ABSTRACT

DUTTA, TITAS. Nanostructured Transparent Conducting Oxides for Device Applications. (Under the direction of Professor Jagdish Narayan).

Research on transparent conducting oxides (TCOs) alternative to indium tin oxide (ITO) has attracted a lot of attention due to the serious concern related to cost and chemical stability of indium tin oxide. The primary aim of this research is to develop low cost alternative transparent conducting oxides with an eye towards 1) increasing the organic solar cell efficiency and 2) fabricating transparent electronic devices utilizing p-type TCOs. To investigate the fundamental properties, the novel TCO films have been grown on sapphire and economical glass substrates using pulsed laser deposition (PLD) technique. The films were also grown under different deposition conditions in order to understand the effect of processing parameters on the film properties. The characteristics of the thin films have been investigated in detail using (X-ray diffraction, TEM, X-ray photoelectron spectroscopy (XPS), UV- photoelectron spectroscopy (UPS), four probe resistivity and UV-Vis transmittance measurements) in order to establish processing-structure-property correlation.

ZnO doped with group III elements is a promising candidate because of its superior stability in hydrogen environment, benign nature and relatively inexpensive supply. However, ZnO based TCO films suffer from low work function (4.4 eV, compared to that of 4.8 eV for ITO), which increases the energy barrier and affects the carrier transport across ZnGa_{0.05}O/organic layer interface. To overcome this issue of ZnO based TCOs, the growth of bilayered structure consisting of very thin MoO_{x} (2.0 < x < 2.75), and/or p-Li_{x}Ni_{1-x}O (0 ≤ x ≤ 0.07) over layer on Zn_{0.95}Ga_{0.05}O (GZO) film by pulsed laser ablation is proposed. The multiple oxidation states present in the over layers (Mo^{4+}, Mo^{5+} and Mo^{6+} in MoO_{x} and Ni^{2+}}
and Ni\textsuperscript{3+} in NiO\textsubscript{1+x}), which result in desired TCO characteristics were determined and controlled by growth parameters and optimal target composition. These optimized bilayer films exhibited good optical transmittance (≥ 80%) and low resistivity of ~ 10\textsuperscript{-4} Ω-cm. The optimized NiO\textsubscript{1+x} / GZO and MoO\textsubscript{x} / GZO bilayers showed significant increase in work function values (~5.3 eV). The work function of the bilayer films was tuned by varying the processing conditions and doping of over layers. Preliminary test device results of the organic photovoltaic cells (OPVs) based on these surfaces modified TCO layers have shown an increase in the open circuit voltage (Voc) and/or increase in Fill factor (FF) and the power conversion efficiency of these devices. These results suggest that the surface modified GZO films have a potential to substitute for ITO in transparent electrode applications.

To gain a better understanding of the fundamentals and factors affecting the properties of p-type TCO, NiO thin films have been grown on c-sapphire and glass substrates with controlled properties. Growth of NiO on c-sapphire occurs epitaxially in [111] direction with two types of crystalline grains rotated by 60\textdegree with respect to each other. We have also investigated the effects of the deposition parameters and Li doping concentration variations on the electrical and optical properties of NiO thin films. The analysis of the resistivity measurement showed that doped Li\textsuperscript{+} ions occupy the substitutional sites in the NiO films, enhancing the p-type conductivity. The minimum resistivity of 0.15 Ω-cm was obtained for Li\textsubscript{0.07}Ni\textsubscript{0.93}O film. The results of this research help to understand the conduction mechanisms in TCOs and are critical to further improvement and optimization of TCO properties. This work has also demonstrated interesting possibilities for fabricating a p-Li\textsubscript{x}Ni\textsubscript{1-x}O/ i-MgZnO /n-ZnO heterojunction diode on c-sapphire. It has been demonstrated that epitaxial Li\textsubscript{x}Ni\textsubscript{1-x}O can be grown on ZnO integrated with c-sapphire. Heteroepitaxial growth of the p-n junction is
technologically important as it minimizes the electron scattering at the interface. The insertion of i-MgZnO between the p and n layer led to improved current-voltage characteristics with reduced leakage current.

An attempt has been made to elucidate the role of point defects, in controlling the carrier concentration and transport characteristics of nanostructured TCO films. This study presents the systematic changes in structural, electrical and optical properties of NiO thin films introduced by nanosecond duration Ultraviolet Excimer laser pulses. NiO films show transformation from p-type semiconducting to n-type conducting behavior with three order of magnitude decrease in resistivity, while maintaining its cubic crystal structure and good epitaxial relationship. This phenomenon is reversible via oxygen annealing. From XPS analysis, a strong correlation has been established between n-type conductivity and non-equilibrium concentrations of laser induced Ni$^{0}$-like defect states.
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by

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DEDICATION

To My Parents

Sipra Dutta and Dr. Somaditya Dutta
BIOGRAPHY

Titas Dutta was born in Sainthia, a town in West Bengal State in eastern India. She completed her high schooling at K.V.O.N.G.C., Dehradun. Her penchant for science and electronic circuits prompted her to pursue a Bachelor’s degree in Technology in the field of Electronics and Communication Engineering. She graduated in 2004. Her interest in research in an area where electronics and materials science abridge instigated her to go for further studies. She joined Materials Science Programme at Indian Institute of technology (IIT), Kanpur and received a master’s degree in Technology in Materials Science in spring 2006. For her master’s thesis, she worked under the guidance of Prof. Jitendra Kumar. In fall 2006, she joined the PhD program in department of Materials Science and Engineering at North Carolina State University. She worked under the guidance of Prof. J. Narayan for her PhD on Nanostructured Transparent Conducting Oxides for Device Applications at the NSF Center for Advanced Materials and Smart Structures (CAMMS).
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- S3: NiO$_{1+x}$ (8 nm)/ GZO ($P_{O2(NiO)} = 10^{-3}$ Torr)
- S4: NiO$_{1+x}$ (8 nm)/ GZO ($P_{O2(NiO)} = 7 \times 10^{-2}$ Torr)
- S5: Li$_{0.05}$Ni$_{0.95}$O (8 nm)/ GZO ($P_{O2(NiO)} = 7 \times 10^{-2}$ Torr)
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Chapter 1

