NiOx based device structures

Kamruzzaman Khan
University of Toledo

Follow this and additional works at: http://utdr.utoledo.edu/theses-dissertations

Recommended Citation
Khan, Kamruzzaman, "NiOx based device structures" (2017). Theses and Dissertations. 2128.
http://utdr.utoledo.edu/theses-dissertations/2128

This Thesis is brought to you for free and open access by The University of Toledo Digital Repository. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of The University of Toledo Digital Repository. For more information, please see the repository's About page.
A Thesis

entitled

NiO$_x$ Based Device Structures

by

Kamruzzaman Khan

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the
Master of Science Degree in Electrical Engineering

Dr. Daniel Georgiev, Committee Chair

Dr. Richard G. Molyet, Committee Member

Dr. Anthony Johnson, Committee Member

Dr. Amanda Bryant-Friedrich, Dean
College of Graduate Studies

The University of Toledo
July 2016
Semiconducting oxides are really important for their use in optoelectronics and photo catalytic applications. While other semiconducting oxides (e.g., ZnO, TiO$_2$, and SnO$_2$) have been widely studied for various applications, the potential applications of NiO have not been explored to any significant degree. NiO$_x$ based devices can open up new horizons in this relevant field. Nickel oxide (NiO), zinc oxide (ZnO) and hafnium oxide (HfO$_2$) films and sandwich structures were fabricated and characterized after first identifying the desired growth conditions. NiO$_x$ based p-n junction (NiO/ZnO) and Metal-insulator-semiconductor (MIS) structures (Ni/NiO/HfO$_2$/Ni) were fabricated and characterized. In the NiO/ZnO case, rectifying behavior based on the current-voltage characteristics was observed, which also depend on the contact resistance i.e., Al:ZnO in our case. Capacitance vs. voltage measurements at various frequencies were performed as well and the dependence of capacitance on frequency and the depletion region width was examined. In the case of Ni/NiO/HfO$_2$/Ni, this MIS structures with three different thickness were systematically studied and negative differential resistance (NDR) characteristics were found for over a narrow HfO$_2$ thickness range. A possible mechanism for this NDR behavior was proposed based on the energy band diagram structure bending and bias induced changes, involving a tunneling current. In addition, weak visible light emission from both types of structures under bias was observed and a possible explanation was presented.
To those who sacrificed their lives to change the lives of others
and
To my family for their continued supports & sacrifices.
Acknowledgments

On my strenuous and stressful, but enjoyable journey to Master’s degree, I was blessed with so many co-operating and encouraging people without whom this would be impossible. I want to convey my heartiest gratitude to all of them. First and foremost, I would like to express my deepest appreciation to my thesis adviser and committee chair Dr. Daniel Georgiev. I consider Dr. Georgiev as an exemplary mentor who motivated and taught me how to conduct research effectively by maintaining a work life balance. He has a rare attitude to guide his students to think out of the box. Last but not least, it would be impossible to finish this research within just one year without his continuous advices and directions. The thesis writing would be far from perfection without his scrutiny and numerous proof reading. Besides, I want to give my sincerest gratitude to other committee members Dr. Richard Molyet and Dr. Anthony Johnson who took time to go through the thesis and gave me some feedbacks to make the thesis perfect.

I would like to extend my gratitude to my group-mates (Ryan O’Dell, Srikanth Itapu and Vamsi Borra) who not only helped me in various ways (training on and setting up different facilities) in my research but also made me a better person. I also want to mention the technical support from Wright Center for Photovoltaics Innovation and Commercialization (PVIC) and their affiliates.

Finally, I have been able to come to the University of Toledo from a developing nation and finish my Masters degree because of my family and friends. The continued love, support and sacrifices of my family have made me what I am and will be.
Contents

Abstract iii

Acknowledgments v

Contents vi

List of Tables xi

List of Figures xii

List of Abbreviations xvi

List of Symbols xvii

1 Introduction 1
   1.1 Background .................................................. 1
   1.2 Motivation ................................................... 3
   1.3 Objective .................................................... 4
   1.4 Thesis Outline ............................................. 4

2 Literature Review 5
   2.1 Wide-bandgap Semiconductors ............................ 5
   2.2 Oxides ....................................................... 6
   2.3 Insulating Oxides .......................................... 7
      2.3.1 Hafnium Oxide .................................. 10
2.4 Semiconducting Oxides ................................................. 11
  2.4.1 Nickel Oxide ......................................................... 13
  2.4.2 Zinc Oxide ........................................................... 15
2.5 Common Defects in Crystals ........................................... 18
  2.5.1 Point Defects ......................................................... 19
  2.5.2 Line Defects .......................................................... 20
  2.5.3 Planar Defects ....................................................... 21
2.6 Defects in Semiconducting Oxides .................................... 22
  2.6.1 Defects in Nickel Oxide Crystals .................................. 22
  2.6.2 Defects in Zinc Oxide Crystals ................................... 24
2.7 Homojunctions and Heterojunctions .................................. 27
2.8 P-n Junctions ............................................................. 28
  2.8.1 NiO/ZnO Heterojunction ........................................... 30
2.9 Metal Semiconductor Contacts ........................................ 31
2.10 Metal Insulator Semiconductor ......................................... 33
  2.10.1 Current Transport in MIS Structures ............................ 35
2.11 Tunneling ................................................................. 37
  2.11.1 Tunnel Diode ......................................................... 37
2.12 MIS Tunnel Devices ..................................................... 38
  2.12.1 Fowler-Nordheim Tunneling ...................................... 39
  2.12.2 Direct Tunneling .................................................... 40
  2.12.3 MIS Tunnel Diode Behavior ..................................... 40
  2.12.4 MIS Tunnel Diode in Degenerate Semiconductors ............. 42
  2.12.5 ZnO-based MIS Structures ....................................... 45

3 Thin Film Fabrication and Characterization Techniques ............. 46
  3.1 Fabrication Methods ................................................... 46
3.1.1 Molecular Beam Epitaxy ........................................ 47
3.1.2 Chemical Vapor Deposition .................................... 47
3.1.3 Atomic Layer Deposition ...................................... 48
3.1.4 Sol-Gel Technique ............................................. 49
3.1.5 Pulsed Laser Deposition ...................................... 49
3.1.6 Sputtering Deposition .......................................... 51
   3.1.6.1 Types of Sputtering Deposition ......................... 52
   3.1.6.2 Properties of Nickel Oxide Thin Film with RF Sputtering Growth Parameter ............... 54
3.2 Characterization Techniques .................................... 58
   3.2.1 Four Point Probe Resistivity Measurement ............... 58
   3.2.2 Hall Effect Measurement (Vander Pauw Method) ............. 60
   3.2.3 Transmittance and Absorption ............................... 63
   3.2.4 Energy Dispersive X-ray Spectrometry (EDS) ............... 65
   3.2.5 X-ray Diffraction(XRD) .................................... 66

4 Experimental Details ............................................. 69
   4.1 Fabrication Procedures ........................................ 69
   4.1.1 Hafnium Oxide Deposition .................................. 69
      4.1.1.1 Sputtering Deposition System from AJA International Inc. ...................... 69
   4.1.2 Zinc oxide Deposition ....................................... 70
      4.1.2.1 Magnetron Sputtering System from Torr International Inc. .................. 70
   4.1.3 Nickel Oxide Deposition .................................... 71
   4.1.4 Contacts Deposition ......................................... 71
   4.2 Samples Characterization ...................................... 71
5 Results

5.1 Properties of Semiconducting Oxides .......................... 75
  5.1.1 Electrical Properties of Nickel Oxide .................. 75
  5.1.2 Crystalline Structure of Nickel Oxide ................. 77
  5.1.3 Crystalline Structure of Zinc Oxide .................. 78
  5.1.4 Crystalline Structure of Hafnium Oxide ............ 79

5.2 Optical Transmittance Measurements .......................... 80
  5.2.1 Hafnium Oxide ........................................ 80
  5.2.2 Zinc Oxide ........................................... 81
  5.2.3 Nickel Oxide .......................................... 81

5.3 Study of ZnO/NiO Heterojunctions .......................... 82
  5.3.1 Device Fabrication ................................... 82
  5.3.2 Current-Voltage Characterization .................... 84
  5.3.3 C-V Measurements .................................... 85
  5.3.4 Light Emission ....................................... 86
  5.3.5 Applications ......................................... 87

5.4 Study of MIS (Ni/HfO$_2$/NiO/Ni) Heterostructures ....... 88
  5.4.1 Device Fabrication ................................... 88
  5.4.2 Band Diagram .......................................... 88
  5.4.3 Current-Voltage Characteristics .................... 89

ix
5.4.4 Explanation of Negative Differential Resistivity ............ 92
5.4.5 Light Emission ................................................. 93
5.4.6 Applications of NDR Characteristics .......................... 94

6 Conclusions ........................................................... 96
List of Tables

2.1 Properties of hafnium oxide [1]. ........................................... 11
2.2 Properties of nickel oxide [2]. ........................................... 15
2.3 Properties of zinc oxide [3]. ........................................... 18

5.1 Resistivity of nickel oxide for different conditions. ................. 76
List of Figures

2-1 (a) Crystal structure of NiO as a unit cell (black circle is Ni atom and red circle is oxygen atom); (b) As a bulk (green circle is oxygen atom and blue circle is Ni atom) [2]. .......................................................... 13

2-2 ZnO crystal structures: a) Cubic zincblende and b) Hexagonal wurtzite [4]. 16

2-3 Vacancy formation by atom transfer to the surface by breaking bond and the subsequent vacancy diffusion into the bulk: (a) Perfect crystal without any defects; (b) An atom at the surface breaks the bond and jump outside to a neighboring place on the surface. This creates a vacancy; (c) An atom in the bulk diffuses to fill the vacancy pushing the vacancy toward the bulk from the surface; (d) Atomic diffusions cause vacancy to diffuse in the bulk. .......................................................... 19

2-4 Point defects in the crystal structures: (a) Vacancy, (b) Larger substitutional impurity, (c) Smaller substitutional impurity and (d) Interstitials. 20

2-5 Solidification of polycrystalline film from the melt. The square box shows atoms [5]. .......................................................... 21

2-6 The structure of grain boundaries [5]. .......................................................... 22

2-7 Vacancy in nickel oxide crystal: (a) Nickel vacancy and (b) Oxygen vacancy. Here, yellow and blue circles define oxygen and nickel atoms, respectively, along with the dashed lines corresponding to vacancies. .... 23
2-8 (a) Energy band diagram of two isolated semiconductors of opposite type and different band gap $E_g$ (where b and gap n-type material is smaller than that of p-type material); (b) Their idealized anisotype heterojunction at thermal equilibrium. (c) & (d) With the different band gap i.e., band gap of p-type material is smaller than n-type.

2-9 Properties of equilibrium p-n junction: (a) Isolated p-type and n-type material and energy band for the isolated region; (b) Junction showing space charge in transition region, the resulting electric field and contact potential and separation of energy bands.

2-10 Energy-band diagram for p-NiO/n-ZnO heterojunction under zero bias.

2-11 Energy band diagram of a metal-semiconductor contact: metal and semiconductor (a) in separated system (b) connected into one system.

2-12 Metal-insulator-semiconductor structure in simplest form.

2-13 Flat Energy band diagram of ideal MIS structures (V=0): (a) n-type semiconductor. (b) p-type semiconductor.

2-14 Energy band diagram showing conduction mechanism of (a) Direct tunneling, (b) F-N tunneling, (c) Thermionic emission, and (d) Frenkel-Poole emission [53].

2-15 Characteristics of tunneling diode (a) Energy band diagram in thermal equilibrium; Static current-voltage characteristics of a tunnel diode: (b) $I_p$ and $V_p$ are the peak current and peak voltage, respectively. $I_v$ and $V_v$ are the valley current and valley voltage, respectively. (c) The total current shown into three current components.

2-16 Tunneling mechanism depending on oxide thickness: (a) In thicker oxide F-N tunneling, (b) Direct tunneling and (c) MIS tunnel diode in non-equilibrium ($E_{Fn} = E_{Fn}$) with both type of carrier tunneling.
2-17 Energy-band diagram of MIS tunnel diode on non-degenerate substrate (p-type) with (a) Low metal-insulator barrier $\phi_{mi}$ and (b) High metal insulator barrier. ................................................................. 41

2-18 Simplified band diagram of MIS tunnel diodes on degenerate substrate including interface traps states for p+ substrate. (a) Flat bland diagram; (b) Reverse bias and ((c)-(e)) Forward bias. .............. 43

2-19 Simplified band diagram of MIS tunnel diodes on degenerate substrate including interface traps states for n+ substrate. (a) Flat bland diagram; (b) Reverse bias and ((c)-(e)) Forward bias. .............. 44

2-20 ZnO-based MIS structure. ................................................................. 45

3-1 The principle of pulsed laser deposition (PLD). AT and S represents an ablation target and a substrate, respectively. The darker color between the ablation target and substrate is the plume. ......................... 50

3-2 (a) Glow discharge formation process inside the vacuum chamber (b) Schematics of a conventional DC sputtering system [6]. ......................... 51

3-3 (a) Two terminal and (b) Four terminal resistance measurement technique [7]. ................................................................. 58

3-4 Resistivity measurement for four point measurement. ...................... 60

3-5 Geometry for Van der Pauw method. ................................................. 60

3-6 Main components of EDS. ................................................................. 65

3-7 Bragg diffraction by crystal planes. .................................................... 66

3-8 Geometric arrangement of X-ray diffraction. ........................................ 67

5-1 XRD of NiO thin film fabricated at RT, 300°C & 400°C. ...................... 77

5-2 XRD spectrum of (a) ZnO fabricated at RT & (b) HfO2 thin film fabricated at 400C. ................................................................. 78

5-3 Transmittance spectra of (a) HfO2 & (b) ZnO as a function of wavelength. 80
5-4 Transmittance of NiO as a function of wavelength.  
5-5 Schematic diagram of NiO/ZnO heterojunctions. The bottom cyan and violet planes show the Al doped ZnO on top of glass and ZnO, respectively. The green and yellow circle stands for NiO and Ni electrodes of the sample.  
5-6 I-V characteristics of NiO/ZnO heterostructure (left). Ohmic contact characteristics between NiO/Ni and Al:ZnO/Cu. The red line is flat after 16V because the limiting current for our characterization system is 100mA.  
5-7 Reverse-bias C-V characteristics of NiO/ZnO heterojunctions at various frequencies: (a) for 100nm Al:ZnO (b) 440nm Al:ZnO.  
5-8 Photographic image of the light emission from a biased ZnO/NiO heterojunction device.  
5-9 Band diagram of MIS structure (a) before any connection (b) After connection, at equilibrium (zero applied bias, V=0).  
5-10 Band diagram of MIS structure with three oxide thickness: 20nm, 50nm & 120nm under forward bias.  
5-11 Current-voltage (I-V) characteristics of MIS structure with different thickness.  
5-12 Simplified band diagram of MIS tunnel diodes on degenerate NiO including surface/interface states and trap states: (a) For reverse bias (positive voltage in Ni and negative voltage at NiO) (b-d) For forward bias (negative voltage in Ni and positive voltage in NiO).  
5-13 (a) Photographic image of the light emission from a biased MIS structure (b) Explanation of light emission by band diagram.
List of Abbreviations

MIS ..................... Metal-insulator-semiconductor
MS ...................... Metal-semiconductor
WBG ..................... Wide-bandgap
NDR ...................... Negative differential resistance
XRD ...................... X-ray diffraction
PLD ...................... Pulsed laser deposition
MOSFET .................. Metal-oxide-semiconductor field effect transistor
MIM ...................... Metal-insulator-metal
MIIM ..................... Metal-insulator-insulator-metal
IR ...................... Infra-red
UV ...................... Ultra-violet
LED ...................... Light emitting diode
MOS ...................... Metal-oxide-semiconductor
RRAM .................... Resistive random access memory
F-N ..................... Fowler-Nordheim
MOCVD ................... Metal organic chemical vapor deposition
MBE ..................... Molecular beam epitaxy
PDA ..................... Post deposition annealing
RTA ..................... Rapid thermal annealing
CVD ..................... Chemical vapor deposition
ALD ..................... Atomic layer deposition
RF ..................... Radio frequency
DUT ..................... Device under test
EDS ..................... Energy-dispersive X-ray spectroscopy
PVD ..................... Physical vapor deposition
List of Symbols

\( \alpha \) ............ Attenuation coefficient
\( \epsilon \) ............ Permittivity of dielectric material
\( V_{Ni} \) ............ Nickel vacancies
\( V_{O} \) ............ Oxygen vacancies
\( V_{Zn} \) ............ Zinc vacancies
\( Zn_i \) ............ Zinc interstitials
\( ZnO \) ............ Zinc antisites
\( O_i \) ............ Oxygen interstitials
\( O_{Zn} \) ............ Oxygen antisites
\( \chi \) ............ Electron affinity
\( \phi_m \) ............ Work function of metal
\( \phi_s \) ............ Work function of semiconductor
\( \phi_{Bna} \) ........ Barrier height of n-type materials
\( \phi_{Bpo} \) ........ Barrier height of p-type materials
\( \phi_n \) ............ Fermi level potentials w.r.t. conduction band edges for n-type
\( \phi_p \) ............ Fermi level potentials w.r.t. conduction band edges for p-type
\( \psi_n \) ............ Fermi level potentials w.r.t. midgap for n-type
\( \psi_p \) ............ Fermi level potentials w.r.t. midgap for p-type
\( A^* \) ............ Richardson constant
\( R_\square \) ........ Sheet resistance
\( \mu \) ............ Mobility
\( \rho \) ............ Resistivity
\( T \) ............ Transmittance
\( R \) ............ Reflectance
Chapter 1

Introduction

1.1 Background

Wide-bandgap semiconductors are very important materials because of their use in various applications, including high-voltage and high-power, high-temperature and even high-speed devices [8–11]. Two unique features (possibilities for band gap engineering and the large band gap itself) have made them an appropriate candidate for optoelectronics [12]. Oxides are really important in glass and electronics industry irrespective of their conductivity (insulating or semiconducting). Nowadays, semiconducting oxides, in particular, have also become a topic of research because of having large band gap and transparency in the optical range of the spectrum [8–11]. The group of the oxide semiconductors includes nickel oxide (NiO), zinc oxide (ZnO), titanium oxide (TiO$_2$), tin oxide (SnO$_2$) and others. Transparent conductor applications of some of these materials have already found an important place in technology [13]. Because of their direct band gap, they are considered suitable for optoelectronic devices, mostly in solid state lighting. Solid state lighting is already replacing incandescent light sources because of its much better efficiency and reliability [12]. The use of these semiconducting oxides in such applications is restricted due to issues with intrinsic defects and conductivity along with challenges with their doping prop-
erties. These issues and challenges have motivated a great deal of experimental and computational research in this field [14–18].

