in conjunction with an Evercool-2 vibrating sample magnetometer (VSM) attachment (Quantum Design). For magnetization measurements, rectangular sample strips of 3 mm x 4 mm were used. Hysteresis measurements were performed by scanning the magnetic field from -10 to +10 kOe at different temperatures; viz., 10, 100 and 300K. The magnetic field was applied parallel to the film plane. Great care was exercised not to contaminate the samples by handling the samples with non-magnetic plastic tweezers.
7.3 Results and discussion

XRD 0-2θ spectra of as-deposited and laser annealed samples are shown in Fig. 7.1. In both cases, the films are single-phase monoclinic (M\textsubscript{1}) VO\textsubscript{2} a unique [020] out-of-plane orientation. No new vanadium oxide phase or grain orientation formed as a result of laser

Fig. 7.1 XRD 0-2θ scans from: (a) pristine and (b) laser annealed VO\textsubscript{2} thin films. The inset shows high resolution scans of the VO\textsubscript{2}(020) reflection.
treatment. As is seen in high resolution scans of the VO$_2$(020) reflection, the peak shifted slightly toward lower 2θ values. This shift is attributed to the interaction of point defects during the laser treatment since these defects change the inter-planar spacing. Because the VO$_2$(020) peak shifted toward lower 2θ values, it is deduced that the formation of defects shoulder on the left hand side of the VO$_2$ peak in the high resolution 0-2θ pattern of the annealed sample (inset of Fig.1). We ascribe this shoulder to the near surface region, of the VO$_2$ film, which was melted and quenched during its laser anneal leading to a high concentration of vacancies and therefore a significantly different inter-planar spacing from that of the pristine region. A low magnification cross-section TEM image and the corresponding selected area electron diffraction pattern from the laser annealed VO$_2$ thin film is shown in Fig. 7.2. The laser affected region is clearly observed near the surface of the sample. It is seen that the interface between the pristine and laser irradiated VO$_2$ is flat and parallel to the surface. The SAED pattern shown in the inset following the relation of the film and substrate confirms the epitaxial growth and, more importantly, reveals that the initial monoclinic structure and single crystalline nature of the VO$_2$ thin film has been preserved after laser annealing. Taking the 0-2θ and SAED patterns into consideration, the epitaxial relationship for the VO$_2$/NiO/c-YSZ/Si heterostructure is $\text{VO}_2$(010)||NiO(111)||c-YSZ(001)||Si(001) and $\text{VO}_2[100]||\text{NiO}[110]||c-\text{YSZ}[100]||\text{Si}[100]$.

The XPS was used to study the effect of laser treatment on stoichiometry and defect structure of the samples. High resolution scans performed through V(2p$_{3/2}$) core level, for the as-deposited and annealed samples, are shown in Fig. 7.3. The results indicate that the
concentration of the $V^{4+}$ species decreased by $> 15\%$ and that of $V^{3+}$ species increased after laser treatment. In fact, no the $V^{3+}$ cation was detected in the pristine as-deposited sample. It is surmised that coupling of the high energy laser beam with the material drives oxygen out of VO$_2$ thin films resulting in the formation of oxygen vacancies. The formation of oxygen vacancies

![Laser annealed region](image)

Fig. 7.2 Low magnification cross-section TEM micrograph taken from the laser annealed VO$_2$/NiO/c-YSZ/Si heterostructure. In the SAED pattern, shown in the inset, the Si(004), c-YSZ(004), NiO(111), and VO$_2$(020) reflections are denoted by S, Y, N, and V letters, respectively.
Fig. 7.3 V(2p_{3/2}) core level binding energy in pristine and laser annealed samples.
vacancies is accompanied by the release of electrons to the lattice which are subsequently trapped by $V^{4+}$ cations to preserve charge neutrality. This phenomenon results in the formation of $V^{3+}$ cations. The formation of oxygen vacancies and $V^{3+}$ species can be explained by the following reaction:

$$2\text{VO}_2 \rightarrow \text{V}_2\text{O}_3 + \text{V}_0^- + 2e^-$$

(7-3)

where $\text{V}_0^-$ represents an oxygen vacancy. This reaction stipulates that the laser annealed VO$_2$ thin films has a higher charge carrier concentration ($e^-$) and must exhibit a lower resistivity in the semiconducting state. Carrier concentration and resistance of the pristine and laser annealed samples was measured by Hall technique. It was found that the carrier concentration increased from $5.3 \times 10^{17}$ to $7.4 \times 10^{19}$ cm$^{-3}$ and resistivity decreased from $2.6 \times 10^1$ to $1.8 \times 10^{-1}$ Ω.cm after the laser treatment.

Fig. 7.4 shows room temperature magnetization curves as a function of applied magnetic field were collected for both pristine and laser annealed VO$_2$ thin films and the corresponding results are presented. Data were smoothed by using a 10-point Savitzky-Golay procedure. The diamagnetic contribution of the substrate was subtracted from the data using the negative slope of the high-field data. As is observed, the pristine sample shows diamagnetic behavior which turned ferromagnetic after laser treatment. The inset displays the magnified M-H loops.
Fig. 7.4 The isothermal field dependence of magnetic moment curves of laser annealed VO$_2$/NiO/c-YSZ films deposited on Si(100) substrates measured at 10, 100 and 300 K. Plotted in the bottom inset are the low field M-H hysteresis loops between ± 500 Oe deciphering clearly the coercivity. The diamagnetic contribution due to the Si substrate has been subtracted. The coercivity increases from ~60 Oe at RT to 250 Oe at 10K. The top inset plot shows the diamagnetic behavior of the pristine VO$_2$/NiO/c-YSZ/Si(100) sample.

for the annealed sample, which clearly show the presence of hysteresis that is characteristics of ferromagnetic behavior. We already showed that the crystalline structure, phase structure, and growth orientation of VO$_2$ thin films remained unaltered after laser annealing. In addition, the XPS survey scan (Fig. 7.5) showed similar elemental compositions and the
absence of magnetic impurity elements in the two VO\textsubscript{2} samples, i.e. pristine and annealed samples. As a consequence, the change in magnetic behavior is attributed to the formation of oxygen vacancies or V\textsuperscript{3+} defects with unpaired electrons. Therefore, the formation oxygen vacancies or non-stoichiometric oxidation state of vanadium in VO\textsubscript{2} are envisaged to be responsible for the observed room-temperature ferromagnetic characteristics.