Introduction

Transparent conducting oxides (TCOs) are wide band gap semiconductors which are optically transparent and show conductivities intermediate to metals and semiconductors. For most of the applications mentioned above, including solar cells, the basic requirements for the TCO materials are to possess transmittance of > 80% and resistivity < $10^{-3}$ Ω-cm [1]. Its conductivity is attributed to high carrier concentration (n) arising from defects (intrinsic and extrinsic), whose energy levels lie close to the conduction band [2]. Depending on the carrier type the TCOs can be classified into two types, n – type and p – type, where the electrons and holes are the majority carriers, respectively. There is a renewed interest in research on TCOs, mainly due to its numerous applications. The major applications include larger flat-screen high-definition televisions (HDTVs), larger and higher-resolution screens on portable computers, photovoltaic cells (PV) and a plethora of new hand-held and smart devices, all with smart displays [3]. Another important application for the TCOs is energy efficient windows, which is gaining significance in the global regions with cold or moderate climates [4]. These applications primarily used n type TCOs. The second type of applications is termed as transparent oxide semiconductors (TOSs), which emerges after the discovery of CuAlO$_2$, the first “real” p-type TCO, in 1997 [5]. This discovery has led to intensive research on developing various p-type TCOs and electronic and opto-electronic devices such as light emitting diodes (LEDs) and photo-detectors [6].
The total global energy consumption of oil, coal, natural gas, nuclear and hydropower, etc., is estimated to be some 10,000 million ton oil equivalents per year [7]. With the recognition of the vast potential of photovoltaic technology, worldwide production levels for terrestrial solar cell modules have been growing rapidly over the past several years (fig. 1.1).

Figure 1.1. World photovoltaic module production (in megawatts), total consumer, and commercial per country [8].

The current cost of ~$4/Wp (Wp = watt peak) is still too high to significantly influence energy production markets [8]. To make these solar units affordable (fig. 1.2), power conversion efficiency has to be increased. But these units are limited by thermodynamic considerations under direct AM1.5 sunlight. Currently best values of efficiencies are ~ 42.3% for the CIGS and GaAs based multijunction photovoltaic cells.
The efficiency can be increased continuously by better understanding of materials and device properties. One key development of any photovoltaic technology is to develop moderate-efficiency devices (~15%) at extremely reduced costs which lead to rapidly emerging Organic photovoltaic device technology. With the improvement in properties of TCOs, the performance of solar cells can be further enhanced which is discussed in chapter 2.

Figure 1.2. Cost-efficiency analysis for first- (I), second- (II), and third- (III) generation PV technologies [9].

Currently, indium tin oxide (ITO) is the most widely used material for TCO applications. With the growing market of electronic and opto-electronic applications mentioned above, it seems to be difficult to maintain the constant supply requirements of ITO because of the rapidly diminishing supply of In. In the recent times the production of In has dropped by ~12% and increasing the production is itself a topic of intense research [10]. The primary reason for the limited availability of In is that it is produced as a by-product of Zn, Sn and Pb
production. The concentration of In in earth’s crust is extremely low (0.1 ppb), which prohibits direct mining of this element [11]. Thus, increasing the output of In would require drastic improvement in the extraction processes and equipment resulting in the high prices of In. In fact, during the last 3 years, the price of indium has increased by a factor of ten. The price is even higher for higher grade In and its alloys. In 2005 – 06, 70% of the In produced globally was used in the form of ITO coating for various TCO applications. The market of flat panel displays (FPDs) is expected to grow to 150 billion US$ by 2012. Moreover, roughly 30% of produced indium is consumed by other industrial applications. For example, indium based compound semiconductors like indium phosphor and indium antimony are widely explored for their applications as transistors and sensors. Indium is also a critical component in CIGS (CuInxGa1-xSe2) based PV cell, which is one of the major commercial thin film PV cells in the solar industry. In addition to the high cost of In, ITO also suffers from poor chemical stability in hydrogen atmospheres and exhibits relatively poor diffusion barrier characteristics [12]. Stability in hydrogen is a particularly important property for the Si based photovoltaic applications, where H passivation is a key processing step in the solar cell fabrication. This problem motivated researchers to explore new and cost-effective TCO materials for divergent applications. Some of the alternative TCOs are (Ga,Al): ZnO, F:SnO2, Nb:TiO2. Among these, ZnO doped with Ga or Al is a promising candidate because of its superior stability in hydrogen environment, benign nature and relatively inexpensive supply. The Ga doped ZnO films with electrical and optical properties comparable to ITO can be grown on sapphire as well as inexpensive glass substrates. Although, low resistivity and high %T are the prerequisite for the superior device performance, some other factors including work
function, band alignment, materials cost, compatibility and processing are also crucial for device performances such as for PV applications [13]. Another important issue is interface stability between the TCO and organic layer in the device, which is critical for reliability and long-term performance. Therefore, diffusion barrier characteristics of TCO play an important role in determining reliability and performance of these devices.

**Proposed Research and Research Objectives**

The main objective of this thesis includes:

1. To develop high work function TCO while maintaining the overall transmittance and conductivity with a goal toward applications for organic solar cells.
2. To develop high efficiency p-type TCO for transparent p-n junctions.

In this present work, nanostructured transparent conducting oxides consisting of MoO\(_x\) (2.0 < x < 2.75)/ Zn\(_{0.95}\)Ga\(_{0.05}\)O (GZO) and p- NiO\(_{1+x}\)/ Zn\(_{0.95}\)Ga\(_{0.05}\)O (GZO) have been developed. This approach utilizes the high work function properties of MoO\(_x\) and NiO\(_{1+x}\) for the energy band alignment at the interface of the TCO layer and the donor of the organic device so that the energy barrier at the interface could be reduced, which will lead to the increased power conversion efficiency of the solar cell. This work also focuses in developing p-type undoped and Li doped Nickel Oxide thin films and evaluate the electrical and optical properties for their potential application as a transparent conducting oxide. The broader goal is to develop alternative low- cost TCOs with properties better than or comparable to ITO for a range of applications such as displays, solar cells, solid-state lighting and sensors.
The following aspects are addressed in this thesis:

- The establishment of process - properties - structure correlation to optimize the performance for TCO applications.
- In the case of p- NiO TCO films, the conduction mechanisms are investigated and modeled through in-depth structural characterization, chemical analysis, and temperature dependent electrical property measurements.
- The suitability of using these TCO layers in photovoltaic application is evaluated through characterization of organic solar cells fabricated using the optimized TCO films.
- Better understanding of the role of point defects/non-stoichiometry in NiO electrical transport properties.

Rest of the thesis is organized in the following chapters.

*Chapter 2:* In this chapter background knowledge and current issues pertinent to TCO is presented.

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

*Chapter 4:* Experimental results on growth and characterization of MoO$_x$ modified ZnGaO based Transparent Conducting Oxides are presented.

*Chapter 5:* Experimental results on growth and characterization of NiO$_{1+x}$ modified ZnGaO based Transparent Conducting Oxides are presented.
Chapter 6: Experimental results on growth and characterization of p-type NiO on sapphire (0001) and glass substrates are presented.

Chapter 7: Results on effect of Li doping in NiO thin films on its transparent and conducting properties are discussed.