Among all of the semiconducting oxides, NiO is really of great importance because of the availability of precursors and environmental friendliness [19]. NiO has been explored for gas sensors [2, 20] and catalysis applications [21] whereas the optoelectronics and tunneling diode applications have seen relatively limited interest. NiO is attractive because of its wide-bandgap (3.2-4.0eV) which can be used for UV applications [22–24]. Besides, NiO can be used in metal-insulator-semiconductor (MIS) structures because of being intrinsically p-type semiconductor. Among the materials for light emission applications, ZnO is the most widely explored oxide semiconductor because of band gap (3.4eV) and large binding energy (60meV) [25–28]. ZnO is intrinsically n-type and the reliable and reproducible p-type doping of ZnO is still under investigation. Most of the p-type dopants are deep acceptor for ZnO, which is why ZnO has not been able to replace GaN in such applications [25, 27, 28]. To deal with the problem of p-type doping of ZnO, MIS structures with n-type ZnO [29–31] or p-n junctions with different p-type materials are now being explored as a solution. The materials they used for replacing p-ZnO are silicon (Si) [32], gallium nitride (GaN) [24, 33–35] nickel oxide (NiO), etc. [22–24]. Among them, NiO as a p-type semiconductor is more promising because of its availability and easy fabrication. So, ZnO/NiO heterojunctions are really important for UV applications [36–38]. The main challenge to the development of ZnO and NiO materials is their intrinsic defect states which make them intrinsically conductive. Defect states are the cause of weak peaks in their light emission spectra [22–24].

Moreover, NiO or ZnO-based p-n junctions are explored to some extent, but MIS structures of NiO or ZnO are not that much studied. ZnO-based MIS structures are explored to some extent for pure UV applications [29–31]. MIS structures are really important in electronics industry for understanding gate oxides in metal ox-
ide semiconductor field effect transistor (MOSFET) [1, 39–41]. For understanding the MIS structures, the use of proper dielectric is essential for device applications. Hafnium dioxide (HfO₂) [1, 42] and silicon dioxide (SiO₂) [40] are the two competitive oxides in MIS structures. Both of them have their own advantages. There are some reports on UV light emission [29–31, 43] and tunneling diode behavior from MIS structures of ZnO [44]. MIS structures of ZnO show negative differential resistance (NDR) in forward bias [43, 44]. Moreover, NiO is also used for tunnel diodes as metal-insulator-metal (MIM)-based tunneling diode [45–48] along with ZnO/NiO heterojunctions used for metal-insulator-insulator-metal (MIIM)-based tunneling applications [49]. This can be used as amplifiers, active filters, oscillators, etc. [45–49].

1.2 Motivation

The motivation of this thesis research is outlined below.

Since the availability of low-cost UV-LEDs is crucially important to solid state lighting, ZnO-based LED devices can be such a low-cost and efficient alternative of GaN-based LEDs. ZnO/NiO-based heterostructures would be of interest to light emitting applications as well. It appears that intrinsic defect states of ZnO and NiO play a vital role in the performance and the efficiency of LEDs. The emission resulting from intrinsic defects is really important to understand the defects of NiO and ZnO as well as improving the efficiency of NiO/ZnO-based LED devices.

NiO-based MIS structures can be an alternative to ZnO-based p-n junctions and ZnO-based MIS structures for LED devices. SiO₂ and HfO₂ can both be used as an insulator in such structures and choosing an appropriate insulator with high dielectric constant and optimum thickness is important for the light emission behavior.

NiO-based MIS structures with a thickness in between thickness for direct tunneling and MIS capacitor like behavior can be used as a tunneling diode and shows
negative differential resistance. This can be highly useful for various applications.

### 1.3 Objective

The objective of this thesis work was to fabricate NiO/ZnO junctions and characterize them in terms of current voltage (I-V) behavior (to verify their rectifying properties), and in terms of light emission behavior by electro-luminescence (E-L) measurements. Samples of various NiO and ZnO thickness and different device stack patterns were to be fabricated and studied.

Another objective was to fabricate and characterize Metal Insulator Semiconductor (MIS) structures, consisting of Ni/NiO/HfO$_2$/Ni stacks. Of specific interest again were the rectifying behavior and light emission properties, together with the potential for negative differential resistance (NDR) behavior.

### 1.4 Thesis Outline

The first chapter (chapter 1) of the thesis describes the background and recent situation of research about nickel oxide. This also includes the motivation and objective for our study along with the organization of the thesis. In the next chapter (chapter 2), a complete literature review on wide-bandgap semiconductor, oxides (semiconducting and insulating), defects, junctions (p-n, metal-semiconductor and metal-insulator-semiconductor) as well as tunneling and MIS tunneling diode are described. Chapter 3 describes conventional thin film fabrication and characterization process for our device structures and materials. Chapter 4 describes the experimental details (fabrication and characterization) of our experiments and device characterization. The findings of our experiments are explained in Chapter 5. Eventually, all our efforts and findings are summed up in chapter 6.
Chapter 2

Literature Review

2.1 Wide-bandgap Semiconductors

Wide-bandgap (WBG) semiconductors are semiconducting materials capable of functioning at a much higher operation voltage, frequency and temperature than conventional semiconductors e.g., silicon (Si) [8–11]. Typically, the band gap of WBG semiconductors is more than 2eV. Most of the WBG semiconductors are II-VI and III-V-based compound semiconductors e.g., gallium nitride (GaN), zinc oxide (ZnO), aluminum nitride (AlN), etc. [12, 50, 51]. There are only two materials with this property from group IV: diamond and silicon carbide (SiC) [10, 52].

One of the unique features of WBG semiconductors is band gap engineering (modifying band gap to a desired value by alloying two or more different compound semiconductors) [12]. Most of the WBG semiconductors are direct band gap materials (the conduction band minima and maxima of the band structure in the same k value). This results in radiative electron-hole recombination, which is suitable for optoelectronics [53]. There are some exceptions with indirect band gap e.g., SiC and gallium phosphide (GaP) [12, 53]. With band gap engineering and direct band gap, WBG semiconductors can be used for light emission from the infrared (IR) to ultra-violet (UV) range. Solid state lighting with WBG semiconductors is already replacing in-
candescent lights because of its high efficiency and low-cost [12]. GaN and related materials have been widely explored for ultra violet (UV) light emitting diode (LED) applications and solid state lighting [54, 55], but in recent years, ZnO is being considered as a prospective low-cost alternative of GaN for UV applications [26]. Although such LEDs can be used for full color displays, the main applications are in high density optical storage on CD-ROM [9, 10].

WBG semiconductors can be used as transducers because of their large piezoelectric constant. They can serve as gas sensors (GaN HEMT structures) [56] and pH sensors [57]. WBG semiconductors are really vital for high power and high temperature devices and systems too. Mostly, Si-based devices performing at a high temperature (more than 200°C and high operating voltage face high junction temperature and high leakage current. Besides, Si-based power devices have some serious disadvantages due to operating frequency, breakdown voltage and power density. The high breakdown voltage of WBG semiconductors can be beneficial for high power applications [8–11]. SiC is the most mature in this regard because of its availability of substrate [52]. Besides, diamond and GaN are two promising materials in these applications [51]. Diamond has the most promising parameters, but cannot be used because of challenges in fabricating large single crystal and lack of n-type dopants [8–11]. GaN can be used to fabricate heterostructures suitable for quantum well and optoelectronic applications. It has great transport properties, but poor thermal conductivity [51].

2.2 Oxides

Oxides, and binary oxides in particular, consist of oxygen and another element. Metals normally form bonds with the oxygen atom (an anion) with oxidation state of oxygen of -2. Some metals oxidize at ambient temperature e.g., Al foil develops a thin
layer of oxide ($Al_2O_3$) as a passivation layer. This protects the foil from corrosion, whereas in other metals (e.g., Fe) oxidation can continue without self-limiting, resulting in corrosion. There are some common oxides: silicon dioxide ($SiO_2$), iron oxide ($Fe_3O_4$), aluminum oxide ($Al_2O_3$), zinc oxide ($ZnO$), calcium oxide ($CaO$). Oxides are really important in electronics and glass industry. Oxides can be insulating and semiconducting depending on their carrier concentration which depends on their fabrication process and growth temperature. Generally, the breakdown field for oxides is around 5-10MV/cm [58].

2.3 Insulating Oxides

Insulating oxides are really necessary for their remarkable thermal, mechanical, chemical and other high temperature properties. In the electronic industry, some oxides ($SiO_2$, $HfO_2$) have already been used as gate oxides in MOSFET and others are under investigation for future applications. Among the insulating oxides, $SiO_2$, $Al_2O_3$, $HfO_2$ are the most common ones.

Silicon dioxide ($SiO_2$ or silica) is, perhaps, the most well characterized oxide. Silica is available in nature as quartz and sand. Silica is also one of the most abundant materials in the world. It is used in applications ranging from structural materials to microelectronics as gate oxides. $SiO_2$ has widely been used as gate oxide in MOS (Metal-oxide-semiconductor) transistors since mid-20th century because of its mature fabrication technology and availability [40, 42]. After that, with the developments of technology, the structures and materials for MOS structures have not been altered in industry that much. However, the size of transistors has been scaled down drastically. To cope with incessant tendency toward smaller devices and higher density, the thickness of oxide should reduce along with other parameters. It is difficult to fabricate really thin oxide (less than 10nm) because of less control and reliability. Another
crucial challenge is the exponential increase of the tunneling current with decreasing oxide thickness. Leakage current increases seven orders of magnitude with thickness decrease of only a factor of 2. In order to reduce gate leakage current, alternatives to SiO$_2$ are being extensively explored nowadays. Thinner oxides have reduced lifetime along with higher leakage current. The gate capacitance can be written in terms of a parallel-plate capacitor:

$$C = \frac{\epsilon_o \epsilon_r A}{d}. \quad (2.1)$$

$\epsilon_o$ and $\epsilon_r$ is the permittivity in vacuum and relative permittivity of dielectric materials, respectively. A is the area of the capacitor (gate length $\times$ gate width) and $d$ is the thickness of the dielectric.

For keeping the same gate capacitance while reducing leakage current, a thicker dielectric film with higher dielectric constant is needed. However, not all materials with higher dielectric constant than SiO$_2$ are acceptable as gate oxide in MOS devices because other parameters, e.g., barrier height, interfacial layers, effective oxide thickness and interfacial band structure also affect device performance. Gate current is also dependent on barrier height between metal and oxide as well as that of oxide and semiconductor. For replacing the SiO$_2$, the oxide should be stable with CMOS process flow. They should not form any kind of silicide, SiO$_2$ or mixture of these two [40, 42].

Other insulating oxides are studied for replacing SiO$_2$ in CMOS devices because of large leakage current. These are $Ta_2O_5$, TiO$_2$, $Y_2O_3$, CeO$_2$, Al$_2$O$_3$, Pr$_2$O$_3$, SrTiO$_3$, BaSrTiO$_3$ (BSTO), ZrO$_2$ and HfO$_2$ [1, 40, 42]. Most of them have drawbacks, such as, for example, $Ta_2O_5$ requires TiN electrode along with a high leakage current as SiO$_2$; TiO$_2$ has very poor band alignment with Si. $Ta_2O_5$, TiO$_2$, STO and BSTO are not thermally stable with Si as a contact and for CMOS devices SiO$_2$ forms at the
interface with oxides normally and during annealing process. This decreases leakage
current, but reduces effective thickness resulting in decrease in dielectric capacitance.
Some of the oxides have low dielectric constant e.g., $Al_2O_3$ (K=12) and $Y_2O$ (K=14).
Transition metal oxides (especially heavy metal elements) are emerging as prospective
candidate because of high dielectric constant. However, stronger polarization
means weaker bonding and weaker bonding referring to smaller separation between
bonding and antibonding energies. That is why BSTO and STO are not applicable
in MOSFET devices [1, 40, 42].

Aluminum oxide ($Al_2O_3$ or alumina) is also called aloxide, aloxite or alundum
depending on its crystalline form. It is found usually in its polymorphic phase $\alpha$ –
$Al_2O_3$ along with precious gemstone ruby and sapphire. $Al_2O_3$ has use in extracting
aluminum, as an abrasive because of its firmness, and as a refractory material due to
its high melting point.

$ZrO_2$ is the only thermodynamically stable solid of zirconium with a simple fluorite
structure [1]. It has monoclinic, tetragonal, cubic crystal structure. It is unstable
and can form $ZrSi_2$ by interacting with Si. $ZrO_2$ has oxygen vacancies in case of non-
stoichiometry. For MOSFET applications, an amorphous phase of $ZrO_2$ is preferable
than other crystal structures for preventing leakage current through grain boundaries
[1].

Titanium oxide, ($TiO_2$), has two phases: anatase (applicable in catalysis and sup-
ports) and rutile (useful in optoelectronics) [1]. It has the highest dielectric constant
(80-110) among IV-B oxides and wide band gap (3.0-3.5eV). The band gap of $TiO_2$
varies with different crystal structures (3.2-3.5eV for amorphous and 3.0-3.2eV for
crystalline). Anatase is thermally unstable along with low dielectric constant. This
phase alters to rutile phase (with high dielectric constant and thermally stable) at
high temperature. These properties make rutile potential candidate as gate oxide [1].

It is not possible to simultaneously optimize $k$, $E_g$ and $E_{bd}$ for simple oxides
For balancing these parameters, a promising high k material should have a dielectric constant 10-30, band gap should be above 5eV and band offset with the substrate should be above 1eV to minimize leakage current. The material should be thermally stable for at least 90s at very high temperature (1000K) to form a good interface. This makes most of the oxides from memory devices such as $Ta_2O_5$ non ideal due to their destructive reactions with Si.

### 2.3.1 Hafnium Oxide

Hafnium oxide, a colorless, clear solid, is the most prevalent and stable oxide of hafnium. There are some IV-B metal oxides of significant interest e.g., HfO$_2$, ZrO$_2$, TiO$_2$. Zirconia (ZrO$_2$) and Hafnium oxide (HfO$_2$) have the same structure consists of seven folds coordinated at room temperature and exposed to oxygen. There are various crystalline phases available with different experimental parameters. These are cubic, tetragonal, monoclinic and orthorhombic [1]. Now HfO$_2$ (hafnia) is being explored for ferroelectric properties. Two orthorhombic polar phases show ferroelectric phases of hafnia [59]. It has a large band gap 5.3-6 eV. The conduction band offset is also high 1.5eV. The dielectric constant is really large (25) which is 4-6 times larger than SiO$_2$. HfO$_2$ is really stable and can be used as a stable contact. Besides, it has a large heat of formation ($\sim$ 271 kcal/mol) higher than SiO$_2$ ($\sim$ 218 kcal/mol) [1, 39]. The effective mass of electron lies between $0.7m_0 - 2.0m_0$. Oxygen vacancies in a wide-bandgap oxides change electrical properties by forming defect states in between the band gap. Oxygen vacancy in oxide increases the conduction band density of states. Other kinds of defects, grain boundaries and dislocations, can also alter properties of devices. For eliminating the dangling bond at Si/HfO$_2$ interface two approaches are taken. These are passivation and introducing another interfacial layer. So, HfO$_2$ can also be used as an alternative of SiO$_2$ for Metal-Insulator-Semiconductor (MIS) structures for diode and UV LED applications [40]. HfO$_2$ can be used in sub 10nm
resistive random access memory (RRAM) because of low leakage current and high ON/OFF ratio [60]. Besides, it can be used as optical coating, refractory material, as insulation of thermocouples because of its high melting temperature [1]. Table 2.1 describes the properties of HfO$_2$ as summary:

Table 2.1: Properties of hafnium oxide [1].

<table>
<thead>
<tr>
<th>IUPAC name</th>
<th>Hafnium (IV) oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other names</td>
<td>Hafnium dioxide, Hafnia</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>HfO$_2$</td>
</tr>
<tr>
<td>Molar mass</td>
<td>210.49g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>off-white powder</td>
</tr>
<tr>
<td>Density</td>
<td>9.68g/cm$^3$, Solid</td>
</tr>
<tr>
<td>Melting point</td>
<td>2,758°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>5,400°C</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Flash point</td>
<td>Non-flammable</td>
</tr>
</tbody>
</table>

### 2.4 Semiconducting Oxides

Though most of the oxides are insulating in behavior, semiconducting oxides are binary oxides with semiconducting properties. One can control the electrical conductivity in oxide thin films and nanostructures by changing growth parameters and/or applying other fabrication techniques. This is crucial for their applications in optoelectronics and electronics. These materials find numerous applications, including gas sensors, transparent conducting layers, catalysis, energy storage and conversion, and optoelectronics [17]. There are many semiconducting oxides that have already found practical applications e.g., zinc oxide (ZnO), titanium oxide (TiO$_2$), tin oxide (SnO$_2$), and to some degree nickel oxide (NiO), among others. These oxides can be intrinsically p-type or n-type because of intrinsic or native defects. These are also
wide-bandgap semiconductors and can be highly conductive. The control of conductivity is really challenging and undoubtedly essential for development of electronic devices. Besides, their nanostructures have been extensively studied as gas sensors because of their small dimensions, low cost and high compatibility with microelectronic processing. Because of their large surface to volume ratio and Debye length, comparable to the small size, they show better performance in surface chemical processes. Sensors show better performance with the size of the nanocrystals less than half of the Debye length. The catalysis effect is dependent upon surface area and other size-related properties [17].

Tin (Sn) has two possible oxidation states i.e., +2 and +4 which constitute Ti(II) oxide (SnO) and Ti(IV) oxide (SnO₂), respectively. SnO₂ is slightly more stable than SnO[56]. The Roman numerals in parentheses are used from now on in this thesis to indicate the oxidation state of the metal. Between these two, tin (IV) oxide (known as stannic oxide) has a large band gap (3.6eV at room temperature) and is highly transparent in visible range. The transparency along with high conductivity makes it useful for transparent conductive electrode in solar cells and other applications. It is highly sensitive to low gas concentration which can be used in gas sensor applications e.g., hydrogen sulfide (H₂S) [61], carbon monoxide (CO), methane (CH₄) [62]. It can be used as oxidation catalyst as well [17, 61].