Fig. 7.5 XPS survey scan acquired from the pristine and the laser annealed VO\textsubscript{2} epilayers.
7.4 Conclusion

Epitaxial VO$_2$(010)/NiO(111)/c-YSZ(100) heterostructures have been integrated Si(100) substrates with the epitaxial relationship VO$_2$(010)//NiO(111)//c-YSZ(001)//Si(001) and VO$_2$(100)//NiO(110)//c-YSZ(100)//Si(100). The VO$_2$ top layers were subsequently annealed by a single pulse from a KrF excimer laser. The crystalline structure of VO$_2$ thin films remained unchanged after laser treatment. However, the formation of oxygen vacancies and V$^{3+}$ species was confirmed. While the pristine sample showed diamagnetic behavior, a ferromagnetic behavior was observed in the laser annealed sample. The electrical conductivity and charge carrier concentration were increased significantly by laser treatment. All these changes in electrical and magnetic properties were envisaged to stem from the presence of point defects.
7.5 References


Chapter 8. A microstructural approach toward the effect of thickness on semiconductor-to-metal transition characteristics of VO$_2$ epilayers

In this chapter the control of semiconductor to metal transition in VO$_2$(010) epilayers integrated with Si(100) substrates buffered with an NiO[111]/YSZ[100] intermediate layer is reported. VO$_2$ epitaxial thin films were grown at different thicknesses varying from 10 to 200 nm using pulsed laser deposition technique. An epitaxial relationship of VO$_2$(010)||NiO(111)||YSZ(001)||Si(001) and VO$_2$(100)||NiO[110]||YSZ[100]||Si[100] was established at room temperature. The crystallographic alignment across the VO$_2$/NiO interface changes to VO$_2$(100)||NiO(111) and VO$_2$(001)||NiO[110] at the temperature of growth giving rise to a misfit strain of about 33.5% and 3.0% along two orthogonal in-plane orientations. The transition temperature was observed to vary from about 353 to 341 K, the transition amplitude increased by about five orders of magnitude, and the hysteresis decreased to about 3 K, as the thickness of VO$_2$ layers increased from about 10 to 200 nm. These observations were explained based on strain characteristics, overall defect content and grain boundaries, and phenomenological thermodynamic models.
8.1 Introduction
Vanadium dioxide (VO₂) exhibits a reversible sharp semiconductor-to-metal transition (SMT) at near room temperature (~ 341 K) where the crystal structure changes from monoclinic to tetragonal phase across the transition temperature making it a potential candidate for sensors,¹,² memory devices,³ switches,⁴,⁵ thermal relays and energy management devices,⁶,⁷ and thermal actuators.⁸ SMT is a first-order phase transition as there is a break in entropy corresponding to the structure of the low temperature monoclinic (M₁) and high temperature tetragonal (Rutile, R) phases.⁹,¹⁰ The transition involves a small lattice distortion along the c-axis of the tetragonal state, which results in dimerization of vanadium atoms and a distinct band structure in M₁ phase. These lattice distortions lead to a failure of bulk single crystals, when subjected to repeated heating/cooling cycles. That is the reason why thin films, being able to withstand the distortions and dissipate heat through the substrate, are critical to a wide range of technological applications¹¹-¹³. Strain plays an important role in the SMT of VO₂ and induces another monoclinic structure of VO₂, i.e. M₂ phase¹⁴. In M₂ structure, only half of the vanadium atoms dimerize, while the other half form zigzag chains. This has been observed in Cr-doped VO₂ samples.¹⁵,¹⁶ Recent experiments show more evidence that under certain strain state, M₂ can act as a transitional structure for the phase transition from M₁ phase to rutile phase.¹⁷-²¹ Working on an ensemble of single-crystal VO₂ nanowires with in situ synchrotron XRD, the complicated phase diagram covering all three phases (M₁, M₂ and rutile) over a wide range of strain has been mapped
It was found that when the VO\textsubscript{2} layer is under tensile strain, two transformation sequences may occur with increasing and decreasing temperature:

**Heating:** \( M_1 \rightarrow M_2 + R \rightarrow R \) \hspace{1cm} (8-1)

**Cooling:** \( R \rightarrow M_2 + R \rightarrow M_1 + R \rightarrow M_1 \) \hspace{1cm} (8-2)

When the VO\textsubscript{2} film is either relaxed or under a compressive strain, the transformation sequence upon cooling and heating is:

\( R \leftrightarrow M_1 \) \hspace{1cm} (8-3)

SMT characteristics of VO\textsubscript{2} are strongly correlated with the strain in the films. According to equations (8-1) and (8-2), when the film is under a tensile stress, with increasing temperature, the \( M_1 \) state of VO\textsubscript{2} initially experiences a phase transformation to the \( M_2 \) intermediate phase, before the final conversion to the metallic phase (R). The presence of \( M_2 \) phase which shows higher carrier activation energy, results in wider hysteresis (\( \Delta H \)) in the films under tensile stress. Hysteresis associated with the SMT defined as the difference in the transition
temperatures during heating and cooling cycles. Higher SMT temperatures are observed in the films under larger strains in comparison to relaxed or low strained films. This is due to strain along c-axis of tetragonal VO$_2$ or a-axis of monoclinic VO$_2$.

Previous works on epitaxial VO$_2$ thin films focused on c-sapphire, r-sapphire, m-sapphire, and Si(100) substrates with yttria-stabilized zirconia (YSZ) buffer layers under the paradigm of domain epitaxy.$^{22-25}$ However, fabrication of high quality VO$_2$ thin films with desirable properties requires good control over the epitaxial growth procedure, as the SMT characteristics of VO$_2$ thin films are known to be a strong function of epitaxial characteristics, defects, microstructure, residual strain, and stoichiometry.$^{26-32}$ Control and reproducibility in the growth of high-quality, single phase VO$_2$ films is also a challenging task because of a large number of stable vanadium oxide crystalline phases that can form in a very narrow range of composition.$^{33}$ In depth understanding of nature of the grain boundaries and their orientation, grain size and distribution, and defect content in modification of SMT characteristics of VO$_2$ thin films, including sharpness, amplitude, width, and hysteresis, is of critical importance for the technological applications.$^{34,35}$ The SMT properties can be adjusted based on the requirement for practical applications. For sensor devices, a sharp SMT transition associated with large changes in electrical and optical properties will lead to a higher sensitivity and efficiency, and smaller hysteresis will result in superior temperature response between the heating and cooling cycles of vanadium oxide films.$^{36}$ The reliability and efficiency of vanadium oxide based devices require the SMT to have a minimum hysteresis and a relatively sharp transition to operate these devices reliably. On the other
hand, for optical memory-type applications, a hysteresis width of 15-20 °C is needed. In both of these regimes, defect nature, and distribution of grain boundaries and other defects play a crucial role. \(^{37}\)

In this chapter, we integrated epitaxial VO\(_2\)(010)/NiO(111) thin film heterostructures of varying thicknesses with silicon substrates where cubic yttria-stabilized zirconia (c-YSZ) was used as a buffer. The epitaxial relationships across the interfaces, in particular VO\(_2\)/NiO interface, were established at room temperature, and at growth temperature of 500 °C. The strain relations and its effect on SMT characteristics are discussed. The effect of thickness on the SMT characteristics of VO\(_2\) epilayers is investigated with a special emphasis on the microstructure where the control of overall defect content and the characteristics of domain boundaries are discussed based on phenomenological thermodynamic models.