Chapter 8: In this chapter, growth and characterization of epitaxial Li doped NiO/ ZnO heterostructures integrated on Sapphire (0001) Substrates are discussed.

Chapter 9: Results of ultrafast p to n type conductivity transformation in NiO induced by laser irradiation are discussed.

Chapter 10: A brief summary of the present work is given. Scope for future work is discussed.
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Chapter 2

Related background knowledge

2.1. Transparent conducting oxide (TCO)

A TCO is a wide band-gap semiconductor that has a relatively high concentration of free carriers with concomitant high transmittance. It shows conductivities intermediate to metals and semiconductors. The high carrier concentration arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. The high-electron-carrier concentration causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between the properties is required. Reduction of the resistivity involves either an increase in the carrier concentration or in the mobility. Increasing the former also leads to an increase in the visible absorption. Increasing the mobility, however, is probably the best direction to follow.

The key requirement for the TCO applications is that transmittance (%T) should be greater than 80%, while resistivity (ρ) is less than $10^{-4} \, \Omega \text{-cm}$. According to Boltzmann’s conductivity equation, a material’s conductivity is given by

$$\sigma = n \mu e$$

(2.1)

where $\sigma$, $n$, $\mu$ and $e$ are electrical conductivity, carrier concentration, carrier mobility and electronic charge, respectively.
Mobility is directly dependent on the relaxation time, which is determined by the scattering events, and is inversely dependent on the effective mass of the carrier. The TCO materials have been widely used in a variety of applications, as mentioned in Chapter 1. The research progress for TCO materials have been repeatedly reviewed from time to time. Holland [1] reviewed the early work of TCO films in 1958. Vossen [2] and Haacke [3] reported comprehensive reviews to the mid-1970s. Manifacier [4], Jarzkeski [5], and Chopra et. al. [6] covered the work in this area up to the early 1980s. Hartnagel et. al. [7] reviewed the growth techniques, properties and applications of TCOs. Some critical issues related to new TCO materials, such as criteria for applications and theoretical models, were addressed in MRS Bulletin [8] in 2000. More recently, Exharhos et. al. [9] summarized up-to-date TCO research with an emphasis on the microscopic description of electronic conduction properties and guidelines for designing new TCO materials.

2.2. TCO properties

2.2.1. Electrical properties

An effective TCO should have high electrical conductivity combined with low absorption of visible light. Thus figure of merit defines the quantitative measure of the performance of TCO which is equivalent to the ratio of the electrical conductivity $\sigma$ to the visible absorption coefficient $\alpha$,

$$\frac{\sigma}{\alpha} = - \left\{ R_s \ln(T + R) \right\}^{-1}$$

(2.2)
n which $R_s$ is the sheet resistance in ohms per square, $T$ is the total visible transmission, and $R$ is the total visible reflectance. A larger value of $\sigma/\alpha$ indicates better performance of the TCO [8].

The conductivity is determined by the product of the concentration of free electrons ($n$) and the mobility ($\mu$). In wide band gap semiconductors, the $n$ and $\mu$ cannot be solely increased, which limits the conductivity. At high electron concentration ($n$), carrier transport is limited primarily by ionized impurity scattering, i.e., the Coulomb interaction between electron and the ionized dopant. So the carrier mobility drops and the conductivity also starts decreasing, and it decreases the optical transmission at the near-infrared edge. With increasing dopant concentration, the resistivity reaches a lower limit, and does not decrease beyond it, whereas the optical window becomes narrower. It was proposed that the mobility and conductivity of TCOs (ITO, SnO$_2$, ZnO) are intrinsically limited by ionized impurity scattering for carrier concentration above $10^{20}$ cm$^{-3}$ [10]. Conductivity is associated with excess oxygen vacancies or metal ions. Doping of these wide bad gap oxides like indium oxide with tin and zinc oxide with Al or Ga can increase the conductivity. However, the mobility is not only governed by ionized impurity scattering but also by lattice scattering, neutral impurity scattering, electron–electron scattering, electron–impurity scattering. Impurity scattering is the dominant scattering mechanism in TCOs. For highly degenerate semiconductors, the contribution of ionized impurity scattering is given by (Eq. 2.3) [11].

$$\mu_{iIS} = \frac{4e}{h} \left(\frac{\pi}{3}\right)^{1/3} n^{-2/3} \text{ (2.3)}$$
Resistivity for an electron gas of density $n$ is given by

$$\rho = \left[ \frac{N_e Z e^2 (m^*)^2}{24\pi^2(\varepsilon\varepsilon_0)\hbar^3 n^2} \right] f(k_F)$$

(2.4)

Where,

$$f(k_F) = \ln(1 + \beta^2) - \frac{\beta^2}{1 + \beta^2}, \quad \beta = \frac{2k}{k_{TF}}$$

And $k_{TF} = \left( \frac{3n}{\pi^2} \right)^{1/3} \frac{m^* e^2}{\hbar^2 \varepsilon \varepsilon_0}$

In the case of polycrystalline TCOs, grain boundary scattering is an important scattering mechanism. These boundaries generally contain fairly high densities of interface states, which trap free carriers from the bulk of the grain and scatter free carriers by virtue of the inherent disorder and the presence of trapped charges. The interface states result in a space charge region in the grain boundaries. According to the petriz model [12]

$$\mu_g = \mu_o \exp\left( \frac{\Phi_b}{kT} \right)$$

(2.5)

where

$$\mu_o' = \left( \frac{L^2 e^2}{2\pi m^* kT} \right)^{1/2}$$

(2.6)

$L$ is the grain size and $\Phi_b$ is the grain boundary potential.

It was found in theoretical simulation that the mobility decreases with decrease in grain size and increase in the grain boundary potential [13]. The calculated value of mobility for grain boundary potential of $\sim 0.01$ eV was greater than $200 \text{ cm}^2 \text{ V}^{-1}\text{ s}^{-1}$ where the average grain size is $\geq 100 \text{ nm}$.
However, mostly the mobility values $< 100 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$ has been reported in the literature. This large deviation observed in the calculated mobility and the experimental data suggests that grain boundary scattering may not be a dominant scattering mechanism for ITO. However, carrier mobility in some materials having high grain boundary potential e.g, ZnO may be effected by grain boundary scattering [14].

![Graphs showing theoretical calculation of mobility at different (a) grain boundary potentials and (b) grain sizes](image)

Figure 2.1. Theoretical calculation of mobility at different (a) grain boundary potentials and (b) grain sizes [13].