Titanium has a wide range of oxidation state i.e., +4, +3, +2, +1, -1, -2. Among them, titanium (IV) oxide (TiO₂, known as titanium dioxide or titania) is only stable in air [17, 61, 63]. The band gap is 3.05eV. This can be used as heterogeneous catalysis, as a photo-catalyst, as transparent conductor, in solar cells for hydrogen and electric energy, as gas sensors, as white pigment, as corrosion protecting coating and in electric devices. It can be used in nanostructured form in Li-based batteries and electrochromic devices [17, 61, 63].
2.4.1 Nickel Oxide

Figure 2-1: (a) Crystal structure of NiO as a unit cell (black circle is Ni atom and red circle is oxygen atom); (b) As a bulk (green circle is oxygen atom and blue circle is Ni atom) [2].

Nickel oxide (NiO) is the only extensively studied oxide of nickel. However, there are reports about $Ni_2O_3$ [64]. This is categorized as a binary transition metal oxide. NiO is intrinsically a p-type semiconductor. The band gap of NiO is 3.3-4eV. The stable crystal structure of NiO at room temperature is polymorph bunsenite which can be transformed to rhombohedral by cooling. These crystals are formed during thermodynamically stable (near-equilibrium) transitions [2]. The lattice constants for face centered rombohedral crystal are a=4.1Å, $\alpha = 3.8^\circ$ at room temperature [19]. Different fabrication techniques can produce different non-stoichiometric structures e.g., simple cubic at room temperature. The crystal structure of NiO is cubic, (sometimes called rocksalt structure) with octahedral $Ni^{2+}$ and $O^{2-}$ sites. The lattice parameter for this structure is 4.178Å [65]. Figure 2-1 (a) & (b) show the crystal structure of NiO as a unit cell and as a bulk, respectively. NiO crystal is usually a solid with a periodic crystal structure. One of the specialties of NiO is the availability
of Ni as a precursor material. Nickel is really cheap, earth abundant and environment friendly [19]. Below Neel temperature of \( T_{\text{N}} = 523\text{K} \), NiO is antiferromagnetic [2, 65].

An ideal stoichiometric semiconducting NiO without any defects acts as an insulator. The resistivity is around \( 10^6-10^{13}\Omega.cm \) at room temperature [19]. One can alter the electrical, optical and mechanical property of oxide by introducing defects. Because of growth techniques and parameters, NiO can be changed from stoichiometric to non-stoichiometric. For example, \( \text{Ni}_{1-\delta}\text{O} \) where \( 0 < \delta < 0.005 \). At \( \delta \) close to upper boundary, the color of NiO is black / brownish while with smaller \( \delta \) value, the color is green. The optical properties change based on fabrication parameters and film thickness [19, 65]. Generally, it is opaque to visible light, but absorbs in IR range of electromagnetic spectrum. This is why it can also be used in bolometric applications [65].

The actual conduction process in nickel oxide is really still under debate. According to some research groups, thermal excitation of the holes from the shallow acceptor levels or thermal excitation of polarons (small polaron hopping) can be a possible reason of conduction [19, 65]. With the increase of temperature, the resistance of NiO thin film decreases and with decreases of temperature, the resistance increases. This is a proof for nickel oxides semiconducting properties [66].

Moreover, the band gap can be easily engineered by alloying NiO with MgO and CdO. The band gaps of MgO and CdO are 7.2eV and 2.18eV, respectively [67]. \( \text{Ni}_x\text{Mg}_{1-x}\text{O} \) has applications in ultra-violet optoelectronics mostly in solar blind photodetectors (220-280nm) [68]. Solar blind photodetectors are getting a lot of attentions recently because of their diverse applications in missile plume sensors, flame detector, chemical biological agent sensors, underwater/submarine communication systems and space communication [68]. \( \text{Ni}_x\text{Mg}_{1-x}\text{O} \) is much better than its competitor \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) in this regard because of large lattice mismatch and the high growth temperature of the later one [68]. Table 2.2 provides the general properties of
NiO:

Table 2.2: Properties of nickel oxide [2].

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Rock Salt (Octahedral)</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>3d⁸</td>
</tr>
<tr>
<td>Cation</td>
<td>Ni²⁺</td>
</tr>
<tr>
<td>Binding energy (O1s)</td>
<td>530eV</td>
</tr>
<tr>
<td>Optical basicity</td>
<td>0.915</td>
</tr>
<tr>
<td>Oxide ion polarizability</td>
<td>High</td>
</tr>
<tr>
<td>Molar mass</td>
<td>74.6928g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>6.67g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1957°C</td>
</tr>
<tr>
<td>Band gap</td>
<td>2.0-4.3eV</td>
</tr>
<tr>
<td>Type of conductivity</td>
<td>P-type</td>
</tr>
<tr>
<td>Resistance</td>
<td>$10^9 - 10^{11}$Ω.cm</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>10</td>
</tr>
<tr>
<td>Coefficient of refraction</td>
<td>2.23</td>
</tr>
<tr>
<td>Refractive index (n)</td>
<td>2.18</td>
</tr>
<tr>
<td>Other names</td>
<td>Nickel Monoxide, Oxonickel</td>
</tr>
<tr>
<td>Appearance</td>
<td>Green crystalline solid</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Negligible, soluble in KCN</td>
</tr>
<tr>
<td>$H_f$ for metal oxide formation per oxygen atom @ 298 K</td>
<td>245.2kJ/mol</td>
</tr>
</tbody>
</table>

2.4.2 Zinc Oxide

The continued interest in ZnO for last several decades is because of its large exciton binding energy (60meV) and wide band gap (~3.3eV) [25, 27, 28]. ZnO is considered as a possible low-cost substitute for GaN, another widely used wide band gap semiconductor for green, blue, UV and white LEDs [26]. ZnO has some advantages over GaN because of easily available high-quality ZnO bulk single crystals, simple crystal growth technology resulting in cheap devices. ZnO and GaN both have wurtzite crystal structure with same lattice parameter, but ZnO is available as bulk
single crystal. So, ZnO can be used as substrate for epitaxial growth of high quality GaN [27]. It is preferable to other wide band gap semiconducting oxides because of its high energy radiation stability and feasible wet etching. Higher resistivity to radiation makes it suitable for space applications. It can be etched in acids and bases resulting in fabrication of small and low-cost devices [25–28].

The large exciton binding energy can be used for intense near band edge excitonic emission at room and higher temperature because the exciton binding energy is 2.5 times higher than room temperature thermal energy (kT=25meV) [25–28, 69]. The exciton binding energy refers to the strength of bond between an electron and a hole in an electron-hole pair (exciton). Higher exciton binding energy leads to less dissociation of pairs by thermal energy and other effects. The proximity of electron hole pairs increases the chances of electron hole recombination and improves the probability of a photon emission. For optoelectronics applications, this binding energy is the key factor for efficient devices. Since for GaN exciton binding energy is 25meV
which is equal to room temperature thermal energy, the probability of dissociation of exciton by thermal energy at room temperature is high. This limits GaN use in optoelectronics applications whereas ZnO has a binding energy of 60meV higher than room thermal energy 25meV. This ensures, the excitons will be bound at much higher temperature than GaN resulting in higher efficiency [69].

ZnO and GaN have similar, wurtzite crystal structure under ambient conditions [17]. At pressures above 8GPa, ZnO transforms to rocksalt structure. It has a zincblende phase as a thin film on GaAs substrates [27, 69]. Figure 2-2 shows all of the structures of ZnO unit cells. In the wurtzite structure, there are 4 atoms per unit cell. The lattice parameters of ZnO with wurtzite structures are a = 3.2495Å and c = 5.2069Å [28]. The ratio of c/a is 1.602 which is consistent with ideal hexagonal structure, 1.633 [17]. The Zn atoms have a tetrahedral coordination with four oxygen atoms where the Zn d orbital hybridizes with the p orbitals of the O atoms [17, 69].

For wider use of ZnO in devices, the reliable and reproducible growth of p-type ZnO should be achieved. There are some reports on p-ZnO using various growth methods and group V dopant elements (In, P, As, Sb), but these reports lack reproducibility and reliability [27]. The cause of intrinsic n-type behavior of ZnO is still under debate [25, 27]. For extensive use of ZnO, the type of conductivity should be confirmed for proper doping concentration. It is alleged that intrinsic defects e.g., oxygen vacancy, interstitial zinc atom or hydrogen impurity can be the cause of n-type behavior [25, 27]. Because of problem with p-type doping, some heterojunctions with Si, NiO, GaN, AlGaN, SiC, ZnTe, CuO and CdTe, etc. have been tried to play role as p-type materials [27]. High electron mobility, high thermal conductivity along with wide-bandgap and large binding energy make ZnO useful for various kinds of devices e.g., thin film transistor, photodiode, light emitting diode, laser diode operating in blue and UV region [26]. Band engineering of ZnO can be obtained by alloying MgO and CdO with ZnO [3, 25, 27]. Adding Mg increases the band gap (as high as
∼5eV) whereas adding Cd decreases the band gap (as low as ∼2eV). Although both of them have rocksalt structure, for moderate doping the alloys take wurtzite structure of parent compound [3]. The tunable band gap of ZnO can open opportunities in heterojunctions and quantum well engineering [3, 25, 27]. Table 2.3 below shows the general properties of ZnO in details:

Table 2.3: Properties of zinc oxide [3].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>ZnO</td>
</tr>
<tr>
<td>Molar Mass</td>
<td>81.38g/mol</td>
</tr>
<tr>
<td>Appearance</td>
<td>White Solid</td>
</tr>
<tr>
<td>Odor</td>
<td>Odorless</td>
</tr>
<tr>
<td>Density</td>
<td>5.606g/cm³</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>1975°C</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>0.004% (17.8°C)</td>
</tr>
<tr>
<td>Band gap</td>
<td>3.3eV</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60meV</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.0-2.5</td>
</tr>
<tr>
<td>Type of conductivity</td>
<td>N-type</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>a=3.25Å, c=5.2Å</td>
</tr>
<tr>
<td>a/c</td>
<td>1.602</td>
</tr>
<tr>
<td>Coordination geometry</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>Expansion co-efficient</td>
<td>a=6.5 × 10⁻⁶°C⁻¹, c = 3.0 × 10⁻⁶°C⁻¹</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6,1~1.2W/mK</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>8.656F/m</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>.24m₀</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>.59m₀</td>
</tr>
</tbody>
</table>

2.5 Common Defects in Crystals

There is no ideal crystal. Above zero temperature, all the crystals have defects. The defects in crystals can be point defects, line defects and planar defects. All of the defects affect the material properties (electrical and optical, etc.). Concentration
of a defect in crystal is mainly related to its formation energy. Low formation energy means higher probability of defect formation whereas high formation energy refers to lower probability of that [27]. That is why, among all the defects, point defects are the most common because of their small size and lowest potential energy.

2.5.1 Point Defects

![Diagram of vacancy formation](image)

Figure 2-3: Vacancy formation by atom transfer to the surface by breaking bond and the subsequent vacancy diffusion into the bulk: (a) Perfect crystal without any defects; (b) An atom at the surface breaks the bond and jump outside to a neighboring place on the surface. This creates a vacancy; (c) An atom in the bulk diffuses to fill the vacancy pushing the vacancy toward the bulk from the surface; (d) Atomic diffusions cause vacancy to diffuse in the bulk.

Point defects can be created by interstitials, substitutions and vacancies mostly. Vacancies present in the crystal for thermal equilibrium are called thermodynamic defects. Vacancy perturbs the periodic arrangement of atoms. According to kinetic molecular theory, all the molecules are vibrating at their equilibrium position. If any of the atoms accumulates sufficient energy to break the bond and gets outside of the arrangement, then the place of that atom creates a vacancy. This vacancy can diffuse
in the bulk with the help of a neighboring atom [5]. Figure 2-3 elaborates the impact of vacancy formation.

![Figure 2-4: Point defects in the crystal structures: (a) Vacancy, (b) Larger substitutional impurity, (c) Smaller substitutional impurity and (d) Interstitials.](image)

There are some other point defects along with vacancies which can result in lattice charge and lattice distortion. These are associated with either intrinsic or intentional impurities. These can be substitutional and interstitials. Mostly substitutional atoms are different in size and valance number. That causes a distortion in the periodic lattice structures. Then the crystal is called strained around a point defect [5]. The figure 2-4 describes all the point defects possible.

### 2.5.2 Line Defects

A line defect is formed when an atomic plane is not continuous in the whole crystal structure from the beginning to the end of the structure [5]. There are two kinds of line dislocations e.g., edge dislocations and screw dislocations. However, line defects can be a mixture of edge dislocations and screw dislocations. For sputtered condition, line defects are not that vital [5].
2.5.3 Planar Defects

Planar defects are mostly related to polycrystalline film [5]. Figure 2-5 describes the solidification of polycrystalline material from melt. In polycrystalline films, there are small crystalline grains or crystallites. Polycrystalline materials have grain boundaries where different crystalline-oriented grains meet. Because of abrupt crystal orientation changes, the atoms at grain boundaries cannot have their regular properties. There are voids, stretched and broken bonds. There are also misplaced atoms which dont follow the behavior of grains from either side. The atoms in the grain boundaries are more energetic than the atoms in bulk. Impurities also like to gather in the grain boundary region [5]. Figure 2-6 shows the defects in the grain boundaries of polycrystalline thin films.
2.6 Defects in Semiconducting Oxides

2.6.1 Defects in Nickel Oxide Crystals

There is no Ni\(^{3+}\) defect in epitaxial nickel oxide (NiO). Ni\(^{3+}\) is only present in thin films, obtained by sputtering, sol-gel and pulsed laser deposition [16]. NiO is a charge transfer type insulator (materials anticipated to be conductors according to conventional band theory, but are in fact insulators due to a charge transfer process). Unlike Mott insulators, the electrons in charge transfer insulators move between atoms within the unit cell [70]. NiO has applications in non-volatile memory because of resistive switching behavior of NiO. The defects of NiO play a vital role in the bi-stable resistance of NiO [14]. NiO is intrinsically p-type because of cation vacancies rather than oxygen vacancies. NiO fabricated in oxygen excess environment is associated with nickel vacancies. Nickel vacancies are the dominant point defects. For neutral behavior, some of the Ni\(^{2+}\) should be converted to Ni\(^{3+}\) which serves as a carrier for
Figure 2-7: Vacancy in nickel oxide crystal: (a) Nickel vacancy and (b) Oxygen vacancy. Here, yellow and blue circles define oxygen and nickel atoms, respectively, along with the dashed lines corresponding to vacancies.

Conduction in NiO thin film [15]. Figure 2-7 shows Ni and O vacancies.

In ambient environment, nickel vacancies ($V_{Ni}$) can be filled with other impurities such as Fe and Li [15]. Lattice defects concentration changes with high oxygen content environment or thermal annealing [71]. The lattice constant increases with increasing oxygen content. Besides, loosely bonded interstitial oxygen atoms in NiO diffuse out upon annealing or heating. NiO film with high oxygen content has poor crystallinity. NiO does not have a perfect crystalline structure, but the crystallinity improves with increasing the annealing temperature because of decrease in the concentration of native defects. Because of this some groups reported dominant defects come from oxygen interstitials [71]. The number of Ni$^{3+}$ decreases with annealing temperature [15]. Although the nickel vacancy is the most common defect in bulk NiO, the growth condition with low oxygen pressure can result in oxygen vacancies. Besides, it is found that nickel vacancies introduce shallow level in the density of states. Specific defect arrangement is favorable for nickel and oxygen vacancies. For nickel vacancies, defect ordering in simple cubic structures is the most stable resulting in half metallic
behavior. The ionized oxygen vacancies have a tendency toward clustering more strongly than in the neutral pairs [14].

Other defects such as dislocations (edge, screw or mixed) are also possible depending on the fabrication technique [2]. The planar (or 2D) defect can be classified in grain boundaries and stacking fault. Grain boundaries are dominant when different crystal orientations are present in one material. The later one is more common in closed packed structures (FCC and HCP) because of misalignment of several stacks of atoms in preferred orientation. The properties of the material can be altered by changing the number of defects in the crystal. Polycrystalline films, mostly fabricated by sputtering, pulsed laser deposition and solgel are most likely have grain boundaries and planar faults [2]. Fabrication procedures, growth temperature, O$_2$/Ar ratio and annealing temperature [71] have a strong effect on the properties of NiO [2].

### 2.6.2 Defects in Zinc Oxide Crystals

Oxygen vacancies ($V_O$) and zinc vacancies ($V_{Zn}$) are the lowest energy defects followed by zinc interstitials ($Zn_i$) and zinc antisites ($Zn_O$) [25, 72]. Oxygen interstitials ($O_i$) and oxygen antisites ($O_{Zn}$) were found in very high energy. The defects that are favored under Zn rich conditions ($V_O$, $Zn_i$, $Zn_O$) are donors while those that are favored under oxygen rich conditions ($V_{Zn}$, $O_i$ and $O_{Zn}$) are all acceptors. Depending on the partial pressure of oxygen upon deposition, there are two common defects in zinc oxide (ZnO) - these are oxygen and zinc vacancies. The oxygen vacancy ($V_O$) has lower formation energy than even zinc interstitials ($Zn_i$) and therefore oxygen vacancies should be much more likely than zinc interstitials under Zn-rich conditions. Under oxygen-rich conditions, zinc vacancies ($V_{Zn}$) should dominate. The oxygen vacancy is the most studied defect in ZnO [25, 72]. Previously, the oxygen vacancy was thought as the main cause of intrinsic n-type behavior of ZnO. However, this assumption is being questioned in recent years [25, 72, 73]. Although the formation
energy is the lowest for oxygen vacancy, $V_O$ is very deep rather than a shallow donor. Consequently, it cannot be the source of conductivity, but it can be a source of p-type ZnO compensation [25, 72, 73].

Zinc vacancies have high formation energies in p-type ZnO and their concentration will be low for p-type materials [25, 72]. In n-ZnO, $V_{Zn}$ has the lowest formation energy among the native point defects indicating $V_{Zn}^{2-}$ can occur in modest concentration in n-type ZnO, acting as compensating center. In fact, Zn vacancies have been identified as the dominant compensating centers in n-ZnO. They are also more favorable in oxygen-rich conditions. Because of high formation energy, it is highly unlikely that $V_{Zn}$ would be a source of p-ZnO [25, 72].