8.2 Experimental

Pulsed laser deposition (PLD) technique was employed to grow VO\(_2\) epitaxial thin films with several thicknesses on an NiO(111)/c-YSZ(100)/Si(100) platform where a Lambda Physik (LPX200) KrF excimer laser (\(\lambda = 248\) nm and \(\tau = 25\) ns) was used to ablate the VO\(_2\), NiO, and cubic zirconia (stabilized by 8-10 mol% yttria) targets. A special target holder with carrousel was used to rotate the targets during the deposition to have a uniform ablation and also to switch between the targets enabling us to deposit multilayers without breaking the
vacuum in the chamber. The c-YSZ buffers were deposited at 750 °C with 1000 pulses in vacuum and 1000 pulses under an oxygen pressure of 5×10⁻⁴ Torr. Zirconia reacts with the SiOₓ native oxide layer on the silicon substrate and effectively removes it. This provides a single crystal platform for the growth of subsequent layers. Subsequently, NiO layers were deposited at 700 °C under an oxygen partial pressure of 5×10⁻⁴ Torr using 3000 pulses. The VO₂ layers, with varying thicknesses, were grown on the NiO intermediate layers under an oxygen pressure of 5×10⁻² Torr at 500 °C. The thickness of the VO₂ thin films were controlled via adjusting the number of pulses between 500, 1000, 2000, 3000, 4500, and 6000. The laser energy density and repetition rate for all layers were set at 3.0-3.5 J.cm⁻² and 5 Hz, respectively.

Out-of-plane orientation of the VO₂/NiO/c-YSZ heterostructures was determined by a Rigaku diffractometer equipped with a copper X-ray source (Kα radiation: λ=0.154 nm). JEOL 2010F (operated at 100 kV) transmission electron microscope with a 0.18 nm resolution and Gatan image filter (GIF) attachment was utilized to acquire cross-section images and selected area electron diffraction (SAED) patterns. These studies were used to confirm the epitaxial growth, investigate the crystallographic alignments across the interfaces, and measure the thickness of VO₂ films. The semiconductor-to-metal transition (SMT) characteristics of the heterostructures were investigated by a Keithley 2400 sourcemeter and labview program. These measurements were done in the temperature range of 310-380 K. The samples were cooled using a closed-cycle helium cryostat and heated by a coiled resistive heater.
8.3 Results and discussion

Fig. 8.1 shows θ-2θ patterns taken from the VO$_2$/NiO/c-YSZ/Si heterostructures, where the top VO$_2$ layer was deposited using different numbers of laser pulses. A single out-of-plane orientation is observed for all layers. As is seen, VO$_2$, NiO, and c-YSZ layers grow such that their (010), (111), and (100) planes are parallel to Si(100) planes, respectively. It is worth mentioning that the signal from VO$_2$ can be assigned to either (020) or (002) reflection of monoclinic (M$_1$) state of VO$_2$; with the aid of φ-scan XRD and detailed TEM studies, in our previous works$^{24,25}$, we unambiguously determined that this signal has its origin in (020) family of planes. The VO$_2$(020) signal intensifies as the number of pulses increase. This is because a thicker VO$_2$ thin film grows when the deposition is done at higher number of pulses or, in other words, for longer times. It was found that the full width at half maximum (FWHM) of the VO$_2$(020) peak decreases when the deposition time gets longer. This is because larger sub-grains form, as the deposition time is prolonged, due to the grain growth phenomenon whose driving force is decreasing the grain boundaries and, therefore, decreasing the Gibb’s free energy of the system. In epilayers, all grains, within a domain, have the same in plane and out-of-plane orientations and are separated by low angle boundaries which are atomically sharp and crystallographically continuous. The formation of larger grains in thicker layers was further ascertained by the AFM 2D images shown in Fig. 8.2.
Fig. 8.1 XRD θ-2θ patterns acquired from the VO₂/NiO/c-YSZ/Si thin film heterostructures for different number of VO₂ pulses: (a) 500, (b) 1000, (c) 2000, (d) 3000, (e) 4500, and (f) 6000 pulses.
High resolution θ-2θ scans conducted on VO$_2$(020) reflection (Fig. 8.3) show that the peaks do not shift, as the thickness changes, so it can be deduced that the strain content within the grain of the films does not change and, therefore, the change in FWHM is attributed to the change in the grain size (defect content).

Bright-field cross-section TEM micrographs of the VO$_2$(010)/NiO(111)/c-YSZ(100)/Si(100) heterostructures as well as their corresponding SAED patterns are displayed in Fig. 8.4 From the cross-section images, the thickness of the VO$_2$ epilayers grown for 500, 1000, 2000, 3000, 4500, and 6000 shots was determined and the results are presented in Tab. 8.1. The different characteristics of the SAED patterns confirm the epitaxial nature of thin films. Indexing these patterns and considering the information from Fig. 8.1, the crystallographic alignment across the interfaces was established to be VO$_2$ (010)||NiO(111)||c-
YSZ(100)||Si(100) and VO$_2$(100)||NiO[110]||c-YSZ[100]||Si[100]. It should be noted that this epitaxial relationship is found at room temperature where VO$_2$ exists in its monoclinic state.