The comparison of the simulated upper limit of mobility and lower limit of resistivity with experimental data for ITO films based on the carrier concentration ionized impurity center correction is shown in fig.2.1 [13]. The simulation due to the ion impurity scattering mechanism with effective mass correction and carrier concentration ionized impurity center correction shows good agreement with the upper limit of mobility and the lower limit of resistivity of the experimental data (fig.2.2).
Thus, based on the discussion of the various carriers scattering mechanism, it can be safely assumed that the ion-impurity scattering sets the limit on the intrinsic limit for maximum value of mobility and hence, on maximum achievable conductivity of TCOs. Some additional scattering mechanism such as defects (dislocation) scattering, electron – electron interaction, electron – impurity interaction and neutral impurity scattering also affect the electrical properties in TCO films, but most of them tend to affect only at low temperatures.

2.2.2. Optical properties

TCO thin films must have a very low absorption coefficient in the near UV-VIS-NIR region. Figure 2.3 shows the typical transmittance spectrum of a TCO film, which exhibits three distinct regions of transmission [15].
The optically transparent region is limited by the absorption edge ($\lambda_{\text{gap}}$) and the plasma edge ($\lambda_{\text{pl}}$). The region is also known as transparent window. The absorption edge ($\lambda_{\text{gap}}$) is associated with fundamental bandgap absorption. The plasma edge ($\lambda_{\text{pl}}$) is determined by free electron plasma absorption.

![Illustration of transmission spectrum of a typical TCO with $\lambda_{\text{gap}}$ and $\lambda_{\text{pl}}$ indicating the wavelength of bandgap absorption and free electron plasma absorption, respectively [15].](image)

The optical properties of TCOs transmission (T), reflection (R), and absorption (A), are determined by its refraction index n, extinction coefficient k, band gap $E_g$, and geometry. n, k and $E_g$ depends on the chemical composition and solid structure of the material, whereas the geometry can be modulated extrinsically by changing the film thickness, thickness uniformity, and film surface roughness.

The transmittance and the absorption can be explained by considering the energy band diagram of the TCOs. Fan et. al. proposed the first energy band model to explain the observed optical spectra in ITO [16].
Since then there have been considerable investigation on the band structures of various TCOs with the aim to explain the experimental measured optical properties [17]. In Fan et. al. model, the conduction band consists mainly of $s$ electrons from the cations and the valence band is formed by O2p electrons. The two bands are separated by a large bandgap ($E_g > 3.2$ eV), which leads to the transparency of TCOs in the visible spectrum region. Upon radiation with energy higher than the bandgap, electrons can absorb photons to be excited from the valence band to conduction band. The intrinsic semiconductor has a Fermi energy ($E_f$) lying in the midgap ($E_g/2$). As the electron concentration increases, $E_f$ is shifted towards the conduction band. With high concentration of electrons generated from the shallow donors (impurities and vacancies), the $E_f$ can move above the conduction band making it a degenerate semiconductor. At sufficiently high electron concentration, the measured optical bandgap can increase with increasing carrier concentration, leading to a shift of the absorption edge towards shorter wavelength. The bandgap widening phenomenon is known as the Moss-Burstein effect, which is due to occupation of the lowest states by electrons in the conduction band. Figure 2.4 shows schematically the proposed band structure of a TCO and the Moss-Burstein effect [18].

Assuming the conduction band (CB) and valence band (VB) are parabolic, the dispersions of the CB and VB in the doped material are given by:

$$E^0_\text{c}(k) = -\frac{\hbar^2 k_F^2}{2m_c}$$  \hspace{1cm} (2.7)

$$E^0_\text{v}(k) = E_g - \frac{\hbar^2 k_F^2}{2m_c^*}$$  \hspace{1cm} (2.8)
The measured band gap is given by:

\[ E^0_g(k) = E_g + \Delta E_{g}^{BM} \]

where \( \Delta E_{g}^{BM} = \frac{\hbar^2 k_F^2}{2} \left( \frac{1}{m_v} - \frac{1}{m_c^*} \right) \)

Figure 2.4. The schematic of the proposed band structure of a TCO and the Burstein-Moss effect [18].

In Figure 2.5, the measured \( E_g \) does show correlation with electron density \( n^{2/3} \) [19]. However, this theory does not take into account additional effects related to the electron-electron interactions and impurity scattering. It is believed that scattering effects also contribute to the observed change in the bandgap in the doped materials.

Assuming that the Fermi surface is spherical, the Fermi wave vector is given as:

\[ k_F = (3\pi^2 n)^{1/3} \]  

(2.9)
Then

\[ \Delta E_{g}^{BM} = (3\pi^2n)^{2/3} \frac{\hbar^2}{2} \left( \frac{1}{m_0^*} - \frac{1}{m_e^*} \right) \]  

(2.10)

It can be seen that the measured optical band gap is proportional to \( n^{2/3} \).

Figure 2.5. The correlation of \( E_g \) with electron density \( n^{2/3} \). The solid curve is calculated using the B-M theory [19].

The effect of the scattering events can be accommodated by adding a correction term to the dispersion of energy bands. As a result, the actual change in the bandgap is given by:

\[ E_g = \Delta E_{g}^{BM} + W \]  

(2.11)

where \( W \) represents a decrease of bandgap due to scattering terms [19, 20].
Reflectivity is another important parameter which is affected by the degenerate nature of a semiconductor. The plasma frequency for the conduction electrons in a TC divides the optical properties. At frequencies below the plasma frequency, the TC reflects and absorbs incident radiation. For most TC materials, the plasma frequency falls in the near-infrared part of the spectrum, and the visible region is in the higher, transparent frequency range.

From Drude model, \( \omega_p \) the plasma frequency of a conducting material is defined. when \( \omega < \omega_p \) a conductor is highly reflective, since then \( \varepsilon_1 < 0 \). The plasma frequency may be written as:

\[
\omega_p = \left( \frac{n e^2}{\varepsilon_\infty \varepsilon_0 m^*} \right)^{1/2} \tag{2.12}
\]

This has been obtained by considering limit of electron density \( n > 10^{21} \text{cm}^{-3} \) and high mobility \( (> 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}) \) for ITO.

This means that for a film to be non-reflective to light of free-space wavelength \( \lambda_0 \) (i.e. \( \omega_p < 2\pi c/\lambda_0 \)), the electron density \( n \) must satisfy:

\[
n < \frac{4\pi^2 \varepsilon_\infty m^*}{\mu_0 e^2 \lambda_0^2} \tag{2.13}
\]

It was concluded in case of ITO that for efficient transmission of the whole visible spectrum (including red light of free-space wavelength up to 780 nm), the electron density should not exceed \( 2.6 \times 10^{21} \text{ cm}^{-3} \).
The power reflection coefficient $R$ at an interface between a thick ITO layer and free space can now be calculated as Eq. 2.14 and 2.15. This takes the following limiting forms for frequencies below and well above the plasma frequency.

\[ R \approx 1 - 2 \frac{2\omega}{\sqrt{\omega N T}} \approx 1 - 2 \sqrt{\frac{2\omega \varepsilon_0}{\sigma_0}}, \quad (\omega < \omega_p) \quad (2.14) \]

\[ R \approx \left| \frac{\sqrt{\varepsilon_\infty} - 1}{\sqrt{\varepsilon_\infty} + 1} \right|^2 \approx 0.11, \quad (\omega \gg \omega_p) \quad (2.15) \]

Figure 2.6. The power reflection coefficient at the interface between a thick ITO layer and free space as a function of free electron density $n$ for various incident wavelengths in the visible spectrum [21].