A zinc interstitial atom ($Zn_i$) can in principle occupy the tetrahedral site or octahedral site in the ZnO wurtzite structures [25, 72]. Based on size consideration, it is expected that Zn interstitials will be more stable at octahedral sites where the geometrical constrains are less severe. Octahedral sites are stable for $Zn_i$ whereas $Zn_i$ at the tetrahedral site is 0.9eV higher in energy and is therefore unstable as it spontaneously relaxes to octahedral site. Probably, even under extreme Zn-rich conditions, Zn interstitials are not the cause of unintentionally n-type conductivity. On the other hand, the formation energy of $Zn_i^{2+}$ decreases rapidly with p-type doping of ZnO, making the Zn interstitials a potential source of compensation in p-type ZnO [25, 72].

The other native defects (zinc antisites, oxygen interstitials and oxygen antisites) have higher formation energy therefore are not expected to play a role in ZnO under near equilibrium conditions [25, 72]. The $Zn_O$ antisite is a double donor in n-type ZnO, but its high formation energy indicates that it is an unlikely source of unintentional n-type conductivity. The migration of $Zn_O$ would involve splitting the defect into its $Zn_i$ and $V_O$ constituents raising the questions of whether these constituents would remain bound and move in concert or would move independently. The dissociation
barrier of $\text{Zn}_2^+$ into $\text{Zn}_i^2+$ and $V_O^0$ is $\sim 1.3\text{eV}$ in n-type ZnO which can make $\text{Zn}_O^{2+}$ stable at temperature up to $\sim 500\text{K}$. $\text{Zn}_O^{2+}$ may cause n-type conductivity in case of non-equilibrium condition e.g., high energy electron irradiation [25, 72].

The oxygen interstitials ($O_i$) can, in principle, take the octahedral or tetrahedral interstitial sites or form split interstitials [25, 72]. $O_i$ at tetrahedral site is unstable and becomes a split-interstitial configuration where the extra O atom shares a lattice sit with nearest neighbor O atoms. $O_i$(split) has a metastable configuration with a formation energy that is $0.2\text{eV}$ higher than the lowest energy configuration. Oxygen interstitials can also exist interstitials occupying the octahedral site $O_i$(oct). $O_i$ can exist either as electrically in active $O_i^0$(split) in semi-insulating and p-type materials or as deep acceptors at the octahedral interstitial site $O_i^{2-}$ in n-type materials. Both of them have high formation energy (except under high $O_2/(O_2+\text{Ar})$ ratio condition). $O_i$ is the reason for defect recombination on oxygen sub-lattice of n-ZnO [25, 72].

The oxygen antisite ($O_{\text{Zn}}$) is an acceptor type defect with high formation energy even under the most favorable O rich conditions [25, 72]. It is almost impossible that $O_{\text{Zn}}$ would be present at equilibrium. $O_{\text{Zn}}$ can be created under non-equilibrium e.g., laser irradiation or ion implantation. Besides, O on the ideal Zn site is unstable and relaxes to an off-site configuration. $O_{\text{Zn}}$ would become $V_{\text{Zn}}$ and $O_i$ and it is predicted that its migration barrier would be higher than that of those two. So, $V_O$ is a deep donor which can compensate p-ZnO, but it is unlikely to be of the reason for intrinsic n-type behavior of ZnO whereas $Zn_i$ is shallow donor with high formation energy for n-ZnO. $V_{\text{Zn}}$ is a deep acceptor with low formation energies under n-type conditions of ZnO which can likely be a compensating defect of n-ZnO [25].
Figure 2-8: (a) Energy band diagram of two isolated semiconductors of opposite type and different band gap $E_g$ (where $b$ and gap n-type material is smaller than that of p-type material); (b) Their idealized anisotype heterojunction at thermal equilibrium. (c) & (d) With the different band gap i.e., band gap of p-type material is smaller than n-type.

### 2.7 Homojunctions and Heterojunctions

A homojunction is the interface between two differently doped regions of the same semiconductor together with the interfaces immediate vicinity. The homojunctions can be of p-n type, or, if two n-type (p-type) semiconductors with different doping levels are connected, that would also be a n-type to n type (p-p) homo-junction [53].

A heterojunction is a junction between two different materials, which generally have different band gaps as well as other different material parameters [58]. If two of them have same type of carrier, then it is called isotype heterojunction whereas if two of them have different type of carrier, then it is called anisotype heterojunction. The later one is much conventional and useful structure than the former one. Figure 2-8 (a) & (c) show energy band diagram of two isolated semiconductors of opposite type.
prior to the formation of a heterojunction. Two different semiconductors have two
different band gaps $E_g$, different dielectric permittivities $\epsilon_r$, different work functions
$\phi_m$ and different electron affinities $\chi$. The difference in energy of conduction band
edges in the two semiconductors $\Delta E_c$ and the difference in energy of valence band
edges is represented by $\Delta E_v$. The energy band diagram difference is denoted by $\Delta E_g$
[58]. In the ideal case, these quantities and the semiconductor parameters are related
as:

$$\Delta E_c = q(\chi_2 - \chi_1) \quad (2.2)$$
$$\Delta E_v = E_{g1} + q\chi_1 - (E_{g2} + q\chi_2) = \Delta E_g - \Delta E_c \quad (2.3)$$
$$\Delta E_g = E_{g1} - E_{g2}. \quad (2.4)$$

Figure 2-8 (b) & (d) shows equilibrium band diagram of an ideal abrupt hetero-
junction formed between these semiconductors where narrow band gap material is
n-type (b) and p-type (d). This assumes an ideal case where there is a very few traps
and other defects (i.e., recombination centers) at the interface of the two dissimilar
materials. This is valid only for heterojunctions of semiconductors with same lattice
constant. The two basic requirements of energy band diagram of heterojunction:

- The Fermi level must be same for both sides of the material &
- Vacuum level must be continuous and parallel to the band edges [58].

2.8 P-n Junctions

Figure 2-9 (a) shows the band diagram of isolated p-type and n-type material. If
two p-type and n-type semiconductors are brought together to form a junction, diffu-
sion of carrier would happen because of large concentration gradient at the junction
Figure 2-9: Properties of equilibrium p-n junction: (a) Isolated p-type and n-type material and energy band for the isolated region; (b) Junction showing space charge in transition region, the resulting electric field and contact potential and separation of energy bands.

[74]. There is a large concentration of holes and few electrons in p-type material, whereas for n-type materials the situation is totally the opposite. The holes diffuse from the p-type into the n side and electrons of n-type material go from n to p. The diffusion current has a limiting value because of build-up of an opposing electric field. This electric field reaches a value at which the net current is zero under equilibrium conditions. The electric field appears in a region with size $W$ and there is an equilibrium potential difference $V_o$ across $W$. The region where the electric field is not zero is called transition (or depletion) region. The potential difference is called a contact potential. The contact potential across space charge region or depletion region, $W$, is called built-in potential barrier [74].

The built in potential, $V_o$, is given by,

$$V_o = \frac{KT}{q} \ln \left( \frac{N_a N_d}{n_i^2} \right)$$  \hspace{1cm} (2.5)

$$p_p n_p = p_n n_n = n_i^2.$$  \hspace{1cm} (2.6)
Since the Fermi level must be constant throughout the device at equilibrium, one can draw the band diagram of p-n junction. Figure 2-9 (b) shows the band diagram of p-n junction at zero bias [74].

### 2.8.1 NiO/ZnO Heterojunction

![NiO/ZnO Heterojunction Diagram](image)

Figure 2-10: Energy-band diagram for p-NiO/n-ZnO heterojunction under zero bias.

ZnO is intrinsically n-type conductive. To form p-n junction, p-type dopant for ZnO is needed, but very few reports are available for p-type doping of ZnO [75, 76]. For dealing with the problem of p-type doping of ZnO, fabrication of metal-oxide-semiconductor structures [29–31] or to substitute p-type ZnO by another easily available p-type material can be utilized [22–25, 32–35]. Nickel oxide is an example of a material which can be easily fabricated and intrinsically p-type. The band gap of NiO is 3.7eV. The resistivity is also high. Depending on the carrier concentration p-NiO/n-ZnO can be either p-n (high $N_a$) junction or MIS (low $N_a$). Both of them will have a depletion region in n-ZnO [77]. Besides some other alternatives e.g., Si, GaN, AlGaN, SiC, ZnTe, CuO, CdTe, CuAlO$_2$, ZnMgO have been used [25, 27]. These also have the potential to overcome the challenges associated with Si-based UV photodetectors. However, because of leakage current and imperfection at the heterojunction interface
these are major challenges for these devices in UV applications [78]. Figure 2-10 shows the idealized energy band diagram in NiO/ZnO heterojunction from Anderson model. The electron affinity of ZnO and NiO are 4.2eV and 1.46eV, respectively and the band gap of ZnO and NiO are 3.31eV and 3.41eV, respectively. From the model, the energy barrier for the electrons is \( \Delta E_c = \chi_{ZnO} - \chi_{NiO} = 4.2 - 1.46 = 2.74eV \) and energy barrier for holes is \( \Delta E_v = E_g(ZnO) - E_g(NiO) + \Delta E_c = 3.31 - 3.41 + 2.74 = 2.64eV \) [36, 78, 79]. For getting a better understanding of band structure of NiO/ZnO, the energy difference between the fermi level and valence band (p-type), \( \delta p \) or conduction band edge (n-type) \( \delta n \) can be determined by carrier concentration of p-NiO and n-ZnO, respectively. The values of \( \delta p \) and \( \delta n \) from the previous studies are .03 eV and 0.11eV [36]

The NiO/ZnO combination has seen relatively limited interest, but there are reports on the heterojunction used as a photodetector [38], a photodiode [23], memristive devices [80], light emitting diode [22], and in photo catalytic applications [81].

### 2.9 Metal Semiconductor Contacts

When a contact between a metal and a semiconductor is made, a barrier is formed at the metal-semiconductor interface. This barrier is the main factor for controlling the current voltage characteristics as well as its capacitance behavior [58]. Figure 2-11 shows energy band diagram with the ideal case without surface states and other anomalies.

Figure 2-11 (a) shows band diagram of separated high work function metal and n-type semiconductor band. If two systems are connected, charges will flow from semiconductor to metal [58]. In thermal equilibrium, the Fermi level of both materials will line up. The Fermi level of semiconductor is altered (raised or lowered for p-type and n-type, respectively) by an amount equal to the difference of two work functions
Figure 2-11: Energy band diagram of a metal-semiconductor contact: metal and semiconductor (a) in separated system and (b) connected into one system.

[58]. This is shown in figure 2-11 (b).

The work function is the energy difference from the vacuum level to the Fermi level. The quantity is given by $q\phi_m$ for the metal and is $q(\chi + \phi_n)$ or $\phi_s$ in the semiconductor. Here $q\chi$ is the electron affinity from the vacuum level to the conductor band, $E_c$ and $q\phi_n$ is the energy difference between the conductor bands to the Fermi level. The potential difference between these two work functions is called the contact potential [58]. When the metal and semiconductor are connected, for barrier height of n-type, $\phi_{Bno}$ and p-type materials, $\phi_{Bpo}$, respectively, can be expressed as:

$$q\phi_{Bno} = q(\phi_m - \chi)$$ (2.7)

$$q\phi_{Bpo} = E_g - q(\phi_m - \chi)$$ (2.8)

$$E_g = q\phi_{Bpo} + q\phi_{Bno}.$$ (2.9)
2.10 Metal Insulator Semiconductor

Figure 2-12: Metal-insulator-semiconductor structure in simplest form.

The metal-insulator-semiconductor (MIS) is a vital device structure in semiconductor surfaces study and research. A MIS structure is shown in figure 2-12. MIS structures are the basis of learning (metal oxide semiconductor field effect transistor) MOSFET, the most important device for advanced integrated circuit. For the energy band diagram of an ideal MIS with n-type and p-type semiconductor at V=0 is shown in figure 2-13 (a) & (b), respectively [58].

For ideal MIS structures, there are some assumptions to be made. These are:

- the only charges that exist in the interface are from the semiconductor and metal (exact equal and opposite sign to semiconductor). It is assumed that no interface trap or oxide charge is present [58].

- There is no carrier transport through the insulator or the resistivity is infinite. Also, $q\psi_B$ is the energy difference between the Fermi level $E_f$ and the intrinsic Fermi level $E_i$. It is assumed that the difference between the metal work function and the semiconductor work function is zero, or $\phi_{ms}=0$ [58]. This is shown in the figure 2-13 and reflected in the equations below:
\[ q\phi_{ms} = (q\phi_m - q\phi_{sp}) \]
\[ = q\phi_m - (q\chi + \frac{E_g}{2} + q\psi_{Bp}) \]
\[ = q\phi_m - (q\chi + E_g - \phi_p) = 0 \quad (2.10) \]
\[ q\phi_s = q\chi + \frac{E_g}{2} + q\psi_{Bp} \quad (2.11) \]
\[ q\phi_{ms} = (q\phi_m - q\phi_{ns}) \]
\[ = q\phi_m - (q\chi + \frac{E_g}{2} - q\psi_{Bn}) \]
\[ = q\phi_m - (q\chi + \phi_n) = 0 \quad (2.12) \]
\[ q\phi_s = q\chi + \frac{E_g}{2} - q\psi_{Bn}. \quad (2.13) \]

\( \chi_s \) and \( \chi_i \) are the electron affinity for the semiconductor and insulator, respectively, and \( \psi_{Bn}, \psi_{Bp}, \phi_n, \phi_p \) are the Fermi level potentials with respect to the midgap, and band edges, respectively for p-type and n-type material. The band is flat for an applied voltage of zero, that's why it is called flat band diagram.
2.10.1 Current Transport in MIS Structures

The conduction through insulator is zero in MIS structures with an ideal, thick insulator. However, there can be a degree of carrier conduction with sufficiently high electric field and at high temperature [58]. To estimate the electric field in an insulator under biasing condition,

\[ \xi_i = \xi_s \left( \frac{\epsilon_s}{\epsilon_i} \right) = \frac{V}{d}. \]  

(2.14)

\( \xi_i \) and \( \xi_s \) are the electric fields in the insulator and in the semiconductor, respectively and \( \epsilon_i \) and \( \epsilon_s \) are the corresponding permittivities. Negligible oxide charges are assumed and the flat band voltage and semiconductor band bending \( \psi_s \) are considered small compared to the applied voltage. There are five conduction processes in the MIS structures. These are: tunnelling, thermionic emission, Frenkel-Poole emission, ohmic conduction, ionic conduction and space charge limited process [58]. These are explained in detail below:

![Energy band diagram](image)

Figure 2-14: Energy band diagram showing conduction mechanism of (a) Direct tunneling, (b) F-N tunneling, (c) Thermionic emission, and (d) Frenkel-Poole emission [53].

1. Tunneling is the most common conduction mechanism through the insulator under high electric field which is a quantum mechanical phenomenon [58]. This
current transport described in more detail below (in section 2.12). The current is dependent on applied voltage only, but totally independent of the temperature. The tunneling can be of two types: 1) direct tunneling, and 2) Fowler Nordheim (F-N) tunneling (carriers tunnel through only a part of the insulator). This is shown in figure 2-14 (a) and (b). For ultra-thin insulator, tunneling is equivalent to conduction of carriers in metal semiconductor contact. For this case, the barrier is measured at the semiconductor surfaces instead of the insulator and the thermionic-emission current is multiplied by a tunneling factor [58].

2. The Schottky emission process is similar to the process of thermionic emission over metal-insulator barrier or insulator-semiconductor barrier responsible for carrier transport [58]. This is shown in figure 2-14 (c).

3. The Frenkel-Poole emission comes from the emission of trapped electrons in the conduction band [58]. The supply of electrons from the traps is achieved by thermal excitation. The barrier reduction is larger than in the case of Schottky emission by factor of 2 due to the immobility of the positive charge. At low voltage and high temperature, current is driven by hopping of thermally excited electrons from one state to other [58]. This mechanism results in ohmic characteristics exponentially dependent on temperature (see Figure 2-14(d)).

4. The ionic conduction is similar to a diffusion process [58]. Generally, dc ionic conduction decreases with the time of applied electric field because ions cannot be readily injected into or extracted from the insulator. After current flow for a while, opposite charges will build up near the interface which can cause distortion of the potential distribution. After the electric field removal, large internal field stays which can cause some, but not all, ions to flow back toward their equilibrium condition [58].

5. The space charge limited current results from the carriers injected into lightly
doped semiconductors or an insulator where no compensating charge is present. The current for unipolar devices without defects is proportional to the applied voltage [58].

2.11 Tunneling

Quantum tunneling is a quantum phenomenon which refers to a particle (electron) tunneling through a barrier, which is impossible according to classical physics [58]. This is fundamental to many important applications to modern devices such as the tunnel diode, quantum computing, and the scanning tunneling microscope. If two isolated semiconductor samples are separated by a small distance, the electrons can travel across the barrier from one side to another irrespective of the electrons energy. This is called quantum tunneling phenomenon. In classical physics, the particles will always be reflected if the electrons energy is less than barrier height whereas in quantum case, the particles have a finite probability of transmitting or tunneling through the potential barrier even with less energy than the barrier [58].

2.11.1 Tunnel Diode

The tunnel diode was discovered by L. Esaki in 1958 and is often called the Esaki diode after his name. His Ph.D. dissertation was on highly doped germanium p-n junction for high speed bi-polar transistors [58]. He observed some inconsistency in current-voltage characteristics in forward direction- negative differential resistance (dI/dV) and explained it by quantum tunneling theory along with experimental results. A tunnel diode is a simple heavily doped p-n junction with sharp transition in junction. This band diagram of tunnel diode is shown in figure 2-15 (a). In reverse biasing, the current increases monotonically. In forward bias, the current first increases to a maximum value (peak current) at peak voltage then decreases to a
minimum value at a valley voltage. With voltage larger than valley voltage, the current increases exponentially with voltage. The current consists of three currents 1) band to band tunneling 2) excess current 3) diffusion current [58]. The static I-V characteristics are shown in figure 2-15 (b) & (c).

2.12 MIS Tunnel Devices

For metal-insulator-semiconductor devices, the current voltage characteristics depend on the insulator thickness [58]. If the insulator layer is substantially thick, there is negligible current through MIS structures and it behaves as a MIS capacitor. If the insulator layer is too thin, electrons see very small barrier during transport from metal to insulator and it is equivalent to a Schottky barrier diode. In between these two thicknesses, there also exist different tunneling mechanisms. These are related to Fowler-Nordheim tunneling, direct tunneling and MIS tunnel diode. However, negative resistance from MIS tunnel diode on degenerate substrate is also possible for p⁺-type semiconductor [58].
2.12.1 Fowler-Nordheim Tunneling

Figure 2-16: Tunneling mechanism depending on oxide thickness: (a) In thicker oxide F-N tunneling, (b) Direct tunneling and (c) MIS tunnel diode in non-equilibrium \((E_{Fn} = E_{Fp})\) with both type of carrier tunneling.