To calculate the lattice misfit strains as well as to understand the relaxation mechanism of changes to the c-axis of tetragonal VO$_2$ and b-axis of monoclinic VO$_2$ changes to a-axis of tetragonal VO$_2$. With this information, the established epitaxial relationship at room temperature was modified for the temperature of growth. Fig. 8.5a and Fig. 8.5b

Fig. 8.3 High resolution 0-2θ scans through VO$_2$(020) signal acquired from the VO$_2$ epilayers with different thicknesses.
Fig. 8.4 Cross-section TEM images and corresponding selected area electron diffraction patterns obtained from the VO$_2$/NiO/c-YSZ/Si heterostructures for different VO$_2$ thicknesses: (a) 10, (b) 30, (c) 70, (d) 100, (e) 150, and (f) 200 nm.
schematically illustrate the $\text{VO}_2,\text{monoclinic}/\text{NiO}(111)$ and $\text{VO}_2,\text{tetragonal}/\text{NiO}(111)$ interfaces, respectively. Based on Fig. 8.5a, there is a 2.37% tensile strain in monoclinic $\text{VO}_2$ unit cell along its $a$-axis. Meanwhile, Fig. 8.5b shows that the $c$-axis of tetragonal $\text{VO}_2$ experiences a tensile strain of about 3.05%. Such small misfit strains are difficult to relax. The misfit strains relax when the growing film reaches a critical thickness. The critical thickness is the thickness at which it becomes energetically favorable for the film to contain dislocations, and lowers its energy. As soon as the thickness of the $\text{VO}_2$ epilayer reaches the critical thickness, the misfit dislocations nucleate at the free surface of the film and propagate toward the $\text{VO}_2/\text{NiO}$ interface to relax the strain. In small misfit systems, the critical thickness is large, so the dislocations face barriers to glide and reach the interface, even though they nucleate at the surface. In the case of ultrathin $\text{VO}_2$ films where the thickness is below the critical thickness, the epilayer cannot accommodate misfit dislocations and remains under a tensile strain along the $a$-axis of monoclinic or $c$-axis of tetragonal phases. Based on Fig. 8.5b, $\text{VO}_2(020)$ planes are parallel with $\text{NiO}(\bar{1}\bar{1}2)$ planes and both of them are normal to the interface. The inter-planar spacing of $\text{VO}_2(020)$ and $\text{NiO}(\bar{1}\bar{1}2)$ planes are considered as 2.27 

<table>
<thead>
<tr>
<th>No. of Pulses</th>
<th>500</th>
<th>1000</th>
<th>2000</th>
<th>3000</th>
<th>4500</th>
<th>6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>10</td>
<td>30</td>
<td>70</td>
<td>100</td>
<td>150</td>
<td>200</td>
</tr>
</tbody>
</table>
Å and 1.7 Å leading to a -33.53% misfit strain. This strain is compressive in the VO$_2$ layer and relaxes via matching of 2 VO$_2$(020) with 3 NiO(112) planes and 3 VO$_2$(020) with 4 NiO(112) planes with a frequency factor of about 0.98, based on the domain matching epitaxy paradigm.$^{39}$

Fig. 8.5: Schematic delineation of: (a) VO$_2$,$\text{monoclinic}/\text{NiO}$ and (b) VO$_2$,$\text{tetragonal}/\text{NiO}$ interfaces.

Electrical properties of the VO$_2$/NiO/c-YSZ/Si epitaxial heterostructures, where the VO$_2$ top layer has different thicknesses, are depicted in Fig. 8.6. All samples clearly show a semiconductor to metal transition behavior. Fig. 8.7 summarizes the SMT parameters, namely transition temperature, hysteresis, and amplitude, as a function of thickness. A correlation between the SMT properties and microstructure was established based on the phenomenological thermodynamic model by Narayan et. al.$^{40}$ The results show that the SMT
takes place at temperatures higher (353 K) than 341 K in the film grown for 500 pulses. The SMT temperature decreases and reaches to the bulk transition temperature, as the thickness increases. As it was already manifested, the a-axis of monoclinic (M₁) VO₂ (or, in other words, c-axis of tetragonal VO₂) is under a tensile strain in un-relaxed samples. Larger V⁴⁺-V⁴⁺ spacing along the c-axis results in a large activation barrier for direct overlapping of d-orbitals which, in turn, stabilizes the covalent monoclinic phase and hinders the phase transformation of low temperature monoclinic phase to high temperature rutile phase. This is the reason why SMT for these samples was observed at above 341 K. In contrast, the SMT takes place at lower temperatures, if the V⁴⁺-V⁴⁺ distance decreases due to a compressive residual strain along the c-axis of tetragonal VO₂. As the thickness increases, beyond the critical thickness, the misfit strain relaxes and a fully relaxed film, with an SMT close to 341 K, is obtained; a very small deviation from the bulk transition temperature originates from the temperature and defect-related strains which are very small and, therefore, very hard to relax.

Fig. 8.7 shows that the SMT hysteresis monotonically decreases with the film thickness. Our XRD and AFM investigations clearly showed that the grain size increases, as the films get thicker. Considering the single crystalline nature of our VO₂ films having crystallographically equivalent domains separated by atomically sharp and crystallographically continuous boundaries, it can be suggested that the interfacial energy (γ) is almost constant in all samples. If ΔGₚ (= ΔTᵣΔS₀) is assumed to be the change of Gibbs free energy during the phase transition between monoclinic and tetragonal VO₂, critical size
Fig. 8.6: Changes of resistance versus temperature for VO$_2$ epilayers at different thicknesses. A semiconductor to metal transition (SMT) is clearly observed.

of a stable nucleus will be $r_c = \frac{2\gamma}{\Delta G_r}$, where $\gamma$ is the interfacial energy, $\Delta T_r$ is the deviation from the equilibrium transition temperature, and $\Delta S_o$ is the change in entropy between monoclinic
and tetragonal VO$_2$. The Gibbs free energy zero at the transition temperature, however away from the transition, there is driving force for phase transition given by $\Delta G_r$. The SMT hysteresis ($\Delta H$) can be directly related to $\Delta T_r$ and we know that $\Delta T_r = \frac{2\gamma}{r_c\Delta S_0}$. Consequently, the hysteresis decreases with increasing $r_c$ at a constant $\gamma$. The amplitude of the transition ($\Delta A$) is controlled by the concentration of the defects, including vacancies, interstitials, clusters, impurities, dislocations, and grain-boundaries as well as crystalline nature of the films. As it was already confirmed by SAED patterns (Fig. 8.4), all samples in this study have a single crystalline nature. The VO$_2$ films with smaller grains contain a larger density of grain boundaries which results in a narrower amplitude of the transition. The amplitude increases as grain size increases, because the density of grain boundaries decreases. The SMT width or sharpness ($\Delta T$) is also influenced by the overall defect content per unit volume. The sharpness ($1/\text{width}$) is inversely proportional to $C_t\rho_d$, where $C_t$ is a constant and $\rho_d$ is density of the defects. Fig. 8.7 shows that the transition width decreases as the grain size increases, because the number of defective sites per unit volume associated with grain boundaries decreases. Another reason for the narrower SMT width in thick layers compared to the thin layers is the smaller compressive strain along the a-axis of the M$_1$ phase. It has been shown that$^{21}$ the SMT in VO$_2$ obeys reaction in equation (8-3) under smaller compressive strain values, while equations (8-1) and (8-2) when VO$_2$ experiences larger tensile strains. As we discussed earlier, the VO$_2$ epilayer is under larger strains when the thickness is smaller than the critical thickness. This gives rise to the stabilization of M$_2$ phase and, as a consequence, a wider hysteresis. The narrow width in the thick VO$_2$ layers has its
origin in the small residual strain leading to the formation of less M$_2$ phase, and transition directly from rutile to M$_2$ as shown in equation (8-3).