As shown in fig.2.6, for frequencies below the plasma frequency then $R$ is close to 1 (i.e. it is very reflective), with a small amount of electromagnetic absorption within the material (approximately equal to 1- $R$) [21].
This analysis has shown that the requirements for transparency would give an absolute lower limit on the resistivity of $\sim 4 \times 10^{-5}$ $\Omega$-cm. However, these calculations did not take into account the dependence of effective mass on the increase in carrier concentration. Since, the effective mass increases with increasing carrier concentration, the limit for resistivity is $\sim 3 \times 10^{-5}$ $\Omega$-cm and the corresponding carrier concentration is $9 \times 10^{21}$ cm$^{-3}$ with the effective mass correction.

2.2.3. Work function

The energy difference between Fermi energy and vacuum level corresponds to the work function ($\Phi$). The work function corresponds to the minimum amount of energy needed to remove an electron from the metal. In metals, work function and ionization energy are the same. The condition of the surface can strongly affect the work function. The presence of minute amounts of contamination (less than a monolayer of atoms or molecules), or the occurrence of surface reactions (oxidation or similar) can change the work function substantially. Changes of the order of 1 eV are common for metals and semiconductors, depending on the surface condition [22]. These changes are a result of the formation of electric dipoles at the surface, which change the energy an electron needs to leave the sample. Due to the sensitivity of the work function to chemical changes on surfaces, its measurement can give valuable insight into the condition of a given surface.

In a nondegenerate semiconductor (having a moderate doping level), the Fermi level is located within the band gap.
This means the work function is now different from the ionization energy (energy difference between valence bands maximum (VBM) and vacuum level). In a semiconductor, the Fermi level becomes a somewhat theoretical construct since there are no allowed electronic states within the band gap. This means the Fermi distribution needs to be considered, which is a statistical function that gives the probability to find an electron in a given electronic state. The Fermi level refers to the point on the energy scale where the probability is just 50%. Even if there is no electrons right at the Fermi level in a semiconductor, the work function can be measured by photoemission spectroscopy (PES). Figure 2.7(a,b) shows the schematic of energy diagram of the metal and the n-type non-degenerate semiconductor.

![Figure 2.7. Schematic energy diagrams of (a) metal and (b) n–type semiconductor.](image)
In organic devices the work function of the electrode materials is very important since it determines together with the LUMO/HOMO and Fermi-level of the semiconductor whether the electrode forms an ohmic or a blocking contact for the respective charge carrier (holes in VB, electrons in CB). Moreover a large difference in work function of the electrode materials can increase the $V_{oc}$ considerably (section 2.4.2). The variability of work function poses a similar conundrum as balancing the optical properties ($\%T$ and $R$) and the electrical properties. However, optimization of the work function does not always assure the highest efficiency, because the carrier injection is also dependent on the chemical and structural characteristics of the heterojunction interface.

2.2.4. Other critical issues

Apart from the electrical and optical properties, there are some other factors which need to be considered for the development of TCOs. Some frequently discussed issues are described in this section.

1. Thermal and chemical stability

The thermal stability temperature is a threshold temperature, above which TCO films show appreciable change or degradation in its properties. The reported thermal stability temperatures for ZnO, SnO$_2$ and Cd$_2$SnO$_4$ are 250, 500 and 700$^\circ$C, respectively [23]. Above these temperatures, chemical decompositions of the films occur, which degrade the quality of the films. Many commercial substrates are temperature sensitive (glass $< 500$ $^\circ$C, polymer $< 200$ $^\circ$C) and hence, restrict the processing temperature. Moreover, observations of chemical reaction of the TCO films with the substrate and the subsequent layers have been reported in
the literature [24]. Thermal stability is essential for the developed TCOs from the application point of view as these TCOs may be exposed to various extreme environments. Chemical stability of a TCO is determined by its ability to resist corrosive environment and treatment. For applications such as amorphous Si solar cells, the sensitivity of TCO to reducing atmospheres is an important concern. ITO undergoes heavy reduction when exposed to hydrogen environments. Comparatively, doped ZnO films are much more stable in reducing atmospheres and plasmas containing hydrogen species [23, 25]. Therefore, ZnO based TCOs may be preferred for the applications involving hydrogen plasma processing. In contrast, for oxidizing atmospheres, especially at high temperatures, ITO shows better stability compared to other TCOs [25].

2. Surface morphology and etchability

Surface roughness is another important characteristic, which drastically affects the device performance as it affects both the optical and electrical properties of TCO. For most of the applications (e.g. organic LEDs, solar cells based on crystalline materials) it is required to have extremely smooth TCO films (RMS < 5nm). Specifically, for the small device dimensions (~100 nm thickness), low specific contact resistance is needed. Any asperities on the TCO surface with the dimensions comparable to those of the device will hamper the device performance [26]. Furthermore, smoother surfaces usually yield lower contact resistance because of reduced surface scattering and minimized localized field effects [27, 28]. However, sometimes a hazy or textured surface is preferred over a smooth TCO film, f.e., in amorphous Si:H and/or nanocrystalline (nc) Si:H solar cells [29, 30].
The texturing of the TCO surface leads to trapping of the incident light due to enhanced scattering within the absorption layer of the solar cell. Figure 2.8 illustrates schematically the trapping of the incident light due to the corrugated structure of the TCO layers [31]. The amorphous Si has indirect bandgap and the increased optical path length of the incident light can significantly increase the optical absorption in the absorption layer, thereby improving the efficiency of these solar cells.

Figure 2.8. Schematic of the TCLO structure fabricated using ZnO and Mo:In2O3 layers [31].