Fowler Nordheim (F-N) tunneling is characterized by a triangular barrier and tunneling through only a part of the insulator layer. This is shown in figure 2-16 (a). With higher electric field, a much narrower barrier will be in effect. Here, triangular thin barrier is the main obstacle instead of the whole barrier. However, the insulating layer thickness has effect in tunneling current by having an impact on electric field [58]. The F-N current is given by,

\[
J = \frac{q^2E^2}{16\pi^2h\phi_{ox}}exp\left(\frac{-4\sqrt{2m(q\phi_{ox})^{\frac{3}{2}}}}{3hqE}\right) = C_4E^2exp\left(\frac{-C_5}{E}\right). \tag{2.15}
\]

Here, \(C_4\) and \(C_5\) are the constants for thermal oxides. Here the equations have only electric field, but oxide thickness is related to electric field which bolsters the theory.
2.12.2 Direct Tunneling

Direct tunneling occurs with a very thin insulator (∼5nm) [58]. With this small thickness, quantum effects come into effect. Here, the carrier faces the whole insulating layer (shown in figure 2-16 (b)). In quantum mechanics, the peak carrier concentration of the inversion layer occurs at a finite distance from the semiconductor-insulator interface, so effective insulator thickness is more than normal condition. Moreover, the inversion layer is a quantum well and carriers are quantized at energy levels above conduction band edge. Tunneling current is very sensitive to effective oxide thickness [58].

2.12.3 MIS Tunnel Diode Behavior

The tunneling probability for a rectangular barrier with effective barrier height \( q\phi_T \) and width \( d \) can be expressed as:

\[
T_t = \exp\left(-\frac{2d\sqrt{2qm\phi_T}}{h}\right) = \exp(-\alpha_T d\sqrt{\phi_T}).
\]  

(2.16)

Where \( \alpha_T(= 2\sqrt{2qm}/h) \) approaches unity if the effective mass in the insulator equals to the free electron mass, \( \phi_T \) is in volts and \( d \) in Å. The tunneling current can be expressed as:

\[
J = A^*T^2 e^{-\alpha_T d\sqrt{\phi_T}} e^{-\frac{q\phi_B}{kT}} [e^{-\frac{qV}{nKT}} - 1].
\]  

(2.17)

Here, \( A^* = \frac{4\pi m^* q k^2}{\hbar^3} \) is the effective Richardson constant and \( \phi_B \) is the Schottky barrier height. The MIS tunneling diode is shown in figure 2-16 (c). This equation is same as thermionic emission equation for Schottky contact multiplied by an extra term of tunneling probability [58]. For \( \phi_T \) with an order of 1V and \( d > 50\text{Å} \), tunneling probability is really low resulting in low current. In this equation, if \( d \) and \( \phi_T \) decrease,
the current increases exponentially toward thermionic emission. With insulator layer thickness increase, the current decreases rapidly and ideality factor starts to change from unity [58].

![Energy-band diagram of MIS tunnel diode on non-degenerate substrate (p-type) with (a) Low metal-insulator barrier and (b) High metal insulator barrier.](image)

Figure 2-17: Energy-band diagram of MIS tunnel diode on non-degenerate substrate (p-type) with (a) Low metal-insulator barrier $\phi_{mi}$ and (b) High metal insulator barrier.

One of the most vital parameters of MIS tunnel diode is the metal-insulator barrier height [58, 82, 83]. Figure 2-17 shows schematic of energy band diagram at thermal equilibrium for MIS tunnel diodes on p-type substrate with two metal to insulator barrier heights. For low-barrier case the surface of the p-type semiconductor is inverted whereas with high barrier case, the surface is in accumulation of holes. This is explained for low and high barrier height in figure 2-17 (a) and (b), respectively. There are two main tunneling currents. These are $J_{ct}$ carriers from the conduction band to the metal and $J_{vp}$, from the valence band to the metal [58, 82, 83].

For the low barrier case, under small forward (positive voltage on semiconductor and negative on the metal) and reverse biases (positive voltage on the metal and
positive voltage on the semiconductor), the dominant current is the minority carriers (electrons) current, $J_{ct}$ due to the abundance of electrons [58, 82, 83]. With forward bias (positive voltage on semiconductor) increase, the current also increases monotonically. At a given bias, the current increases rapidly with decreasing insulator thickness. This is because of its dependence on the tunneling probability. At reverse bias, the current is independent of insulator thickness. Because the current is limited by the rate of supply of minority carriers (electrons) through semiconductor and the current can be similar to the saturation current in reverse biased p-n junction [58, 82, 83].

For higher barrier, under forward bias, the dominant current is for majority carriers (holes) tunneling current from the valence band to metal [58, 82, 83]. The current increases exponentially with decrease of oxide thickness because of increasing tunneling probability. Under reverse bias for this case, the current is not independent of insulator thickness. The current increases rapidly with decreasing insulator thickness, because for majority carrier transport the current is limited both in directions by the tunneling probability not the rate of carrier supply. So for this case, the tunneling current is always higher specially in reverse direction [58, 82, 83].

### 2.12.4 MIS Tunnel Diode in Degenerate Semiconductors

Negative resistance can be observed in MIS tunnel diode in degenerately doped semiconductor [58]. Figure 2-18 & 2-19 shows simplified band diagrams of MIS tunnel diodes with p+ and n+ semiconductor substrates including interface traps. The band bending, image force lowering and potential drop across oxide layer at equilibrium are omitted for simplicity [58].

For p+ materials, applying a positive bias to the metal (reverse bias) causes electron to tunnel through valence band to metal [58]. The tunneling current increases monotonically and does not show negative resistance. It will also increase with de-
Figure 2-18: Simplified band diagram of MIS tunnel diodes on degenerate substrate including interface traps states for p\(^{+}\) substrate: (a) Flat bland diagram; (b) Reverse bias and ((c)-(e)) Forward bias.

Increasing of effective insulator barrier height (figure 2-18 (b)). With small negative voltage to the metal, electrons will tunnel from metal to the unoccupied semiconductor valence band. With tunneling from metal to unoccupied states of valence band, there will be an increase in effective barrier height. This results in a drop of current with increase of forward bias which can be defined as negative resistance (figure 2-18 (c)). Another current component comes from the electron in the metal with higher energies. Electrons tunnel simultaneously into empty interface traps and momentarily recombine with holes in the valence band (figure 2-18 (d)). Since the effective insulator barrier decreases with bias, the current component has a positive differential resistance. Finally, further increase of bias result in a very fast growing tunneling current component from the metal into the conduction band of the semiconductor (figure 2-18 (e)) [58].

With a n\(^{+}\) semiconductor, the effective insulator barriers for the n\(^{+}\) type are expected to be smaller than those of the p\(^{+}\) type samples [58]. So in general they
will have larger tunneling current. For a negative bias on the metal (reverse bias), electrons tunnel from the metal into the empty states of the semiconductor band. These results in a large and rapidly increasing current (figure 2-19(b)). A small positive voltage on the metal leads increasing electron tunneling from the conduction band of the semiconductor to metal (figure 2-19 (c)). The interface traps are filled with conduction electron by recombination and a further increase in bias gives rise to a second component caused by tunneling of electrons from the interface traps in the metal. This current component increases with increasing bias since the effective insulator barrier decreases (Figure 2-19 (d)). For larger voltage additional tunneling from valence band to metal is possible, but influence on the total I-V characteristics is comparably small because of relatively high oxide barrier (Figure 2-19 (e)). The band structure of $n^+$ semiconductor has less influence on the tunneling characteristics $n^+$ semiconductor compared to $p^+$ type semiconductor. This causes absence of negative resistance of $n^+$ type substrate with respect to the interesting result of $p^+$ substrate [58].
2.12.5 ZnO-based MIS Structures

For solving the problem of p-type ZnO doping, ZnO-based MIS structures can also be used [29–31] The HfO$_2$ or SiO$_2$ both can be used as insulator in ZnO-based devices [29–31]. In figure 2-20 the ZnO-based MIS structure is represented. Ultraviolet emission from MIS structure is not present during reverse bias or a diode without the oxide layer. The device emits light at current of 5mA. There was some fluctuations in the luminescence because of Joules heating of the sample because of high current (10mA) [84]. With even larger forward bias (negative voltage is connected to Si substrate) the UV electroluminescence from such device changes from spontaneous emission to random lasing.
Chapter 3

Thin Film Fabrication and Characterization Techniques

3.1 Fabrication Methods

There are many deposition techniques for thin film fabrication. The feasibility of thin film deposition depends on type of material, its thickness along with its stack. Thin film deposition can be physical e.g., thermal evaporation and chemical, e.g., gas and liquid phase chemical process. Processes based on glow discharge and sputtering are combination of physical and chemical process. Molecular beam epitaxy (MBE), Metal Organic chemical vapor deposition (MOCVD) and atomic layer deposition are mostly used for fabricating perfect crystal structure without any defects or perfect doping profile whereas sputtering and pulsed layer deposition are used for very fast, but cheap process of fabrication. However, all of the processes described earlier need high vacuum pressure and high energy reactions making the processes more expensive. Non vacuum method e.g., pyrolysis method or solgel can increase the throughput of fabrication process. The fabrication method by solgel technique is very unique, low cost, environment safe and can be used to synthesis other oxides.
3.1.1 Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) means epitaxial growth of semiconductors with the reaction of one or more molecular beams with a crystalline surface. MBE is a kind of thermal evaporation, but ensures much better control. With MBE, one can grow heterojunctions with atomically abrupt interface and the molecular beam can change the direction very quickly. Impurities are added to the growing materials by a separate beam resulting in precise doping profile. This precise doping profile and clean growth environments property are really useful for solid state lasers, microwave applications and many other. MBE can grow super lattices, quantum well structures, HEMT structures too [85, 86].

According to our literature survey, very few groups have done NiO growth by using the MBE technique [87]. $\text{HfO}_2$ can be deposited using the KrF excimer LMBE technique. The (100) p-type Si wafers should be directly put into the LMBE deposition chamber after RCA cleaning. During the deposition, configuration of the laser beam should be the following: the wavelength- 248nm, the power density - 1.8 J/cm$^2$ and the laser pulse repetition rate- 2 Hz. The substrate temperature should be 500$^\circ$C. $\text{HfO}_2$ film should be deposited in Ar/O$^2$ ambient. The oxygen partial pressure should be at 2x10$^5$ Torr. Post-deposition annealing (PDA) should be executed ex situ in a rapid thermal annealing (RTA) chamber at 500$^\circ$C for 30s in N$_2$ ambient with residual O$_2$ [41].

3.1.2 Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) is the formation of thin solid films on a substrate by chemical precursors. This is a complex process with continuous gas phase and substrate surface reaction. It is different from physical vapor phase deposition e.g., evaporation, and sputtering because these two are dependent on physical reac-
tions of atoms with the substrate. There are a lot of varieties of CVD. MOCVD is a special type of CVD which uses metal organic precursors. PECVD is one kind of CVD with lower temperature fabrication which is often a major advantage. Here, electrical (plasma) energy is used instead of thermal energy [88].

There are some reports on the deposition of NiO by CVD. The precursor for MOCVD-based NiO thin film deposition is volatile compound Ni(tta)$_2$tmada (H-tta=2-thenoyl-trifluoroacetone, tmada = tetramethylethylenediamine) which is evaporated at 160$^\circ$C. This vapor is carried to the deposition zone by an Ar gas. The Ar and the reactive gas O$_2$ flow rate are the same (150sccm for this deposition and can be varied from 0 sccm to 500 sccm according to purpose) . The operation pressure is 2-3 Torr and the substrate temperature is 450$^\circ$C [89, 90].

3.1.3 Atomic Layer Deposition

Atomic Layer deposition (ALD) is a vapor phase technique for thin film fabrication. The film is fabricated by consecutive and alternative pulses of gaseous chemical precursors. The precursors controlled reaction with the surface of a material result in deposition. ALD can be referred to an upgraded version of CVD where gaseous precursors are introduced in a sequence and the reactor is purged with an inert gas between consecutive the precursor pulses [88]. ALD has several advantages over Chemical Vapor Deposition (CVD) and physical vapor deposition (PVD) due to its high aspect-ratio, angstrom level thickness control and tunable thin film composition [88, 91].

In ALD reactors, argon can be used as a carrier and purge gas for NiO deposition. Boron doped p-type Si wafer (001) is widely used. Ni(dmamp)$_2$ and H$_2$O are the two precursors. The important parameters in ALD growth are precursor temperature, precursor supply time, substrate temperature and the number of ALD cycles [92].

Nickel oxide thin film from ALD can be used in hole transporting layers for poly-
mer solar cells [93] and resistive switching operation [94].

### 3.1.4 Sol-Gel Technique

The sol-gel technique is one of the simplest techniques for fabricating thin films. This means fabrication of solid materials from inorganic nonmetallic material solutions. This solution can be from monomeric, oligomeric, polymeric and colloidal precursors [95].

The precursor solution can be produced by sol-gel method from nickel acetate tetrahydrate powder \((C_4H_6NiO_4.4H_2O)\) as the first material. Nickel acetate is dissolved in 2-methoxyethanol \((C_3H_8O_2)\) then and diethanolamine MEA should be mingled with the solution slowly by magnetic stirring. The ratio of diethanolamine to nickel acetate should be kept at 1.0. The concentration of nickel acetate in the precursor solution should be 0.5M. The stirring should go on for 1h at 80°C. One can fabricate NiO on glass by spin coating. The glass substrate should be cleaned before deposition and the film should be heated after each coating. The procedures from coating to drying should be repeated four times for optimum film thickness [20].

Sol-gel processed NiO can be used to prepare NiO/ZnO-based UV photodiodes with high efficiency [23], gas sensors for ammonia detection [96], to increase the stability of organic solar cells as hole transport layers [97], hydrogen sensing [20], electrochromic applications [98].

### 3.1.5 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a thin film deposition technique by evaporation from one or more targets by using the energy of a focused pulsed laser beam [99]. A pulsed laser is focused onto a target in ultra-high vacuum chamber where it is partially absorbed. When the light is absorbed in the target surface, due to light
matter interaction the electromagnetic energy is converted to electronic excitation e.g., plasmons, unbound electrons and excitons in case of insulators. If power is above a definite critical value, a significant amount of partially ionized materials takes form of luminous plume. The critical value of power depends on the target material, its morphology, laser wavelength and duration. The luminous plume is then re-condensed on a substrate resulting in film growth. The growth of the thin film can be supplemented by a passive or reactive gas or ion source. This can affect luminous plume in the gas phase or the surface reactions which can be referred to reactive PLD [100, 101]. This is shown in figure 3-1. The working principle of PLD is highly complex and depends on the laser source and target materials.

NiO thin film can be grown epitaxially at room temperature via pulsed layer deposition by using a ceramic target [99]. The substrate of atomically stepped sapphire (0001) can be used. The oxygen pressure during deposition should be 1.3mPa. The configuration of pulsed KrF excimer laser is wavelength 248nm, pulse duration 20ns and frequency 5Hz. The target should be rotated continuously for uniform ablation and solving the issue of droplet formation. The distance between the target and the
substrate should be 5 cm. The growth rate depends on the various growth parameters and for this configuration, it would be 0.02-0.03 nm/s. After deposition, the NiO (111) epitaxial thin film should be annealed via rapid thermal annealing. The heating rate should be 20 K/s from room temperature and should be kept at 1373 K for 60 s. Then the thin film should be cooled down to room temperature [99].

3.1.6 Sputtering Deposition

![Figure 3-2](image)

Figure 3-2: (a) Glow discharge formation process inside the vacuum chamber (b) Schematics of a conventional DC sputtering system [6].

Sputtering is an alternative to evaporation because of its step coverage and radiation damage [102]. This was first discovered in 1852 and was used as a thin film deposition technique in 1920s by Langmuir. In this technique, high energy ions collide with the target to create the plasma in plasma chamber set up. The target contains the material to be deposited. The target should be on the electrode with maximum ion flux. The spacing between the target and substrate is kept very small to collect most of the ejected atoms from the target on the substrate. An inert gas is also supplied to the chamber [102]. It is shown in figure 3-2.
3.1.6.1 Types of Sputtering Deposition

There are several sputtering techniques used for producing thin film. The basic model is DC sputtering while the others are improvements of DC sputtering. One has to use different techniques based on different target materials and to be deposited materials properties [6].

1. DC Sputtering

DC sputtering system consists of two planar electrode, target (cathode) and substrate (anode) [6]. Water cooling is used for cooling of the outer face of the cathode. The chamber is kept in low pressure and a few kilovolts is applied between the electrodes to produce the plasma. The positive argon ions in the plasma go toward the cathode causing the deposition of target atoms. For DC sputtering, the target should be conductive (metal). Otherwise an insulator would accumulate charges at the surface causing prevention of ion bombardment. This has two major problems. 1) low deposition rate and 2) heating and structural damage due to electron bombardment [6].

2. RF Sputtering

For sputtering an insulator, continuous plasma is really challenging because of immediate formation a positively charged surface on the face of insulator [6]. In order to get sustainable plasma, a DC power supply is replaced by rf source. For this rf source, the system is called rf sputtering system. With a high peak to peak rf power source, an alternative positive and negative voltage are accumulated on the substrate surface. During one half cycles, the potential is enough to accelerate the ions to make the target sputter to the film surface and during other half cycle, the electrons that reach the target surface prevent the ionization of the surface. It needs an impedance matching network between the power supply and the chamber too [6].
Nickel oxide films can be fabricated by a radio-frequency (RF) magnetron sputtering system from a NiO target. The substrate is 0.7-mm thick Corning 1737 glass substrate. The distance from the target to the substrate should be approximately 8085 mm. The chamber should be evacuated to a pressure below $3 \times 10^4 \text{Pa}$ before deposition. Sputtering deposition should be performed under a gas pressure of 1Pa. The power of target should be kept at a constant RF power of 200W. The substrate temperature can be room temperature or at 400°C. The sputtering time should be adjusted in order to get different film thickness [103].

3. DC Magnetron Sputtering

Here, a permanent magnet is used under the target. In DC sputtering, the electrons from the target are moving from the cathode, but this is not an efficient way for sustaining discharge [6]. The electrons are confined in a closed path by magnetic field generated by the magnets mounted on the target. This results in decrease of electrons bombardment on substrate surface. The electron confinement also ensures ionization probability of neutral molecule of the gas. The increase in ion density ensures increased sputter yield and deposition rate [6].