Fig. 8.7 A summary of SMT parameters of VO$_2$ epitaxial thin films with several thicknesses.

8.4 Conclusions

We were able to integrate epitaxial VO$_2$(010)/NiO(111) thin film heterostructures with silicon substrates buffered with cubic yttria-stabilized zirconia (c-YSZ). The crystallographic alignments across the interfaces were established to be VO$_2$(010)||NiO(111)||YSZ(001)||Si(001) and VO$_2$[100]||NiO[110]||YSZ[100]||Si[100] at
room temperature. An epitaxial relationship of VO$_2$(100)||NiO(111) and VO$_2$(001)||NiO[110] was written for VO$_2$/NiO interface at the temperature of growth. The effect of thickness on SMT characteristics was investigated. It was found that the transition temperature decreases from about 353 to 341 K, the transition magnitude increased by about five orders of magnitude, and the hysteresis decreased to about 3 K, as the thickness of VO$_2$ layers increased from about 10 to 200 nm. A structure-property correlation was established based on the overall defect content and number densities of grain boundaries.
8.5 References


Chapter 9. Semiconductor to metal transition characteristics of VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) epitaxial heterostructures

In this chapter a correlation between microstructure and semiconductor to metal transition (SMT) characteristics of VO$_2$(011) single crystalline thin films integrated with Si(100) substrates buffered with NiO/MgO/TiN intermediate layers is reported. The epitaxial relationship across the interface between monoclinic VO$_2$ and NiO is determined to be (011)$_{\text{VO}_2}$||(100)$_{\text{NiO}}$ and [0$\overline{1}$1]$_{\text{VO}_2}$||[001]$_{\text{NiO}}$ at room temperature. The epitaxial alignment at the temperature of growth where tetragonal VO$_2$ is stable is written as: (110)$_{\text{VO}_2}$||(100)$_{\text{NiO}}$ and [001]$_{\text{VO}_2}$||[100]$_{\text{NiO}}$. A cube-on-cube crystallographic alignment is established across the NiO(100)/MgO(100)/TiN(100)/Si(100) interfaces. The misfit strains across the VO$_2$/NiO interface at the growth temperature are calculated and the mechanism of strain relaxation is discussed. It is shown that the compressive strain of about 31.73% along the [001] direction of tetragonal VO$_2$ is fully relaxed via matching of multiple domains leading to a near bulk SMT temperature. Microstructure of the samples at elevated temperature is investigated in detail by high resolution high temperature X-ray diffraction. A compressive strain along the out-of-plane orientation is found to be present in both monoclinic and tetragonal phase of VO$_2$ originating from an unrelaxed misfit strain along [0$\overline{1}$1] in-plane direction of tetragonal VO$_2$. SMT characteristics of VO$_2$(011) epilayers are assessed where a near bulk transition temperature, an amplitude of near five orders of magnitude, and a hysteresis of below 4 °C
are obtained. This study introduces VO$_2$/NiO thin film heterostructure integrated with silicon chip as a promising candidate for multifunctional devices with novel characteristics where a combination of various properties of two crystals is required.

9.1 Introduction

Several oxides of vanadium undergo a transition from a semiconductor or insulating state to a metal phase at a critical temperature.$^{1-5}$ Vanadium dioxide undergoes this transition near 68°C as it transforms from a low temperature monoclinic structure to a high temperature tetragonal structure.$^{6-9}$ There is no extensive rearrangement of the atoms, only a slight distortion of the original atomic grouping, which is rapidly reversible at $T_c$, the transition temperature. The change in oxide crystal structure is accompanied by strong change in the electrical resistivity and optical behavior at the transition temperature.$^{10-14}$ Most VO$_2$ thin films demonstrate a transition of electrical resistance by as much as $10^3$-$10^4$ at 68 °C with a thermal hysteresis of 2-5 °C upon heating up and cooling down. Since the magnitude of the resistivity change and the narrowness of the hysteresis are very sensitive to the stoichiometry and the crystalline structure of the VO$_2$ thin film, these parameters are good indicators of its quality.$^{15-19}$ Generally the characteristics of the thin films are inferior to those of single crystals. Thin films and nanoparticles of VO$_2$ tend to survive the stress generated during repeated cycles of phase transition better than bulk crystals, and also their switching temperature can be depressed to near room temperature by doping. Therefore, these oxides
have potential use, particularly in thin film form, for a wide variety of applications involving thermally activated electronic or optical switching devices. Such films are of considerable technical interest because of applications in chemical sensors, energy-conserving coatings, transparent conductors, and switching materials.\textsuperscript{18} The numerous potential electronic, optical, and optoelectronic device applications which have been suggested have stimulated work on the preparation of thin films by a variety of techniques, including chemical vapor deposition, solgel, evaporation, and sputter deposition.

It is experimentally well established that the SMT, and hence the physical properties, depend strongly on local microstructure, chemical doping and applied strain.\textsuperscript{19,26-29} This dependence on lattice distortions provides insight into the mechanisms responsible for the SMT. Experimental studies have used a range of sample geometries in order to investigate the effect of microstructure and strain under controlled conditions. Using bulk single crystals, thermal cycling through the structural transition leads to large strains and sample cracking. Studies of VO\textsubscript{2} thin films avoid this problem, allow measurements of substrate-induced strain effects, and are advantageous for device applications. New techniques for growing high-quality micro- and nano-crystals with well-defined geometries have enabled more direct studies of the connections between local strain and phase behavior without sample cracking.\textsuperscript{25,31-35}
In this chapter a correlation between microstructure and semiconductor to metal transition (SMT) characteristics of VO$_2$(011) single crystalline thin films integrated with Si(100) substrates buffered with NiO/MgO/TiN intermediate layers is reported. This study introduces VO$_2$/NiO thin film heterostructure integrated with silicon chip as a promising candidate for multifunctional devices with novel characteristics where a combination of various properties of two crystals is required.