The surface morphology is governed by several parameters such as the deposition temperature, partial pressure and the ambient gas, the plasma characteristics (sputtering, PLD) and the post deposition treatment. Although, as-deposited films are fairly smooth, the post-deposition is often required to achieve desired surface characteristics, namely the work function and chemical activity.
Several methods (plasma processing and etching) have been proposed to modify the surface properties of the TCO films [28]. In case of polymer based LEDs, it has been shown that post-deposition treatment of the ITO films results in the decrease of turn-on voltage, increase in the brightness and significant improvement in the efficiency of the device. The improvement of the device performance is related mainly to the increase of the work function, smoother film, cleaner surface and higher surface energy. However, adsorption of extraneous species such as H, Ar, and oxygen on the film surface during the post-treatment can significantly alter the electrical resistivity of the films, so proper process optimization needs to be done. The chemical activity is also likely to change once the surface is etched or treated with a certain type of plasma, which can change the bonding at the interface and consequently, the kinetics of the charge transfer at the interface. Thus, caution is to be practiced during surface preparation of the TCO films for fabrication of devices that exhibit optimal performance. Etching is also sometimes employed to pattern the TCO films and it is highly desirable that the films can be readily removed. In the industry both wet (or chemical etching) and dry etching using laser ablation technique are currently being used to etch the TCO.

Table 2.1. Various etchants for different TCOs [32].

<table>
<thead>
<tr>
<th>TCO</th>
<th>Etchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Dilute acids and alkalis (HCL, KOH)</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ammonium chloride</td>
</tr>
<tr>
<td>TiN</td>
<td>H₂O₂ + NH₃</td>
</tr>
<tr>
<td>In₂O₃</td>
<td>HCl + HNO₃ or FeCl₃</td>
</tr>
<tr>
<td>SnO₂</td>
<td>Zn+HCl</td>
</tr>
<tr>
<td>SnO₂</td>
<td>CrCl₂</td>
</tr>
</tbody>
</table>
Table 2.1 lists the various chemicals that are used to etch the different TCOs. ZnO tends to etch very easily compared to the other TCOs, while tin oxide based TCOs are the most difficult to etch [23]. Laser etching of TCO layers is used where high precision is required over the processing speed.

3. Diffusion barrier

Generally, SnO₂ films on glass require temperatures higher than 550°C to achieve desirable properties, which causes rapid diffusion of Na (from soda lime glass) into the film. To prevent interdiffusion of impurities, a barrier layer such as SiO₂, TiO₂ or Al₂O₃ is often used [23, 33]. Among these, Al₂O₃ seems to be the most effective in preventing diffusion of Na into the films. Traditionally, ITO has been used in the industry and most of the diffusion related studies have involved ITO. The studies on diffusion of impurities in TCOs is not only important to avoid degradation of the TCO layers but also relevant to prevent transport of dopants from the active semiconductor layers, which might eventually lead to failure of the device. In context of the present study, MoOₓ which is used as an interfacial layer between TCO and active layer of device shows excellent diffusion barrier characteristics.

2.3. Alternative TCO

2.3.1. Doped metal oxides

Mostly TCO research has focused on $n$-type semiconductors consisting of metal oxides. Indium-tin-oxide (ITO) thin films which have mainly been the workhorse for the TCO industry are prepared by magnetron sputtering deposition.
However, transparent conducting oxides (TCOs) that contain a reduced amount or no indium have recently attracted much attention as substitute materials for ITO transparent electrode applications because of the cost and scarcity of indium, the principal material of ITO [25, 34-36]. Many kinds of TCO thin-film materials have been newly developed in recent years [25, 34, 37]; host materials and suitable dopants are shown in Table 2.2 for typical TCO thin-film materials reported up to now.

Table 2.2. Host and dopant materials in TCO thin films [38].

<table>
<thead>
<tr>
<th>Binary</th>
<th>Dopant</th>
<th>Resistivity</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Al, Ga, B, In, Y, Sc, V, Si, Ge, Ti, Zr, Hf, Nb, Ta, W, Ta, Te</td>
<td>★</td>
<td>×</td>
</tr>
<tr>
<td>CdO</td>
<td>In, Sn</td>
<td>★</td>
<td>×</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>Sn, Ge, Mo, Ti, Zr, Hf, Nb, Ta, W, Te</td>
<td>★</td>
<td>×</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>Sn</td>
<td></td>
<td>×</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Sb, As, Nb, Ta, Te</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Nb, Ta</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Ternary</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgIn$_2$O$_4$</td>
<td></td>
<td>Δ</td>
<td></td>
</tr>
<tr>
<td>GaIn$_2$O$_3$</td>
<td>Sn, Ge</td>
<td>Δ</td>
<td></td>
</tr>
<tr>
<td>(Ga, In)$_2$O$_3$</td>
<td></td>
<td>Δ</td>
<td>×</td>
</tr>
<tr>
<td>CdSb$_2$O$_6$</td>
<td>Y</td>
<td></td>
<td>×</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>Nb, La</td>
<td></td>
<td>×</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ternary</th>
<th>Multi-component</th>
<th>Resistivity</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$In$_2$O$_5$, Zn$_3$In$_2$O$_6$</td>
<td>ZnO In$_2$O$_3$ system</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>In$_2$Sn$_2$O$_12$, Cd$_2$In$_2$O$_4$, Cd$_3$Sn$_2$O$_6$, CdSnO$_3$</td>
<td>In$_2$O$_3$ SnO$_2$ system</td>
<td>O</td>
<td>×</td>
</tr>
<tr>
<td>Zn$_2$Sn$_2$O$_6$, Zn$_3$SnO$_3$</td>
<td>ZnO SnO$_2$ system</td>
<td>Δ</td>
<td>×</td>
</tr>
</tbody>
</table>

Recently, transition metal oxides such as TiO$_2$ and MoO$_x$ have also drawn the attention by exhibiting attractive TCO characteristics [39, 40]. The observation of TCO characteristics in these binary compounds (metal oxides) with no intentional doping is attributed to intrinsic donors such as oxygen vacancies and/or interstitial metal atoms. However, the undoped oxide films are unstable when used at high temperature and when exposed to ambient atmosphere. Doping these films with certain impurity elements improves the long term stability and reliability of these films for transparent electrode applications.