4. Ion Beam Sputtering

In ion beam system, ions are generated in a special chamber and are extracted into the sputtering chamber, then hit the target in good vacuum condition. This results in high bombardment rate and ensures less contamination. This is highly for used high performance optical devices [6].

5. Reactive Sputtering

DC sputtering needs conductive target to complete the electric circuit [6]. It is impossible to keep the plasma in case of insulating target. This problem can be solved by reactive sputtering. Oxides, nitrides and hydrides can be deposited with reaction with oxygen, nitrogen and hydrogen in an argon environment. The
interaction between metal and reactive gas can fabricate these materials. The fabricated material composition depends on the metal deposition rate of the metal, growth temperature, reactive gas partial pressure [6].

At the presence of reactive gas, the reaction of reactive gas can happen in three different places, e.g., target surface, in between target and substrate, substrate surface [6]. The reaction happened at the time from target to substrate can be neglected. The reaction at the target surface should be small for continuous plasma generation and uninterrupted deposition. Because of this, the reactive gas/ (reactive gas+Argon) should be reduced to minimum value. The reaction should be in substrate surface and it can be ensured by supplying oxygen in front of the substrate and argon closed to the target [6].

The NiO films can be deposited by dc reactive magnetron sputtering from a Ni target in an O\textsubscript{2} and Ar environment [6]. Si substrate and glass substrates can be used. The apparatus pressure should be less than 5 \times 10^{-4} Pa by a diffusion pump prior to deposition. A sputtering power from (50W-200W) can be used according to growth rate. Both argon inert flow and oxygen reactive flow can be controlled by mass flow controllers. The relative partial pressure defined as \( p(O_2)/ p(O_2+ Ar) \) can be varied from 10% to 50%. The total gas pressure should be kept at 0.5 Pa. Before deposition, the target should be pre-sputtered to remove any contaminants and eliminate any differential sputtering effects [104].

### 3.1.6.2 Properties of Nickel Oxide Thin Film with RF Sputtering Growth Parameter

The lowest resistivity and hall coefficient are 16.7 $\Omega$-cm and 1.99$\text{cm}^3$/C, respectively. This is by sputtering power 100W and substrate temperature 350$^\circ$C. The highest carrier concentration obtained is $3.13 \times 10^{18} \text{cm}^{-3}$ [105].
1. **Crystalline Structure**

At lower oxygen content in the chamber, the NiO film shows amorphous crystal structure [104]. With increasing the oxygen content, it becomes polycrystalline (fcc NiO film). If NiO is grown in less oxygen environment (low $O_2/(O_2+Ar)$ ratio), it shows a strong (200) peak that provides indication of preferred orientation in (100) direction. If NiO is grown in an environment with less oxygen (low $O_2/(O_2+Ar)$ ratio), it shows a strong (200) peak that provides indication of preferred orientation in (100) direction. NiO samples grown in an oxygen rich environment, the diffraction peak at (111) direction and the intensity is also increased [66, 104, 106]. These results show crystallinity that has a relation with the oxygen content in the oxygen and argon sputtering gas mixture.

NiO films deposited on unheated substrates or heated to 150°C show (111) preferred orientation. The preferred orientation changes from (111) to (200) for substrate temperature above 250°C. The crystalline size increases with film thickness due to columnar grain growth in the structure [103, 105]. The grain size increases with increasing substrate temperature. At room temperature growth (i.e., unheated substrates), the deposited atoms have lower mobility. This results in prevention of atom diffusion for energetically favorable site and makes the atom to nucleate at new sites. This causes smaller grains and relatively weaker preferred orientation of crystal structure. With higher energy, atoms have enough energy to diffuse to the preferred nucleation sites. Smooth propagation of atoms in high temperature results in NiO thin film growth in definite direction. The FWHM value of crystals decreases with increasing temperature. With higher growth temperature, the crystallinity improves and NiO film with larger crystalline size was formed. Grain size increases with RF power and larger grains create less grain boundaries resulting in less scattering [107].
2. Electrical Behavior

The conduction mechanism is mostly related to the nickel vacancies is NiO. All prepared film has both Ni\(^{2+}\) and some amount of Ni\(^{3+}\) ions. The color of deposited thin film is dark brown due to the presence of Ni\(^{3+}\) ions in \(Ni_2O_3\) assignment [106].

The electrical properties of NiO are intricately related with the microstructures and composition which are dependent on the deposition parameters of sputtering deposition.

High deposition temperature produces larger grains; it makes better crystalline structure and low vacancies which leads to higher resistivity [103, 107]. With pure Ar gas environment, the film from the Ni target shows metal like color and resistivity is \(10^{-4}\Omega.cm\). With adding oxygen with the argon, the nickel thin film shows an increase in resistivity and a change in film color. With 10% oxygen, the resistivity is 6 times than the pure argon environment NiO thin films. With the oxygen content increasing above 10%, the resistivity starts to decreases rapidly. This is also related to the increase of carrier concentration with increase of oxygen content. The increase in hole concentration can be related to increases in shallow acceptors e.g., nickel vacancies and oxygen interstitials [66]. Presumably, the cause of decrease of resistance is from the crystallinity change from amorphous to polycrystalline [66, 104].

The sheet resistance increases rapidly around 50-150nm this range and then they start to decrease in 150-200nm dramatically. Then resistance increases linearly after 200nm. The minimum value of resistivity is around 200nm. The increase of resistivity after 200nm is for the crystallization process [103].

From the EDS, the film prepared with low oxygen ratio from 15%-25% the Ni/O ratio is .71-.72. With oxygen ratio 35%-50%, Ni/O ratio in the mixture increases to .96-1.02 [104]. This proves the nonstoichiometric behavior and how the vacancy
states are changed in different condition.

With increase of RF power, nickel atoms get ejected more than oxygen creating oxygen vacancies. Besides with increase of RF power some metallic nickel can be deposited. Thats why the resistivity decreases with increase of RF power [107].

The electric property of NiO has a dramatic aging effect. The resistivity of NiO increases dramatically if it is kept in ambient temperature more than 35 days. These show the electrical properties of NiO are unstable. The cause of this increase is still unclear. Residual stress, microstructural defect recovery, oxygen adsorption and desorption can be a reason for this stability problem [105].

3. Deposition Rate

The deposition rate increases with increasing input power, but decreases with oxygen content. The decrease of deposition rate with increase of $O_2/(Ar+O_2)$ ratio is generally due to oxidation of the target. With the $O_2/(Ar+O_2)$ ratio 10%, the target poisoning starts and deposition rate decreases as a result. The oxidation causes low deposition rate because of low sputtering yield of the oxides [104].

The growth rate of NiO thin film increases linearly with increase of RF power. More Nickel atoms get ejected with more rf power resulting in more deposition rate [105]. Oxygen content decreases with the increase of RF power. This results in more oxygen vacancies in the film. Besides, with increase of RF power, some metallic nickel is deposited in the film as non-oxidized nickel. Mixing of metallic nickel phase in the film is the main reason why transmittance decreases and resistivity increases as RF power is raised [107].

4. Optical Transmittance

The trend of conductivity and transmittance are totally opposite because defects are the main cause of conduction in NiO thin film whereas defects result in absorption of light causing decrease in transmittance. With the increase of thin film
thickness, the transmittance decreases. With thin NiO film, the film becomes transparent and the absorption edge becomes sharper. This is because of larger crystalline size resulting in scattered radiation due to surface roughness [103]. The transmittance is reduced for higher oxygen flow rate. With 400°C and higher oxygen flow rate, no absorption band is present in transparent region. This explains the deposited film is without any impurity or defects [107]. Good crystalline thin film with high purity is the best transparent thin film. More than 50% oxygen content in the film means more nickel vacancies and higher carrier concentration. These defects create stress field and interact with incident light resulting in scattering. So with the increase of oxygen content, the transmittance of the NiO film decreases. With increase of RF power, it creates more vacancies and there is some mixing of the metallic nickel phases in the film. These causes decrease in transparency with RF power [107].

3.2 Characterization Techniques

3.2.1 Four Point Probe Resistivity Measurement

![Figure 3-3: (a) Two terminal and (b) Four terminal resistance measurement technique [7].](image)

Figure 3-3: (a) Two terminal and (b) Four terminal resistance measurement technique [7].
A four point probe, an absolute measurement to get a calibrated standard for other measurements, is usually used to measure semiconductors resistivity [7, 58]. A two point probe is much easier, but explanation of the data is much tougher. In two probes measurement, each probe is used as a current and voltage source [7]. This is shown in figure 3-3 (a) The total resistance of device under test (DUT) is given by,

\[ R_T = \frac{V}{I} = 2R_w + 2R_c + R_{DUT}. \]  

Here, \( R_w \) is the wire or probe resistance, \( R_c \) is the contact resistance and \( R_{DUT} \) is the resistance of device under test.

It is almost impossible to determine \( R_{DUT} \) from the equation above and that is why four points measurement is used. This is shown in figure 3-3 (b). The current path is identical to the previous set up and the voltage is measured by two other contacts. The voltage path contains \( R_w \) and \( R_c \), but these are negligibly small. Thus these can be neglected and the measured voltage is the voltage drop across DUT. By using four probes instead of two probes, parasitic voltage drops can be eliminated because voltage probes make contacts with the device on the same contacts pads as current probes [7]. For an ultra-thin wafer, the thickness \( W \) is much smaller than length, \( a \) and width, \( d \). The four point probe configuration is shown in figure 3-4 for square and circular samples.

The sheet resistance \( R_\square \) can be characterized by,

\[ R_\square = \frac{V}{I}.CF \Omega/\square \]  

Here, CF is the correction factor. The resistivity is then,

\[ \rho = R_\square W \Omega.cm. \]
If the width of the sample is much smaller than the distance between the probes, the correction factor will be $\frac{\pi}{\ln 2}$ [58].

### 3.2.2 Hall Effect Measurement (Vander Pauw Method)

Four point probe resistivity measurement determines the product of mobility and carrier concentration [58]. For determining each of them individually, Hall Effect measurement can be used. Hall Effect is named after the scientist who reported its
discovery in 1879. Even today it is still an interesting and practical phenomenon for example, fractional quantum Hall Effect and spin Hall Effect along with their use in magnetic sensors can be mentioned. Nowadays it is still used to determine various parameters more often such as carrier concentration (even as low as $10^{12}\text{cm}^{-3}$), mobility and carrier type. It is really an important measurement technique because simple four point probe resistivity measurement can only give the product of mobility and carrier concentration \[58\]. For Van der Pauw method, the thin film should have an appropriate geometry shown in figure 3-5.

The average diameters (D) of the contacts and sample thickness must be much smaller than the distance between contacts (L). Because relative errors from non-zero values of D, are of order of $D/L$. A permanent magnet / electro-magnet, constant-current source, high input impedance voltmeter and sample temperature measuring probe are required. Four leads are connected to the four ohmic contacts on the sample labeled as 1,2,3,4 (counterclockwise) as shown in figure 3-5 (a). Same batch of wire should be used for decreasing thermoelectric effect and all the ohmic contacts should be from same material. By applying a current in any two points, the voltage in two alternative probes is measured and the polarity of current and voltage probes is reversed then \[108\]. For simplicity, a resistivity measurement from voltage and current measurements is shown below:

$$R_{21,34} = \frac{V_{34}}{I_{21}}. \quad (3.4)$$

$I_{12}$ = a dc current I injected from contact 1 to contact 2 same for $I_{23}, I_{34}, I_{41}, I_{21}, I_{14}, I_{43}, I_{32}$ (in amperes, A).

$V_{12}$ = a dc voltage measured between contact 1 and 2 ($V_{1} - V_{2}$) without applied magnetic field (B=0) for $V_{23}, V_{34}, V_{41}, V_{21}, V_{14}, V_{43}, V_{32}$ in volts, V.

The sheet resistance $R_s$ can be determined by these two resistance described below:
\[
R_A = \frac{R_{21,34} + R_{12,43} + R_{43,12} + R_{34,21}}{4} \tag{3.5}
\]
\[
R_B = \frac{R_{32,41} + R_{23,14} + R_{14,23} + R_{41,23}}{4}. \tag{3.6}
\]

If the conducting layer thickness \( d \) is known, the bulk resistivity which can be calculated by \( R_s \rho = R_s d \).

With the help of magnetic field, this method can be used to determine sheet carrier density \( n_s \) and the bulk carrier density \( n \) or \( p \) (for n-type or p-type materials) if the conducting layer thickness of the sample is known. The hall voltage for thick heavily doped samples can be quite small \((\text{in } \mu)\). To deal with this small voltage, one value for positive and another for negative magnetic field are determined \([108]\). The sample resistivity is determined by equation described above.

\[
V_C = V_{24p} - V_{24n} \tag{3.7}
\]
\[
V_D = V_{42p} - V_{42n} \tag{3.8}
\]
\[
V_E = V_{13p} - V_{13n} \tag{3.9}
\]
\[
V_F = V_{31p} - V_{31n}. \tag{3.10}
\]

Here, the additional subscript \( p \) and \( n \) shows presence of positive and negative magnetic field.

The carrier type is determined from the polarity of the voltage sum \( V_C + V_D + V_E + V_F \). If the sum is positive (negative), the sample is p-type (n-type) \([108]\).

The sheet carrier density, bulk carrier density can be determined by equations
shown below:

\[
\rho_s = \frac{8 \times 10^{-8}IB}{q(V_C + V_D + V_E + V_F)} \quad (3.11)
\]

\[
\rho_n = \left| \frac{8 \times 10^{-8}IB}{q(V_C + V_D + V_E + V_F)} \right| \quad (3.12)
\]

\[
n = \frac{n_s}{d} \quad (3.13)
\]

\[
p = \frac{p_s}{d}. \quad (3.14)
\]

The hall mobility can be expressed by the equation below:

\[
\mu = \frac{1}{qn_s R_s}. \quad (3.15)
\]

The unit of hall mobility is $cm^2 V^{-1} s^{-1}$, bulk carrier density is $cm^{-3}$, resistivity is $\Omega cm$ and sheet carrier density is $cm^{-2}$.

### 3.2.3 Transmittance and Absorption

It is crucial to determine intensity or irradiance of the reflected and transmitted waves when the light is traveling from medium of index $n_1$ to a medium with index $n_2$ \[53\]. In some cases, normal incidence ($\theta_i=0$) is a matter of interest i.e., in laser diodes where light is reflected from the ends of an optical cavity at the interface of two mediums. For a light wave travelling with a velocity $v$ in a medium with relative permittivity $\epsilon_r$, the light intensity $I$ can be described by the formula with $E_0$ shown below:

\[
I = \frac{1}{2} v \epsilon_r \epsilon_o E_0^2 = v \times \text{Energy in the field per unit volume}. \quad (3.16)
\]

The light intensity means the rate at which energy is transferred through a unit area.
Reflectance (R) measures the intensity of the reflected light with respect to that of the incident light and can be defined separately electric field component parallel and perpendicular to the plane of incidence [53]. With normal incidence, reflectance can be described by,

\[ R = R_{\parallel} = R_{\perp} = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2. \] (3.17)

The transmittance (T) is related to intensity of transmitted light to that of incident light same as reflectance [53]. One has to consider transmitted wave in a different medium and its direction with respect to the boundary which is different from that of incident wave by refraction. For normal incident, the incidence and transmittance beam are normal and transmittance can be described by,

\[ T = T_{\parallel} = T_{\perp} = \frac{4n_1n_2}{(n_1 + n_2)^2}. \] (3.18)

The addition of fraction of light reflected and that of transmittance should be unity. Thus,

\[ R + T = 1. \] (3.19)

At the time of light propagation through a material, it gets attenuated in the direction of propagation by two effects-absorption and scattering. Both of them cause a loss of intensity in the regular direction of propagation. In absorption, the loss in the power in propagating electromagnetic wave is due to the conversion of light energy to other form of energy e.g., lattice vibration (heat). The attenuation constant (\(\alpha\)) refers to the fractional decrease in the irradiance I of a wave per unit distance along the direction of propagation [53]. So,

\[ \alpha = -\frac{\delta I}{I\delta z}. \] (3.20)
When the irradiance decreases, $\delta I/\delta z$ is negative resulting in positive the attenuation constant. If the attenuation is only for the absorption only, then $\alpha$ is absorption co-efficient. The transmittance and absorbance can be determined from infrared to ultraviolet ranges [53].

### 3.2.4 Energy Dispersive X-ray Spectrometry (EDS)

![Diagram of EDS](image)

Energy Dispersive X-ray Spectrometry (EDS), elemental analysis or chemical characterization of materials in a sample, uses the X-ray spectrum emitted by a solid sample caused by bombardment with a focused beam of electrons to do chemical study [109]. In ambient condition, an atom within the sample contains unexcited electrons in discrete energy shells which are bound to nucleus of an atom [109, 110]. The incident beam of X-rays may excite an electron in inner shell and transfer it from the level to an upper shell resulting in a hole in that position where the electron was. An electron from outer energy level then releases some energy and comes back to lower shells to fill the hole. The difference in energy between the higher energy shell and lower energy shell can cause an X-ray emission. The number and energy of X-ray can be measured by a spectrometer. This can be used to find the elemental composition of the sample [109, 110]. All the elements from atomic number 4 to 92 (Beryllium...
to Uranium) can be distinguished in this principle. However, all the instruments are not proper for light elements (atomic number, $Z < 10$) [109].

Figure 3-6 shows the EDS setup with a sample spectrum. One needs an excitation source (electron beam or X-ray beam), the X-ray detector, the pulse processor and analyzer. Similar setup can be used in electron microscope, scanning electron microscopes and scanning transmission electron microscopes [110]. EDS started as a commercial product in 1970s and rapidly replaced wavelength dispersive spectra (WDS) because of not having a moving parts i.e., rotation detector in WDS and being faster. This is faster than WDS because the detector collects the signals of characteristics X-ray energies from a whole range rather than collecting that of X-ray independently [110].

3.2.5 X-ray Diffraction (XRD)

![Bragg Diffraction by Crystal Planes](image)

Figure 3-7: Bragg diffraction by crystal planes.