9.2 Experimental

Pulsed laser deposition (PLD) was employed to grow VO$_2$ epilayers on an NiO/MgO/TiN/Si(100) platform. A Lambda Physik (LPX200) KrF excimer laser source ($\lambda = 248$ nm and $\tau = 25$ ns) was used to ablate the targets. The silicon substrates were ultrasonically cleaned in acetone and methanol at room temperature for 5 minutes each, followed by rinsing in DI-water. Then, they were etched for 30 seconds in diluted HF solution at room temperature to remove the silicon oxide layer and obtain a hydrogen terminated surface which can prevent subsequent surface oxidation before loading the substrates to the vacuum chamber. The cleaned substrates along with the high purity VO$_2$, NiO, MgO, and TiN targets were loaded to the PLD chamber and the chamber was pumped down to a background pressure of $< 8 \times 10^{-7}$ Torr. We used TiN as a buffer material to destroy and remove the amorphous SiO$_x$ layer from the surface of the silicon substrates. The TiN thin film was deposited at 750 °C for 1000 pulsed under the background pressure. Then, an MgO
layer was deposited at 700 °C for 1000 pulses. To deposit the NiO layer, oxygen was injected to the chamber and the pressure was set at $5 \times 10^{-4}$ Torr. The NiO film was grown at 700 °C for 3000 pulses. Finally, VO$_2$ films were grown on the NiO/MgO/TiN platforms under an oxygen partial pressure of $5 \times 10^{-2}$ Torr for 4000 pulses at 500 °C. The laser energy density and repetition rate were set at 3.0-3.5 J.cm$^{-2}$ and 5 Hz for all layers.

A Rigaku diffractometer with Cu-Kα radiation ($\lambda=0.154$ nm) was used to study the out-of-plane orientation of the films. A Philips X’Pert Pro X-ray diffractometer was also employed to collect φ-patterns. A JEOL 2010F transmission electron microscope with a 0.18 nm resolution and Gatan image filter (GIF) attachment was used to take cross-section images and selected area electron diffraction patterns. The microscope was operated at 200 kV. Semiconductor-to-metal transition characteristics of the samples were investigated by a Keithley 2400 sourcemeter and labview program. The measurements were done in the temperature range of 40-80 °C. The samples were warmed by a resistive coil heater and cooled using a closed-cycle helium cryostat.

9.3 Results and discussion

Fig. 9.1 displays XRD θ-20 pattern collected from VO$_2$/NiO/MgO/TiN/Si(100) thin film heterostructure. As is observed, all MgO, NiO, and TiN intermediate layers grow along their [100] axes, while monoclinic (M$_1$) VO$_2$ grows along the normal of (011) family of planes.
The absence of other out-of-plane orientations confirms the growth of a highly textured or epitaxial heterostructure. From the information of Fig. 9.1, the out-of-plane crystallographic alignments across the interfaces are written as: $(011)_{\text{VO}_2} || (100)_{\text{NiO}} || (100)_{\text{MgO}} || (100)_{\text{TiN}} || (100)_{\text{Si}}$. To confirm the epitaxial growth and figure out the in-plane alignments across the interfaces, $\phi$-scan XRD was used whose results are shown in Fig. 9.2. The crystallographic parameters considered to acquire these patterns are listed in Tab. 9.1. The results reveal a cube-on-cube growth as for NiO, MgO, TiN, Si crystals. To find the crystallographic alignment across the VO$_2$(011)/NiO(100) interface, the VO$_2$(200) and NiO(220) reflections were taken into

Fig. 9.1 A $\theta$-2$\theta$ XRD pattern acquired from VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) thin film heterostructure.
Fig. 9.2 XRD ϕ-patterns taken from VO$_2$(011), NiO(220), MgO(220), TiN(220), and Si(220) reflections.
account. According to Fig. 9.2, the azimuthal distance between \( \varphi \)-peaks from these reflections equals 90.0°. The geometrical intersection between (011) and (100) planes of monoclinic (M1) VO\(_2\) is the \([0\bar{1}1]\) vector; meanwhile, the [001] vector represents the geometrical intersection between the (110) and (100) planes in NiO. Because the \( \varphi \)-pattern peaks from two crystals appears at the same \( \varphi \)-angles, the \([0\bar{1}1]_{\text{VO}_2}\) and \([001]_{\text{NiO}}\) vectors must be parallel, while the out-of-plane relationship, i.e. \((011)_{\text{VO}_2}\parallel(100)_{\text{NiO}}\), is satisfied. In view of the above discussion, the in-plane alignment across the VO\(_2\)/NiO interface is written as \([0\bar{1}1]_{\text{VO}_2}\parallel[001]_{\text{NiO}}\), assuming a [100] out-of-plane direction for NiO crystal. The epitaxial relationship at room temperature for the entire heterostructure is determined to be: \([0\bar{1}1](011)_{\text{VO}_2}\parallel[100](100)_{\text{NiO}}\parallel[100](100)_{\text{MgO}}\parallel[100](100)_{\text{TiN}}\parallel[100](100)_{\text{Si}}\). At the temperature of growth, where tetragonal state of VO\(_2\) is stable, the alignment between VO\(_2\) and NiO crystals differs from what is written for room temperature. Taking the model presented by Goodenough\(^{36}\) into consideration, the a-axis of monoclinic (M1) VO\(_2\) changes to the c-axis of tetragonal VO\(_2\) and the b-axis of monoclinic (M1) VO\(_2\) changes to the a-axis of tetragonal VO\(_2\). This monoclinic and tetragonal phases of VO\(_2\) is schematically illustrated in Fig. 9.3 which reveals that the (011) planes of monoclinic VO\(_2\) change to the (110) planes of the
tetragonal VO$_2$ at temperatures above the SMT temperatures. These two planes are highlighted in pink and blue in Fig. 9.3a and Fig. 9.3b, respectively. With this information, the epitaxial relationship at the temperature of growth between VO$_2$ and NiO thin films is written as: [001](110)$_{VO2}$|[010](100)$_{NiO}$ and [110]$_{VO2}$|[001]$_{NiO}$.