Impurity-doped ZnO, In$_2$O$_3$ and SnO$_2$ and multicomponent oxides composed of combinations of these binary compounds are some useful TCOs. Some of the multicomponent oxides such as ZnO-In$_2$O$_3$, In$_2$O$_3$-SnO$_2$ and ZnO-In$_2$O$_3$-SnO$_2$ (or Zn-In-Sn-O) [37] are also examples of reduced-indium TCO materials. In addition, ternary compounds such as Zn$_2$In$_2$O$_5$ and Zn$_3$In$_2$O$_6$ (zinc indates) and In$_4$Sn$_3$O$_{12}$ (indium stannate) contained in the ZnO-In$_2$O$_3$ and In$_2$O$_3$-SnO$_2$ systems, respectively, and multicomponent oxides composed of combinations of these ternary compounds, such as Zn$_2$In$_2$O$_5$-In$_4$Sn$_3$O$_{12}$, are promising as reduced-indium TCO thin-film materials. Examples of indium-free materials include ZnO and SnO$_2$ and ZnO-SnO$_2$ multicomponent oxides as well as ZnSnO$_3$ and ZnSn$_2$O$_4$ (zinc stannates), ternary compounds in the ZnO-SnO$_2$ system. However, impurity-doped SnO$_2$, zinc stannates and SnO$_2$-based materials are unsuitable for use in most FPDs because of the difficulty of producing low-resistivity films in low-temperature depositions required for substrates. In addition, there is the problem of patterning, i.e., the difficulty of wet etching using acid solutions.
Table 2.3 summarizes a comparison of properties of reduced-indium-content TCO films and ITO. Even though the amount of indium used in these materials can be reduced approximately 50%, the underlying availability problem remains. As a result, at present, the best, and only practical, indium-free candidate for an alternative TCO material is impurity-doped ZnO, such as Al:ZnO (AZO) and Ga:ZnO (GZO). There have been several reports of substituting transparent conducting AZO thin films for ITO [25, 34, 36]; AZO, with source materials that are inexpensive and non-toxic, is the best candidate. In addition, the lowest resistivity obtainable in AZO thin films is comparable to that found in ITO, as evidenced from theoretical analyses and experimental results. ZnO films with a low resistivity of the order of $10^{-4} \, \Omega \cdot \text{cm}$ were reported by Chopra et al. in 1983 [41].

For the purpose of improving stability at high temperatures, Minami et al. reported in 1984, that ZnO:Al films prepared by rf-magnetron sputtering with a resistivity of $1.9 \times 10^{-4} \, \Omega \cdot \text{cm}$ were stable in use at temperatures as high as 400°C [42].
Table 2.4 summarizes the minimum resistivities and the maximum carrier concentrations obtained for ZnO films prepared with optimal doping content for various dopants and deposition methods reported to date.

Table 2.4. Resistivities, Carrier Concentrations, and Dopant Content for ZnO Films Doped with Various Impurities [34].

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Doping Content (at.%)</th>
<th>Resistivity ($\Omega$-cm)</th>
<th>Carrier Concentration ($\text{cm}^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>16-32</td>
<td>13</td>
<td>50</td>
</tr>
<tr>
<td>Ga</td>
<td>17-81</td>
<td>12</td>
<td>145</td>
</tr>
<tr>
<td>B</td>
<td>46</td>
<td>20</td>
<td>54</td>
</tr>
<tr>
<td>Y</td>
<td>22</td>
<td>79</td>
<td>58</td>
</tr>
<tr>
<td>In</td>
<td>12</td>
<td>12</td>
<td>39</td>
</tr>
<tr>
<td>Sc</td>
<td>25</td>
<td>31</td>
<td>59</td>
</tr>
<tr>
<td>Si</td>
<td>80</td>
<td>48</td>
<td>88</td>
</tr>
<tr>
<td>Ga</td>
<td>16</td>
<td>74</td>
<td>88</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>56</td>
<td>62</td>
</tr>
<tr>
<td>Zr</td>
<td>54</td>
<td>52</td>
<td>65</td>
</tr>
<tr>
<td>Hf</td>
<td>41</td>
<td>55</td>
<td>35</td>
</tr>
<tr>
<td>F</td>
<td>05</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

It is evident that Al and Ga are the most effective donors for ZnO and lead to the lowest resistivity films. Recently, Ga has attracted much attention as a dopant, and low-resistivity ZnO:Ga films have been prepared by PLD and dc-arc discharge ion plating (ADIP) [34]. It has been reported that the resistivity initially decreases with increasing Ga/Zn ratio up to 2-3 %, and then increases with Ga additions (fig. 2.9 (a)) [43].

A similar trend has been observed for the case of Al doped ZnO and Sn doped In$_2$O$_3$ [44]. The lowest value of resistivities reported for Al:ZnO and ITO are $8.5 \times 10^{-5}$ $\Omega$-cm and $7.2 \times 10^{-5}$ $\Omega$-cm, respectively [45, 46]. It is believed that the increase in resistivity beyond a critical concentration of dopant is related to the increase in ionized impurity scattering. Fig. 2.9 (a) illustrates the variation of electrical properties of ZnO as a function of % Ga. It is apparent
from the figure that the increase in carrier concentration leads to a decrease in mobility due to the increased ionized impurity scattering. It can also be seen from the fig. 2.9 (b) that the resistivity shows a similar dependence on % Ga as observed in fig. 2.9 (a), except that the critical concentration in this case is found to be ~5% [47].

![Graph showing resistivity vs %Ga and Resistivity, n, μ vs %Ga](image)

Figure 2.9. (a) Resistivity vs %Ga [43], (b) Resistivity, n, μ vs %Ga [47].

The difference in optimal dopant concentration corresponding to the lowest resistivity films is mostly related to the variation in the processing conditions, which considerably affects the activation of dopants and the intrinsic defects (vacancies and interstitials). It should also be noted that the resistivity values ranging from $10^{-4}$ to $10^{-2}$ Ω-cm have been reported for impurity-doped ZnO deposited under varying deposition conditions.

However, impurity-doped and undoped ZnO films were also affected by grain-boundary scattering. The grain boundary scattering is characterized by the increase in Hall mobility with increased carrier concentration, up to approximately $10^{21}$ cm$^{-3}$, resulting from increases
in the potential barrier height as well as the trapping of free electrons due to oxygen adsorbed on grain boundaries and the film surface. The oxygen adsorption is affected by the oxidizing atmosphere during the deposition. Note, particularly, that a Hall mobility of 120 cm²/V.s could be obtained in an undoped ZnO film with a carrier concentration of about 2 x 10²⁰ cm⁻³ as long as the oxidizing atmosphere was controlled during magnetic sputter deposition (MSD) [48]. It can be concluded that controlling the oxidizing atmosphere during the deposition is very important for the preparation of low-resistivity transparent conducting thin films of ZnO; a more spatially uniform and weaker oxidizing atmosphere is required than for the deposition of other TCO materials. It is also known that the resistivity distribution is worse in AZO and GZO thin films than in ITO thin films. Consequently, this non-uniform resistivity distribution results in an increase of resistivity of AZO and GZO thin films deposited on large area moving substrates developed for practical applications. Therefore, improving the resistivity distribution is necessary to obtain lower resistivity. The non-uniform resistivity distribution is mainly attributable to the spatial distributions of both the amount and the activity of oxygen reaching the substrate surface [49, 50], and not to a bombardment by high energy particles [51]. Recently, newly developed deposition techniques that incorporate rf power into the dc-MSD methods have been employed in order to resolve the spatial distribution problem.
Figure 2.10. RF power dependence of resistivity at substrate locations that correspond to the erosion area and the center of the target for AZO films prepared by (rf and dc)-MSD [38].