Two in phase X-ray beams incident on the crystal will be diffracted by the two
crystallographic planes [111]. The deflected waves will be in phase when the equation given below is satisfied:

\[ n\lambda = 2d\sin\theta. \] \hspace{1cm} (3.21)

This is also called basic law of diffraction or Bragg’s Law. The Bragg’s law can be simply achieved by calculating the difference between two beams in figure 3-7. The wavelength of incident beam and diffracted beam is \( \lambda \). After getting the spacing between atomic planes of crystal at the constructive interference based on Bragg’s Law, one can have crystal structure of materials [111]. For the plane of spacing of cubic crystal relates to the lattice parameter (a) by the equation given below:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \] \hspace{1cm} (3.22)

Here, the Miller indices (hkl) are a series of parallel planes in crystal with spacing dhkl.

Figure 3-8: Geometric arrangement of X-ray diffraction.
XRD, the most common X-ray diffraction technique in materials characterization was used for examining the crystal structure of powder samples at first. That is why it is called X-ray powder diffractometry [111] and this instrument is called X-ray diffractometer. In this, single wavelength X-ray beam is used to examine polycrystalline film. By continuous change of incident angle of X-ray, a spectrum of diffraction intensity vs. the angle between incident and diffraction beam is collected. This gives us the crystal structure and quality. Figure 3-8 shows the geometrical arrangement of X-ray source, specimen and detector [111].
Chapter 4

Experimental Details

4.1 Fabrication Procedures

4.1.1 Hafnium Oxide Deposition

Hafnium oxide (HfO$_2$) was deposited by reactive sputtering by an AJA sputtering system described below. The target used was Hf. HfO$_2$ was fabricated with different O$_2$:Ar ratio (from 6:6 to 3:9, with total of 12sccm) and their characteristics were explained by some characterization methods. Besides DC power was kept at 100W to have an optimum deposition rate. Moreover, the temperature of substrate during HfO$_2$ deposition was kept at 400$^\circ$C. During the fabrication process, the substrate was rotated for uniform heating and deposition. For this deposition, the vacuum pressure was less than $2 \times 10^{-7}$ Torr. The distance between the sample and target was 10cm. The working pressure was 5mtorr.

4.1.1.1 Sputtering Deposition System from AJA International Inc.

The utilities important for this system are chiller (20$^\circ$C), compressed air (80-100psi), purged nitrogen and argon (10psi). It has integrated ion gauge, isolation valve for bartatron, gate valve for controlling working pressure, pressure gauge (convection and CDG) and manual vent valve. It also has a view-point with manual
shutter. There are two RF power sources with matching network. One can do DC sputtering, RF sputtering and reactive sputtering with oxygen and nitrogen in this system. The heater can go above 800°C. The substrate holder can be rotated (0-100rpm) for uniform heating and uniform sample fabrication. The gas flow of oxygen and argon can be controlled separately by gas gauge. The substrate height can be 10-50cm. There is a side gate for attaching a load lock with the system.

4.1.2 Zinc oxide Deposition

Zinc oxide (ZnO) deposition was done by a system by magnetron sputtering system from Torr International, by using a target of ZnO. ZnO thin films were fabricated by rf sputtering of ZnO instead of dc sputtering because it would cause discontinuity in the circuit. ZnO was fabricated at room temperature. The distance from the sample to the target was 8cm. The working pressure was kept 10mtorr. The target used was 2" diameter and .125" thick ZnO target (with 99.99% purity and density 5.25g/cc) from Kurt J. Lesker company.

4.1.2.1 Magnetron Sputtering System from Torr International Inc.

The system has non-magnetic stainless steel vacuum chamber with a vacuum system including a turbo molecular pump and roughing pump. In the chamber there is a 4" viewing window and fully opening front door which can be helpful for substrate and target loading and unloading as well as chamber cleaning and maintenance. It also comes with one 600W DC power supply above 20 kHz, one 300W RF power supply with an automatic matching network. It consists of a FTM-2000 deposition controller that uses a quartz crystal thickness sensor and oscillator cables to measure film thickness and deposition rate. This includes one RF 2" magnetron sputtering gun, one DC 3" magnetron sputtering gun and motorized and heated substrate stage (6" diameter). The substrate can be rotated (0-20rpm) and heated up to 400°C.
handled by a PID controller.

4.1.3 Nickel Oxide Deposition

We deposited nickel oxide (NiO) by both of the sputtering system described above. We tried to fabricate NiO at room temperature, 300°C and 400°C. In addition, we tried reactive sputtering of Ni with different O and Ar ratio by controlling flow mass rate. The substrate was rotated during fabrication process for getting uniform deposition and uniform heating. The substrate used was 3.00” diameter and .0625” thick 99.99% Pure nickel (Ni) target from Kurt J. Lesker company.

4.1.4 Contacts Deposition

For most of the devices, we used Ni, Al, Al doped ZnO (Al:ZnO) and ITO as contacts with the semiconductor layer. For fabricating thin and continuous films for contact, sputtering and evaporation are the most common deposition processes, and in our study, we used rf magnetron sputtering in the Torr International system.

4.2 Samples Characterization

4.2.1 I-V & C-V Characterization

The 4200 SCS Semiconductor Characterization System consists of 4 SMU and one pre-amplifier for current measurement (1fA-100mA). It usually includes with capacitance-voltage (C-V) unit capable of measuring capacitance and conductance at various frequencies. This is attached with a SemiProbe Lab Assistant specifically designed for universities and individual researchers with simple and easy operation, portability, affordability and modularity. The Lab Assistant has features and options of both DC and HF/Microwave testing that are usually available in much more ex-
pensive systems. Numerous accessories can be added later to enhance the system functionality. This configuration along with preloaded software enables the measurement of various device parameters.

### 4.2.2 Four Point Probe Measurements

The Signatone Pro4 can measure sheet and bulk resistivity. For measurements, the four-point probe head is lowered onto sample then the test button is selected in the software. The computer automatically controls the instrument and determines the ideal current for perfect measurement by a number of current. A V/I measurement is taken and recorded. The Pro4-440N system includes Keithley 2400, two four-point probe heads, Pro4 software, Pro4 stand, and a notebook PC. Besides, it has the Dual Configuration test method of ASTM Standard F84-99 to compensate for errors in probe spacing and errors from proximity to the edge of the conducting layer. Proper use of the NIST traceable calibration standards and the calibration procedure can give better than 1% accuracy. The standard range of the system is 1 mΩ up to 800KΩ-per-square.

### 4.2.3 Van der Pauw Hall Effect Measurements System

The MMR Hall Effect Measurement System provides automatic measurements of the electrical properties of semiconductor materials using the Van der Pauw measurement technique. By measuring using Hall Effect described above, properties of the material, such as sheet resistance, doping type, carrier density, and mobility of majority carrier can be calculated. The variable temperature Hall Effect measurement (70 K- 500 K) is also possible. It has a simple sample mounting which allows rapid interchange of samples. It comes with VTHS Hall measurement controller, the H5000 and connection between a laptop and the system via USB or RS-232 interface. It also
includes MMRs Benchtop electromagnet and programmable power supply.

4.2.4 UV-VIS-NIR Transmittance Measurements

The UV/Vis/NIR spectrophotometer (LAMBDA 1050) uses a photometer to determine the intensity of light in a wavelength range. It uses visible light, near-ultraviolet, and near-infrared (or any combination) light and ranges for 190nm to 3300nm. A double beam spectrophotometer compares the light intensity between two paths (one as a reference and the other the test). It can achieve a greater level of sensitivity, resolution and speed in the NIR range. It can simplify the analysis of difficult samples e.g., glass with high absorbing capability, optical coating or thin film filters. It has two large sampling compartments and a variety of snap-in modules and accessories along with conventional optical bench, integrating spheres and a universal reflectance accessory. It has tungsten-halogen and deuterium interfaces. It can calculate the transmittance, reflectance of the sample (diffuse and specular), and pseudo absorbance.

4.2.5 Thickness Measurements

A profilometer (Dektak 150) calculates the vertical depth of a thin film (film thickness). A diamond stylus or contact is moved laterally across the sample with a specified distance and contact force. The stylus makes contact with the film surface. Then the stage is moved front to back while the stylus is held static to calculate the changes in surface height. The average change in surface height is equal to the thin film thickness. This system can be utilized to measure etch depth, deposited film thickness, and surface roughness.
4.2.6 Rigaku Ultima III High Resolution XRD Instrument

X-ray diffraction (XRD) is one of the most important measurement systems to investigate all kinds of matters (from fluids, to powders and crystals). From research centers and industry to academia, XRD is an indispensable technique for materials characterization and quality control. Rigaku has developed a range of diffractometers. To determine the crystal structure of materials, we did XRD characterization by the Rigaku Ultima III high resolution X-ray diffraction (XRD) instrument. This can be utilized for a lot of applications e.g., in-plane and normal geometry phase identification, quantitative analysis, lattice parameter refinement, crystallite size determination and depth-controlled phase identification. With standard Bragg Brentano geometries, the system can determine grazing incidence diffraction (GIXRD), transmissive and reflective small-angle X-ray scattering (SAXS). This consists of a generator, detector, goniometer, optics and accessories. It has a Cu target (rated tube voltage of 20-60KV operated at 40KV and 44mA) generator with scintillation counter detector. Automatic alignment of the tube height, goniometer, optics and detector is possible. The divergence, scattering and receiving slits are fixed or auto variable. Monochromator, Transmission SAXS holder and related software (Jade v8.0, Nano-solver v3.4) also come with the system.
Chapter 5

Results

5.1 Properties of Semiconducting Oxides

5.1.1 Electrical Properties of Nickel Oxide

According to some reports on nickel oxide (NiO) growth, NiO characteristics mostly depend on growth temperature, O₂/Ar ratio, thickness [66, 71, 103–107, 112]. The conduction mechanism is mostly related to nickel vacancies in NiO. All the NiO thin films have both Ni²⁺ and some amount of Ni³⁺ ions. The color of deposited thin film is dark brown because of the presence of Ni³⁺ ions in Ni₂O₃. That is why, with the increase of conductivity, the film takes brown color from the greenish color of ideal NiO [104, 106]. The resistivity, mobility, density, Hall co-efficient and sheet resistance are given below in table 5.1 for 5 different samples where type of carriers is always holes.

Sample-1 was a 200nm sample grown in 300°C whereas sample-3 was grown at same temperature with thickness of 500nm. The resistivity drastically increases from 12.21 Ω.cm to 311.59 Ω.cm which coincides with the previously reported results [103]. The cause of resistivity increase is because of crystallization process. The sheet resistance increases rapidly in 50-150 nm thickness range and then it decreases with oxide thickness in 150-200nm range. The resistance increases linearly after 200nm [103].
Table 5.1: Resistivity of nickel oxide for different conditions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Resistivity (Ω.cm)</th>
<th>Mobility (cm²/(V.s))</th>
<th>Density (cm⁻³)</th>
<th>Hall Coeff. (cm³/°C)</th>
<th>Sheet Res. (Ohm.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.21</td>
<td>1.29</td>
<td>3.95 x 10¹⁷</td>
<td>15.8</td>
<td>610540.2</td>
</tr>
<tr>
<td>2</td>
<td>351.81</td>
<td>27.69</td>
<td>6.41 x 10¹⁴</td>
<td>9740.2</td>
<td>7036190</td>
</tr>
<tr>
<td>3</td>
<td>311.59</td>
<td>6.66</td>
<td>1.83 x 10¹⁵</td>
<td>3415.1</td>
<td>1.03 x 10⁷</td>
</tr>
<tr>
<td>4</td>
<td>512.96</td>
<td>20.95</td>
<td>9.56 x 10¹⁴</td>
<td>6526.4</td>
<td>6231763</td>
</tr>
<tr>
<td>5</td>
<td>20.30</td>
<td>0.23</td>
<td>1.35 x 10¹⁸</td>
<td>4.61</td>
<td>8273300</td>
</tr>
</tbody>
</table>

All the samples except sample-2 were grown with O₂/(O₂+Ar) =80% ratio while sample-2 was grown with O₂/(O₂+Ar) =50% ratio. For comparison between sample-1 & sample-2, with increase of O₂ in environment during growth makes the NiO much conductive. This is because of increase in carrier concentration with increase of oxygen content in environment [66, 104, 106]. The increase of hole concentration is related to increase in shallow acceptors e.g., oxygen interstitials and nickel vacancies. Presumably, this can be due to change of crystallinity from amorphous to crystalline [104]. According to some other reports [66, 104, 106], with pure Ar environment growth, the film from Ni target shows a metal like color and its resistivity is 10⁻⁴ Ω.cm. With addition of O₂ in Ar environment, the NiO thin film resistivity increases and changes the film color. With 10% oxygen, the resistivity is 6 times than the pure argon environment. With the increase of O₂ content above 10%, the resistivity starts to decrease rapidly [66, 104]. The sample-5 was grown in high temperature (grown in 400°C) than that of other sample-1. High deposition temperature is favorable for larger grains which makes better crystalline structure and low vacancies which leads to higher resistivity [103, 107]. The sample-3 was kept in ambient environment for two months and then recalculated the values and noted as sample-4. The resistivity of NiO increased with time from 311.59 Ω.cm 512.96Ω.cm which is due to oxidation of NiO thin film surface. This is equivalent to aging effect of NiO due to instability.
Some groups reported that, the resistivity increases if the NiO film is kept in ambient for more than 35 days [105]. The cause of these effects is still unclear. There are several causes in consideration e.g., residual stress, microstructural defect recovery, oxygen absorption and desorption [105]. For a decrease of resistivity, the carrier concentration should increase and the increase of carrier concentration decreases carrier mobility and vice versa.

5.1.2 Crystalline Structure of Nickel Oxide

![XRD of NiO thin film fabricated at RT, 300°C & 400°C.](image)

Figure 5-1: XRD of NiO thin film fabricated at RT, 300°C & 400°C.

The nickel oxide (NiO) was fabricated at room temperature, 300°C and 400°C to see the changes in crystal structure with different temperatures. This is shown in figure 5-1. The preferred orientation is (111) for room temperature growth which is similar to previous reports [103, 105, 107]. The NiO thin film fabricated at 300°C
shows a weak peak at (200) along with the strong peak at (111). The preferred orientation becomes (200) with a weak peak at (111) orientation in much higher temperature e.g., 400°C. This (200) preferred orientation gives an indication of preferred orientation in (100) direction. This can be explained with mobility and its effect on crystal structure. At room temperature growth i.e., unheated sample holder, the deposited atoms will have lower mobility. This obstructs atoms diffusion for energetically convenient site and forces atoms to nucleate at new atom sites. This results in smaller grains and weak crystalline peak. With higher energy e.g., high temperature, the atoms can have much more energy to diffuse to their preferred nucleation sites. Smooth and easier propagation of atoms during high temperature growth makes NiO thin film preferred orientation in a definite direction. With the fabrication temperature increase, the crystallinity improves which results in a decrease in FWHM value and NiO film with larger crystalline size was formed [107].

5.1.3 Crystalline Structure of Zinc Oxide

Figure 5-2: XRD spectrum of (a) ZnO fabricated at RT & (b) HfO₂ thin film fabricated at 400°C.
The sputtered zinc oxide (ZnO) shows plural ZnO hexagonal wurtzite peaks. ZnO prefers c-axis orientation with a single peak at 34° which is related to diffraction of (002) plane of ZnO [113]. Besides the main peak at (002), the XRD has three very weak peaks at 36°, 48° and 63° which correspond to (101), (102) and (103) orientation, respectively. This is shown in figure 5-2 (a). This weak phases were reported before [114, 115]. Some of these reports mentioned a (101) peak at RF power more than 200W and its increase with increase in RF power [115]. In their results the intensity of (002) is much higher than that of (101) orientation. This indicates most of the samples would be c-axis oriented. The (002) peaks decreases with increasing RF power more than 175W. This proves RF power increase causes faster deposition rate resulting in insufficient time for formation of the initially preferred crystal orientation [115].

5.1.4 Crystalline Structure of Hafnium Oxide

The XRD of HfO$_2$ with lot of weak peaks indicates the thin film has a mixed structure of amorphous and polycrystalline. The XRD of HfO$_2$ shown in figure 5-2 (b) has a strong peak at (111) with (002), (211), (220) and (221) weak peaks. Two peaks of (111) and (002) can be attributed for monoclinic phase (reported by other groups [116, 117]). Besides, other weak peaks (211), (220) and (221) can also be present in the XRD. Excess oxygen environment makes it more crystalline whereas excess argon environment makes it amorphous thin film. The cause of these weak peaks in Ar rich environment is higher sputtering rate where atoms dont have sufficient time to orient themselves in preferred direction. With oxygen rich environment, the deposition rate is slower due to low ejection rate of target materials (Hafnium). So hafnium will get enough time to react with oxygen to fabricated reactively sputtered HfO$_2$. Thus it will have enough time to orient them in preferred direction [116]. Besides, high temperature also helps to get the highly oriented HfO$_2$ thin film. For
getting the crystalline nature, the growth temperature should be more than 200°C for monoclinic phase and for room temperature it becomes amorphous [118].

5.2 Optical Transmittance Measurements

5.2.1 Hafnium Oxide

![Transmittance spectra of HfO₂ and ZnO](image)

Figure 5-3: Transmittance spectra of (a) HfO₂ & (b) ZnO as a function of wavelength.

From the hafnium oxide (HfO₂) transmittance spectra in figure 5-3 (a), the optical band gap of HfO₂ can be approximated. The value from the transmittance spectra is around 4.8eV for reactive sputtered HfO₂ which is pretty much similar to electric band gap (5.3-5.7eV) [119]. This is pretty good for optical devices because of its transmittance above 85%. Besides, its sharp edge in transmittance spectra is useful
for transparent electronics. Besides the transmittance is totally constant for the whole range of 325-700nm (around 80%) [118, 119]. The transmittance decreases linearly from 325 to 250nm.

5.2.2 Zinc Oxide

From the Transmittance spectra of zinc oxide (ZnO) in figure 5-3 (b), one can easily find the optical band gap of ZnO. From the slope of the edge for ZnO, the band gap is around 3.35eV. The transmittance of ZnO in 375-700nm range varies in 65%-90% range. This can be because of layered structure of thin film [120]. The transmittance of ZnO is really high resulting in low reflectance. This property makes ZnO an important anti-reflecting coating material. The transmittance decreases sharply almost as a vertical line at 375nm. The transmittance at low range (330-375nm) is not constant too.