A bright field cross-section TEM micrograph obtained from epitaxial VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) heterostructure is depicted in Fig. 9.4. The results clearly show that TiN, as a buffer layer, has been able to effectively remove the SiO$_x$ amorphous layer from the surface of the silicon substrate and provide a single crystalline

---

**Fig. 9.3** Schematic delineation of: (a) monoclinic and (b) Tetragonal VO$_2$ unit cells. The (011) and (110) planes in monoclinic and tetragonal VO$_2$ unit cells are highlighted in pink and blue, respectively. The crystallographic relationship between two crystals are based on the Goodenough’s model.
platform for the subsequent layers. The reason why MgO was deposited in between TiN and NiO films is that MgO is an extremely stable material, particularly at high temperatures, and is able to prevent the formation of titanium oxides at the interface (from the reaction between TiN and NiO) which might adversely affects the epitaxial growth.
Based on the information in Fig. 9.5 where the VO$_2$/NiO interface at the growth temperature is schematically illustrated, the misfit strains along the [001] orientation of tetragonal VO$_2$ at the growth temperature is calculated as 31.73% which is compressive. In accordance with the domain matching epitaxy paradigm, such a huge lattice misfit strain relaxes very quickly within the very first few monolayers of VO$_2$ thin film growing on an NiO platform through alternation of 4/3 and 3/2 domains with frequency factors of about 0.85 versus 0.15. The mechanism of relaxation of misfit strain stems from nucleation of dislocations at the free surface of the VO$_2$ film followed by their propagation toward the VO$_2$/NiO interface. Large strains are easier to relax, since the critical thickness beyond which the system (thin layer) can, from a thermodynamic point of view, accommodate misfit dislocations is smaller; as a consequence, the misfit dislocations are able to glide and reach the interface to relax the strain easily, as the glide distance is very small, i.e. a couple of monolayers. As explained earlier, the misfit strains along two orthogonal in-plane orientations of VO$_2$ layer are both compressive which are easier to relax as compared to tensile strains. Dislocation nucleation and glide phenomena lead to the formation of surface steps. The step formation energy is negative if the dislocations relax a compressive stress. This phenomenon gives rise to a decrease in the surface energy. In contrast, the formation energy of surface steps is always positive if the misfit dislocations relax a tensile stress. Under compressive strain conditions, the step formation process decreases the number of dangling bonds and, hence, the surface energy. However, the number of surface dangling bonds increases when the strain is tensile, as one extra half plane, i.e. misfit dislocation, needs to be inserted in the lattice. Hence, one
extra row of dangling bonds is added to the surface. We will show in the future that the formation of a VO₂ thin film with a fully relaxed c-axis leads to a near bulk semiconductor to metal transition.

Fig. 9.5 A 2D schematic illustration of (110) and (100) planes of tetragonal VO₂ and NiO at the VO₂/NiO interface at the temperature of growth.
Results of high temperature high resolution θ-2θ XRD performed on epitaxial VO$_2$ thin films grown on an NiO/MgO/TiN/Si(100) platform are depicted in Fig. 9.6. The results show that the (011) planes of monoclinic (M1) VO$_2$ change to the (110) planes of tetragonal VO$_2$ across the SMT, as it was discussed in detail earlier. The (110) and (011) signals from tetragonal and monoclinic VO$_2$ crystals advent at 2θ angles of about 27.72° and 27.90°, respectively. These values are slightly higher than the 2θ values of bulk (relaxed) VO$_2$ showing that the crystals are under a compressive strain along their out-of-plane directions. Based on the established epitaxial relationship as well as Fig. 9.5, [1̅0] orientation of tetragonal VO$_2$ is parallel to [001] orientation of NiO at the temperature of growth. Along the [1̅0] orientation of tetragonal VO$_2$, there are two sets of oxygen anions with an alternating distances of about 2.44 Å and 3.99 Å. These atoms couple with nickel cations, having a spacing of about 4.176 Å, along the [100] orientation of NiO. This results in a small tensile misfit strain of about 4.45%. Such a small strain is very hard to relax, as explained earlier. We already showed that the in-plane strain is fully relaxed along the other in-plane orientation of VO$_2$, i.e. its c-axis. Consequently, the unrelaxed in-plane tensile strain along the [1̅10] direction of VO$_2$ leads to a compressive strain along the out-of-plane orientation which is the reason behind the peak shift toward larger 2θ values in Fig. 9.6. From the high resolution θ-2θ patterns in Fig.6, the inter-planar spacings of (110) and (011) family of planes of tetragonal and monoclinic (M$_1$) VO$_2$ as a function of temperature were calculated using the Boltzmann’s model and the results are presented in Fig. 9.7. The results confirm the compression along the out-of-plane orientation in both tetragonal and monoclinic phases which is induced by the NiO platform.
Fig. 9.6 High resolution θ-2θ scans through (110) and (011) reflections of tetragonal and monoclinic VO₂ at different temperatures during: (a) heating and (b) cooling cycles. The insets show the change of peak intensities as a function of temperature.
and originates from the unrelaxed misfit strain along the [1\(\bar{1}\)0] in-plane direction of VO\(_2\). The inset of Fig. 9.6 shows the intensity change of (110) and (011) signals as a function of temperature. The monoclinic to tetragonal phase transformation begins at about 63 °C and gets completes at about 71 °C during the heating cycle, as is seen in Fig. 9.6a and Fig 9.7. Furthermore, Fig. 9.6b and Fig. 9.7 show that the tetragonal to monoclinic phase transformation begins at about 67 °C and gets completes at about 56 °C during the cooling

![Graph](image)

**Fig. 9.7** The temperature dependence of inter-planar spacing for (110) and (011) planes of tetragonal and monoclinic (M\(_1\)) VO\(_2\).
cycle. The heating/cooling cycles were repeated for four times (The data shown here belong to the forth cycle) and the largest hysteresis was determined to be about 3.7 °C. No significant change was observed in the peak positions and full width at half maximum of the films which confirms the durability of our VO₂ epilayer.

Electrical resistance of VO₂ epilayers as a function of temperature was measured for nine consecutive heating/cooling cycles and the results are displayed in Fig. 9.8 where a semiconductor to metal transition behavior is obvious. A near bulk transition temperature was obtained which stems from the relaxed c-axis of tetragonal VO₂ and a-axis of monoclinic VO₂. A transition amplitude of above four orders of magnitude and a hysteresis of about 4 °C were obtained. The start and finish temperatures of the monoclinic ⇌ tetragonal phase transformation are in a complete agreement with those in Fig. 9.6 and Fig. 9.7. No significant change is observed after 20 heating/cooling cycles which shows the stability of our VO₂ single crystalline thin films.

9.4 Conclusions

VO₂(011) epitaxial thin films were grown on an NiO/MgO/TiN platform integrated with Si(100) substrates by pulsed laser deposition technique. The epitaxial relationship across the VO₂/NiO interface was determined to be and [0\bar{1}1](011)_{VO₂}||[001](100)_{NiO} at room temperature and [001](110)_{VO₂}||[100](100)_{NiO} at the temperature of growth. A cube-on-cube
Fig. 9.8 Change of electrical resistivity of epitaxial VO$_2$(011)/NiO(100)/MgO(100)/TiN(100)/Si(100) thin film heterostructure as a function temperature.
crystallographic alignment was observed for the NiO(100)/MgO(100)/TiN(100)/Si(100) interfaces. The misfit strains at the interface between tetragonal VO$_2$ and NiO platform at the growth temperature were calculated along two orthogonal in-plane directions. We showed that the huge 31.73% compressive strain along the c-axis of tetragonal VO$_2$ is fully relaxed. However, there is an unrelaxed small misfit strain along the [0\bar{1}1] in-plane direction which leads to a compressive residual strain along the out-of-plane orientation. The fully relaxed structure along the c-axis of tetragonal VO$_2$ or a-axis of monoclinic VO$_2$ was understood to be the origin of the near bulk SMT temperature. High resolution X-ray diffraction was employed to study microstructure of the VO$_2$ epilayers at low and elevated temperatures. A compressive strain along the out-of-plane orientation was observed in both monoclinic and tetragonal phase of VO$_2$ originating from an unrelaxed in-plane misfit strain. SMT characteristics of VO$_2$(011) epilayers were investigated. A near bulk transition temperature, an amplitude of near five orders of magnitude, and a hysteresis of below 4 °C were observed.
9.5 References


Chapter 10. Conclusions and suggestions for further work

10.1 Conclusions

1. In this research, we integrated single crystalline NiO thin films with Si(100) substrates using cubic yttria-stabilized-zirconia (cYSZ) buffer. The epitaxial relationship and the crystallographic arrangement across the interfaces were studied. We were able to create a p-n junction within a single NiO epilayer through subsequent nanosecond laser annealing. We show that the interface between the p-NiO and n-NiO is atomically sharp leading to an enhanced charge transfer and, therefore, prominent photocatalytic efficiency. Considering our results, the p-NiO/n-NiO single crystalline heterostructures can be considered for an efficient and promising photoanode for hydrogen production and environmental remediation.

2. Epitaxial NiO thin films are integrated with silicon(001) substrates via buffering with cubic yttria-stabilized zirconia (c-YSZ). Special emphasis is placed on epitaxial growth and controlling the crystallographic alignment in NiO/c-YSZ(001)/Si(001) heterostructures in the light of the domain matching epitaxy (DME) paradigm where integral multiples of planes match across the interfaces. We are able to precisely tune the out-of-plane orientation of NiO epilayers from [111] to [100] by adjusting the growth pressure. This observation is attributed to the nature of the surface termination and bonding characteristics of c-YSZ(100) face. Interestingly, we show that the p-type electrical conductivity of the NiO thin films grown under medium and high
oxygen partial pressures turns n-type at lower pressures where we envisage that nature of the point defects plays a critical role in determining the electrical conductivity. This study is important for practical applications of NiO based devices where different and controlled crystallographic and electrical characteristics are required.

3. In another part of this study, special emphasis is placed on the growth of high quality single crystalline thin film heterostructures and explaining the epitaxial relationships across the interfaces in accordance with the domain matching epitaxy (DME) paradigm where integral multiples of planes match across the film-substrate interface. We could achieve a near bulk and sharp SMT in the VO$_2$/NiO/YSZ heteroepitaxy through engineering the interfaces and relaxing the strains.

4. Next chapter of this study focuses on the generation of point defects into the VO$_2$ lattice by nanosecond laser annealing. We show that the diamagnetic behavior of as-deposited sample changes to ferromagnetic behavior and the concentration of charge carrier increases after laser treatment. These findings might introduce VO$_2$ as interesting candidate for spintronic applications where both semiconducting and ferromagnetic behavior are required, in addition SMT characteristics.

5. We integrated epitaxial VO$_2$(010)/NiO(111) thin film heterostructures of varying thicknesses with silicon substrates where cubic yttria-stabilized zirconia (c-YSZ) was used as a buffer. The epitaxial relationships across the interfaces, in particular VO$_2$/NiO interface, were established at room temperature, and at growth temperature
of 500 °C. The strain relations and its effect on SMT characteristics are discussed. The effect of thickness on the SMT characteristics of VO₂ epilayers is investigated with a special emphasis on the microstructure where the control of overall defect content and the characteristics of domain boundaries are discussed based on phenomenological thermodynamic models.

6. A correlation between microstructure and semiconductor to metal transition (SMT) characteristics of VO₂(011) single crystalline thin films integrated with Si(100) substrates buffered with NiO/MgO/TiN intermediate layers is reported. This study introduces VO₂/NiO thin film heterostructure integrated with silicon chip as a promising candidate for multifunctional devices with novel characteristics where a combination of various properties of two crystals is required.

10.2 Future Work

From our previous work and the literature studies, it would be worthwhile to investigate the ferromagnetic source of VO₂ and potential applications as Resistive random-access memory (RRAM) devices. Thus, some suggestions for the future work are presented as follows:

- VO₂ films showed the room temperature ferromagnetism. However, the details of defect contributing the magnetic moments are still unclear. Investigation of the magnetic source in VO₂ films is important. This needs a thorough investigation in
ferromagnetic VO₂ films by varying the oxygen pressure during growth and annealing. In addition, a comprehensive study in Electron Energy Loss Spectroscopy (EELS) can provide the types of the intrinsic defects and their distribution.

- VO₂ films has been successfully grown on silicon substrate. Fabricating a real VO₂-based device with silicon substrates, such as: Microbolometer, is worth investigating.

- The other big breakthrough opportunity for VO₂ is related to Resistive random-access memory (RRAM) if the semiconductor to metal transition can be triggered by an applied electrical field. Since, the rate of VO₂ phase transformation is ultra-fast it could lead to an extremely high performance RRAM device.