5.2.3 Nickel Oxide

The figure 5-4 shows nickel oxide (NiO) transmittance spectra for different O$_2$/Ar ratio. NiO film with O$_2$: Ar ratio 60:40 are more transparent than that of O$_2$:Ar 80:20. With the increase in O$_2$/(Ar+O$_2$), the NiO becomes polycrystalline from amorphous which is equivalent to increasing band gap [66, 104, 105]. The decrease in transmittance spectra edge also coincides with this result. The cause of conductivity and transmittance is totally opposite. Defects are the primary carriers of conduction in NiO, whereas defects in thin film cause absorption of light causing decrease in transmittance. However, very thin films are transparent. The transmittance edge is also very sharp (almost vertical) because the larger crystalline size causes scattered radiation due to surface roughness [103]. More than 50% oxygen content in the film causes nickel vacancies and higher carrier concentration. These defects can create
stress field and interact with incident light resulting in scattering. That is why NiO grown in more oxygen environment is less transparent.

5.3 Study of ZnO/NiO Heterojunctions

5.3.1 Device Fabrication

The individual fabrication process of ZnO, NiO and Ni was described in experimental details chapter. The substrate was 3″ × 1″ × 1mm glass substrate. The substrate was cleaned with micro90 concentrated cleaning solution and deionized water. Ultrasonic cleaning was done with acetone first and then with ethanol. After that the substrate was rinsed with deionized water. In between each of the steps, the substrate was blown dry with nitrogen. The device structure is shown in figure 5-5. Then Al:ZnO was fabricated on glass substrate to be used as a substrate for ZnO/NiO heterojunctions. For our experiment, we had two thickness of Al:ZnO e.g.,
Figure 5-5: Schematic diagram of NiO/ZnO heterojunctions. The bottom cyan and violet planes show the Al doped ZnO on top of glass and ZnO, respectively. The green and yellow circle stands for NiO and Ni electrodes of the sample.

440nm and 100nm with sheet resistance 39.9 $\Omega/\square$ and 116$\Omega/\square$, respectively. At the top of it ZnO was fabricated with DC sputtering at room temperature with shadow masking. The thickness of ZnO was 100nm. The circular shaped NiO was fabricated on top of ZnO with shadow masking at 280°C. The thickness of NiO was 400nm and the diameter of circle 5/16 inch. After that the Ni contact was fabricated on NiO with a circle of diameter 1/8 inch. Shadow masking was used in this step too. The top contact was 300nm. For making a good contact with Al:ZnO, a piece of Cu tape was used, since highly doped Al:ZnO can make ohmic contact to most of the metals. The working pressure for all of the steps was 10mtorr.
Figure 5-6: I-V characteristics of NiO/ZnO heterostructure (left). Ohmic contact characteristics between NiO/Ni and Al:ZnO/Cu (right). The red line is flat after 16V because the limiting current for our characterization system is 100mA.

5.3.2 Current-Voltage Characterization

The current voltage characterization was obtained by using a Keithley Instrument (4200 SCS Semiconductor Characterization System). In ZnO/NiO heterojunctions, ZnO is the n-type material while NiO is the p-type material. Both of them behave as semiconductors because of their intrinsic defects and optimum growth condition. The I-V characteristics of NiO/ZnO is shown in figure 5-6(left).

In the figure 5-6 (left), both devices show a good rectifying behavior. The rectification ratio (forward current/ reverse current) of the devices with 400nm & 100nm Al:ZnO are determined to be 20:1 and 7:1, respectively. Here, for both of the devices, the turn on voltage is almost same e.g., 1V. The reverse current is in 1µA-1mA range. The Ni/NiO and Al:ZnO/Cu make perfectly ohmic contact which can be verified by figure 5-6(right).
The device with 400nm Al:ZnO substrate gives much more current than 100nm Al:ZnO because thicker Al:ZnO makes a better contact with the metal than the thinner one. So, the series resistance of thicker Al:ZnO is smaller than thinner Al:ZnO which gives easier current path for electron flow. This goes to saturation value (100mA) of our characterization system at 15V whereas the maximum value of sample on 100nm Al:ZnO is 30mA. The characteristics coincide with the previous studies [38, 78] which show rectifying behavior with turn on voltage of 3.5V and 0.5V, respectively.

5.3.3 C-V Measurements

![C-V Characteristics](image)

Figure 5-7: Reverse-bias C-V characteristics of NiO/ZnO heterojunctions at various frequencies: (a) for 100nm Al:ZnO and (b) 440nm Al:ZnO.

Capacitance-voltage (C-V) measurements were performed at several different frequencies by using the same Keithley instrument (4200 SCS Semiconductor Characterization System). Figure 5-7 shows the reverse-bias C-V characteristics of NiO/ZnO heterojunction in the -10 - 0V range. The frequency was changed from 1kHz to 1MHz. The depletion layer capacitance of the junction, $C_D$, can be defined by the equation below:
\[ C_D = \frac{\varepsilon_s}{d} \] (5.1)

Hence, the depletion layer capacitance depends on depletion layer thickness which is related to the applied voltage. Besides, it is independent on the frequency.

At low frequencies, e.g., 1 KHz, the capacitance is dependent on the applied voltage from -3 - 0V and after that the value saturates to a constant. For other frequencies that are less than 100 KHz i.e., 5 KHz, 10 KHz, 50 KHz, 100 KHz the same behavior is observed. On the other hand, at frequencies higher than 100 KHz, it shows voltage independent behavior, e.g., 50 KHz and 1 MHz. For ideal p-n junctions (without any interface states, trap states and defects) the capacitance should decrease continuously with the increase of the reverse bias because of the increase in the depletion width. Moreover, the variance in capacitance should be independent of the frequency, so, the observed both voltage and frequency dependent behavior of the capacitance is likely due to trap states and/or other defects. At low frequency operation, the trap states can contribute to the charge carrier conduction because of being slow process. The released charges from the traps decrease the depletion width at the junction and give a high capacitance. With frequency decrease, the capturing and releasing of charge increases which results in increase of capacitance. At high frequencies, the switching of charge carrier is too fast to affect depletion width [36, 58].

5.3.4 Light Emission

With forward biasing (> 14V), the ZnO/NiO showed some light emission which shown in the figure 5-8. We tried to characterize the light from ZnO/NiO, but because of our less sophisticated E-L setup and low intensity of light we were unable to do so. The probable cause of light emission can be the recombination of holes from NiO
and electrons of ZnO in the depletion region. Most probably, the intensity of light is low because both of the materials are intrinsic resulting in low carrier concentration.

5.3.5 Applications

The rectifying characteristics can be used for studying its applications in optoelectronics. This heterostructure can be used as photodiodes, photodetectors, LEDs and lasers. Because of their band gap, NiO/ZnO can be used for devices in or near the ultraviolet range. Besides, NiO/ZnO has much better photo catalytic characteristics than only NiO, ZnO or mixture of them. This heterojunction can be used in transparent electronics as transparent diodes as well. The C-V studies of NiO/ZnO can be used to study the defects of NiO/ZnO heterostructure and their effect in electric properties of material such as for studying interface traps of NiO/ZnO heterojunctions.
5.4 Study of MIS (Ni/HfO\(_2\)/NiO/Ni) Heterostructures

5.4.1 Device Fabrication

The individual process for Ni, HfO\(_2\) and NiO was described in details in experimental details section. 78 × 38 × 1mm glass substrate was used for metal-insulator-semiconductor (MIS). The same cleaning procedure mentioned above was performed for wafer preparation and cleaning. Ni was fabricated at room temperature by DC sputtering of Ni target. Then NiO was fabricated on top of Ni layer by reactive sputtering of Ni target at 280°C with \(\text{O}_2:\text{Ar}\) ratio of 4:1 in sputtering environment. The thickness of NiO was 200nm. The HfO\(_2\) was fabricated by reactive sputtering of Hf target at 400°C with \(\text{O}_2:\text{Ar}\) ratio 1:1. The total of \(\text{O}_2\) and Ar pressure was 12sccm. The thickness of HfO\(_2\) was varied for three different thicknesses i.e., 20nm, 50nm and 120nm. The diameter of HfO\(_2\) is 3/8 inch. At the top of it, circular Ni (diameter 1/4 inch) was fabricated from Ni target. For making devices, shadow mask was used instead of mask aligner. Same device geometry as described above (figure 5-5) was used for this device fabrication as well.

5.4.2 Band Diagram

For drawing the band diagram of MIS structure, one needs to know the values of material parameters such as electron affinity, workfunction and band gap. The work function of Ni is 5.01eV. The electron affinity and band gap of HfO\(_2\) are 1.75eV and 5.7eV, respectively [121]. For NiO, these values are 1.8eV and 3.2eV, respectively. The band diagram before any connection between them and after connection with zero bias (V=0) is shown in figure 5-9 (a) & (b), respectively.

At equilibrium, the Fermi level of metal Ni and semiconductor NiO should be in
the same position. For lining up, the Fermi level of semiconductor goes down to be in the same level as Fermi level of metal. Because of band structure, the valence band and conduction band bend upward for this alignment. Bending of valence band makes valence band to go beyond Fermi level of semiconductor resulting in degeneracy.

5.4.3 Current-Voltage Characteristics

For understanding the current voltage characteristics of NiO/HfO$_2$-based MIS structures, three batches of devices with three different thicknesses were fabricated: 20nm, 50nm and 120nm. Band diagrams for these three cases are given below in figure 5-10.

The thickness is a key factor for the negative resistance behavior of MIS structure. For MIS structure with 20nm HfO$_2$, the oxide barrier is so thin that it can be considered as a Ni/NiO ohmic contact. This can be compared to a simple metal-semiconductor contact. For this case, there are very few electrons accumulated in NiO and HfO$_2$ interface (shown in figure 5-10(a)). Current in MIS structure with 20nm
HfO₂ comes from electron emission from the metal through the potential barrier into the p-NiO. Fowler-Nordheim tunneling does not have significant impact in this device with 20nm HfO₂ thickness because of having ultra-thin oxides. The I-V curve for this shows almost the same characteristics as Ni/NiO. This is shown in figure 5-11. Among 20 devices with 20nm HfO₂, most of them showed ohmic behavior, but some of the devices with 20nm HfO₂ (4 devices) showed somewhat flatter negative differential resistance NDR characteristics. This can be explained by the oxide growth non-uniformity. Since, the devices were fabricated by sputtering (rf sputtering of the oxide), some devices with little thicker oxide might cause this NDR characteristics. The current goes to a peak value of 20mA at 12V then decreases gradually (shown in figure 5-11 ). The flatter curve of devices with 20nm HfO₂ than that with 50nm HfO₂ can be explained by less electrons in the semiconductor-oxide interface and lack of substantial F-N tunneling.

With the devices with HfO₂ 120nm, the oxide layer is too thick and the energy barrier is too wide for the electrons to go through it from Ni layer to NiO under forward bias. Although, a lot of electrons accumulate in the oxide-semiconductor interface, the capacitance decreases due to large oxide thickness. So for the same
Figure 5-11: Current-voltage (I-V) characteristics of MIS structure with different thickness.

forward bias, carrier density confined in the interface of the device with 120nm oxide thickness is smaller than that of oxide thickness 50nm (shown in figure 5-10 (c)). That is why the I-V curve is almost flat (horizontal) for devices with 120nm HfO$_2$. It has current in the range of $10^{-12}$A which is pretty low (figure 5-11).

For devices with 50nm HfO$_2$, the electrons accumulate at the interface of oxide and semiconductor and because of upward bend bending due to forward bias; the valence band goes more beyond Fermi level. At that time because of F-N tunneling of electron from metal to semiconductor, the current flow through the MIS structure until the metal Fermi level goes beyond the valence band of semiconductor and the current decreases. For F-N tunneling, the electrons in the metal only face a triangular barrier (shown in figure 5-10 (b)). It increases again after the metal Fermi level goes beyond the conduction band. So, optimum oxide thickness and accumulation of electrons near the oxide and semiconductor interface are the main factor for NDR characteristics. This I-V curve of the device with 50nm HfO$_2$ along with 20nm HfO$_2$ (2 cases) and
5.4.4 Explanation of Negative Differential Resistivity

For explaining the I-V characteristics, the whole voltage range can be divided into 4 portions: 1) Reverse bias, 2) Forward bias 0-5V with positive differential resistance, 3) Forward bias 5-7.5V with negative differential resistance and 4) More than 7.5V with exponential increase.

With reverse bias (negative voltage in NiO and positive voltage in Ni side), electrons tunnel from the valence band of NiO to metal, Ni. The NiO side has a continuous supply of minority carrier electron because of being reverse biased. This current increases monotonically with the increase of bias and it does not show any negative resistivity (figure 5-12 (a)). This current is totally dependent on energy barrier height and thickness.

Forward biasing (positive voltage in NiO and negative voltage in Ni) in 0-5V range results in electrons from Ni to tunnel through the oxide to NiO valence band (figure...
With the tunneling of electrons from the metal to the unoccupied states of valence band, a reverse voltage builds up because of accumulation of electrons in the semiconductor side resulting in an increase in barrier height. Another reason for decreasing the current is because of unavailability of holes in the semiconductor energy band gap region for the electrons in metals when the metal Fermi level is between valence band to conduction band. This decreases the current substantially with increase of bias (5-7.5V). This can be referred as negative differential resistance (figure 5-12 (c)). The voltage range in our I-V curve is significantly higher than a voltage corresponding to the band gap (15V vs 4V) which is due to the series resistance. This series resistance consists of intrinsic sample series resistance and measurement setup series resistance. With an increase of voltage further (more than 7.5V), a very fast growing tunneling current from the metal to the conduction band of semiconductor shows an exponential increase in I-V curve (figure 5-12 (d)). Some portion of this might be coming from the thermionic emission of electron from to semiconductor with higher bias. Moreover, there is a probability of a current from electrons in the metals with higher energies which can tunnel through the oxide simultaneously by hopping on the interface and trap states and recombine with the holes instantaneously. The effective insulator barrier decreases with bias which results in a positive differential resistance for this component.

5.4.5 Light Emission

Under forward bias (positive bias in NiO and negative bias in Ni side), the the MIS structure (Ni/NiO/HfO$_2$/Ni) showed yellow light emission for more than 16V (shown in figure 5-13 (a)). The light is pretty much continuous and visible. We tried to capture the light by our E-L setup, but we could not capture it because of the same reasons mentioned above for light emission from NiO/ZnO heterojunctions (in section 5.3.4). The light can be coming out because of recombination of electrons
Figure 5-13: (a) Photographic image of the light emission from a biased MIS structure (b) Explanation of light emission by band diagram.

which are going from the metal to the conduction band or energetic electrons going by hopping through the trap states. This is shown in figure 5-13 (b).

5.4.6 Applications of NDR Characteristics

NDR properties are really useful for oscillator and amplifier applications [122–127]. A resonator from LC circuit can also be used as a short term oscillator because it can store oscillating electric energy. However, its oscillation goes to zero with time because of its internal resistance or other losses. The negative resistance can negate the positive resistivity of resonator and make a lossless oscillator. They can be used as high frequency or microwave frequency range oscillators. NDR can be used as an amplifier at microwave frequencies. Negative differential resistance devices are also used in nonlinear switching circuits which changes from one step to other dramatically with hysteresis. The advantage of these switching circuits is a relaxation oscillator,
flip flop or memory cell can be made from a single device whereas conventional logic circuit consists of two active devices e.g., transistors.
Chapter 6

Conclusions

We fabricated thin film of semiconducting (zinc oxide (ZnO) & nickel oxide (NiO)) and insulating oxides (hafnium oxide (HfO$_2$)) to study their optical, electrical and structural characteristics. We observed that the electrical properties (resistivity, carrier concentration, mobility, Hall coefficient, sheet resistance) of NiO depend on growth parameters (temperature, O$_2$/Ar ratio and thickness). By changing the O$_2$/Ar ratio, the intrinsic carrier concentration can be modified which can be used in applications of NiO. We found that NiO can be unstable at ambient conditions because its surface oxidizes with time.

Since, NiO is a non-stoichiometric material, we did energy-dispersive X-ray spectroscopy to learn about its stoichiometry. For determining the crystal structure, we did the X-ray diffraction of NiO, ZnO and HfO$_2$. All of them are polycrystalline. HfO$_2$ and ZnO have a preferential peak along with some and a very few weak peaks, respectively. The preferential orientation of NiO changes with growth temperature. Even the O$_2$/Ar ratio can affect the preferential orientation of HfO$_2$ and NiO because they are fabricated by rf sputtering. The transmittance spectra of the oxide layers show that all the oxides are transparent and their optical gap matches the electrical band gap. Changing the O$_2$/Ar ratio can change the transmittance of NiO, so, growth parameters (temperature, O$_2$/Ar and thickness) are important to the fabrication of
the desired nickel oxide.

We fabricated Ni/NiO/ZnO/Al:ZnO heterojunctions with different Al:ZnO thickness by sputtering with proper cleaning procedure and did electrical characterization (current-voltage (I-V), capacitance-voltage (C-V)). The current voltage characterization of this heterojunction showed rectifying characteristics. For finding a proper contact, we also fabricated and characterized Ni/NiO and Al:ZnO/Cu tape which showed perfectly linear I-V characteristics. Device with much thicker substrate (Al:ZnO) gives more current than the thinner substrate because thicker Al:ZnO results in a smaller series resistance and this makes lateral flow of current easier than thinner Al:ZnO. We also performed C-V characterization at various frequencies and found frequency dependence of capacitance of this heterostructure. We showed the relation between depletion width and capacitance in our measurements. We also observed weak transient orange light emission from the heterostructure which we were unable to characterize because of its very low intensity and our less sophisticated E-L setup.

We fabricated and characterized Ni/NiO/HfO$_2$/Ni heterojunctions with different hafnium oxide (HfO$_2$) thickness (20nm, 50nm, 120nm) by sputtering. We did I-V characterization of the heterostructure. The device with 120nm HfO$_2$ behaved as a MIS capacitor because the oxide works as an insulator. The devices with 50nm HfO$_2$ showed negative differential resistance (NDR). We explained this behavior with the help of band diagram and MIS tunneling diode theory of degenerate semiconductor along with some general theories of tunneling and tunneling diodes. This device emits continuous orange light with higher intensity under higher bias. However, we were unable to characterize the light by electroluminescence because of the same reason described above for light emission from NiO/ZnO.

While other semiconducting oxides such as TiO$_2$, ZnO, CuO are widely studied and researched, nickel oxide has not been well understood as a wide band gap and transparent semiconductor. We systematically studied NiO-based heterojunctions
for device applications and our results indicate that. NiO-based structures definitely have a potential for electronics and optoelectronics applications.
References


[78] R. Gupta, K. Ghosh, and P. Kahol, “Fabrication and characterization of NiO/ZnO pn junctions by pulsed laser deposition,” *Physica E: Low-dimensional Systems and Nanostructures*, vol. 41, no. 4, pp. 617 – 620,


111


112