2.3.2. Process optimization of Ga doped ZnO thin films by Pulsed Laser Deposition

Growth of high quality epitaxial films is contingent upon the high quality of the substrate (single crystal) and a high processing temperature. Specifically, the growth of single crystals by equilibrium evaporation and deposition techniques require temperatures exceeding 1000 °C [32, 52]. Epitaxial films of Ga: ZnO have been deposited by pulsed laser deposition (PLD) on single crystal substrates such as (0001) sapphire [53-55]. The substrate temperature in all the cases was $\geq 500$ °C. The high value of mobility and the resultant low resistivity obtained in the epitaxial films are believed to be the result of decreased defect densities and increased relaxation times for the free carriers.

Unfortunately, for practical applications these TCO films will need to be deposited on economical substrates such as glass and polymer, which present an amorphous template and
require relatively low deposition temperatures. The low temperature processing of TCOs leads to formation of polycrystalline films, which is aggravated by the amorphous nature of the template. The electrical and optical properties of the TCO films have been found to be extremely sensitive to the microstructure of the films. The main contribution of microstructure to the resistivity comes from the presence of grain boundaries and their effect on the electrical properties. In general, the resistivity of the films decreases with the increasing deposition temperatures due to improvement in the crystalline quality of the films [44, 56]. In addition, grain size usually increases with increasing deposition temperature, leading to reduced scattering by the grain boundaries. Higher deposition temperature also assists in diffusion of dopants to their desired sites and activation of the dopants, both leading to lower resistivity of the TCO films [57]. The growth of ZnO films with preferred orientation results in better electrical properties, which makes them more suitable for applications involving flexible substrates and low temperature processing.

In this section, we will discuss the electrical and optical properties of Ga doped ZnO thin films on sapphire and glass substrates grown by pulsed laser deposition (PLD).

The resistivity of Ga doped ZnO was found to decrease with increasing Ga dopant concentration (table 2.5). Another important observation was that the increased carrier concentration also leads to a metallic behavior at temperatures closer to the ambient temperature, which is not observed in pure ZnO.
Table 2.5. List of values of resistivity and the metal – semiconductor transition temperature of ZnO films with varying Ga concentrations [58].

<table>
<thead>
<tr>
<th>%Ga</th>
<th>Resistivity ($\Omega$-cm)</th>
<th>$T_c$ (measured) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.59 \times 10^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>$4.71 \times 10^{-4}$</td>
<td>93</td>
</tr>
<tr>
<td>3.65</td>
<td>$4.29 \times 10^{-4}$</td>
<td>135</td>
</tr>
<tr>
<td>5</td>
<td>$1.40 \times 10^{-4}$</td>
<td>170</td>
</tr>
<tr>
<td>7</td>
<td>$2.57 \times 10^{-2}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Metallic conductivity is observed in samples containing 2%, 3.65% and 5 % Ga, due to the formation of a degenerate band appearing in heavily doped semiconductors, as suggested by Mott [39, 59]. The increase in carrier concentration with increase in concentrations of Ga was also consistent with the optical transmittance results, shown in fig. 2.11.

Figure 2.11. Transmission spectra of films with different concentrations of Ga [58].
Figure 2.12. Effect of oxygen partial pressure on carrier concentration of the ZnGa\textsubscript{0.05}O films deposited on glass at different substrate temperatures: (a) RT, (b) 200°C and (c) 400°C [58].

The carrier concentration was also found to depend on the oxygen partial pressure during deposition (fig. 2.12). The films deposited at lower substrate temperature showed increase in \(n\) with the lowering of oxygen pressure due to increase in donor oxygen vacancies and has been verified by the optical measurements in addition to the Hall measurements. Effect of oxygen pressure during deposition on the transmission spectra of the films deposited at RT and 200°C are shown in fig. 2.13, respectively [58]. The absorption edge shifts towards higher energies due to increase in carrier concentration. The increase in \(n\) for films grown at RT and 200°C, especially for the films deposited at lower oxygen pressures of 10\(^{-3}\) torr and 10\(^{-5}\) torr, suggests that the neutral defects which would decrease the carrier concentration are less stable at lower temperatures. For most of the TCOs deposited on glass substrates, the lowest resistivity films are obtained at temperatures between 200 - 400°C [32].
Figure 2.13. Effect of oxygen partial pressure on the transmission spectra of the films deposited on glass at 200°C [58].

The lowest value of resistivity, $1.8 \times 10^{-4} \Omega \text{-cm}$ was achieved for the film deposited at 200°C and $10^{-3}$ torr oxygen pressure, which had an estimated carrier concentration of $5.71 \times 10^{20} \text{cm}^{-3}$ and mobility of $13.06 \text{cm}^{2}/\text{V.s}$ [58]. It was concluded that the formation of defects responsible for the carrier generation/trapping is also governed by the processing temperature. Thus, a thorough understanding of the mechanisms involved in the formation and stability of these defects as a function of oxygen pressure and temperature is critical to ultimately improving the properties of TCOs.

2.3.3. P-type TCOs

A variety of active functions in semiconductor originates from p–n junction. However, due to the lack of high quality p-type TCOs, there is almost no application as transparent semiconductors in active optoelectonic devices. In most metal oxides, the conduction band minimum (CBM) is made of spatially spread spherical metal s orbital.
Therefore, electrons in the metal oxides have small effective masses, and high electronic conduction is possible if high-density electron doping is achieved. This makes it possible to have several n-type TCOs. In contrast, the valence band maximum (VBM) is made of oxygen 2p orbitals, which are rather localized, leading to small hole effective masses. Furthermore, the dispersion of the valence bands tends to be small, and thus the VBM level is so deep that hole doping is difficult. Therefore, until 1997 p-type TCO was not discovered. It has been proposed that the use of metal d orbitals with energy levels close to those of O 2p orbitals may form highly hybridized orbitals with O 2p, expecting that it might raise the VBM level and make hole doping easier. The 3d^{10} configuration of Cu^+ was chosen as a candidate because the Cu 3d energy level is just above the O 2p level. Further, the closed shell configuration of Cu^+ allows for large band gaps and optical transparency. This idea actually led to the discovery of CuAlO₂ [60]. This was followed by the subsequent discovery of new Cu+-based p-type TCOs such as CuGaO₂ and SrCu₂O₂. However, neither high-concentration hole doping nor large hole mobility was achieved in these Cu+-based p-type TCOs.

Table 2.6. Electrical Transport Properties of Thin Films of CuAlO₂, CuGaO₂, SrCu₂O₂ at RT [61].

<table>
<thead>
<tr>
<th>Property</th>
<th>CuAlO₂</th>
<th>CuGaO₂</th>
<th>SrCu₂O₂*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity (S cm⁻¹)</td>
<td>9.5 × 10⁻¹</td>
<td>6.3 × 10⁻²</td>
<td>4.83 × 10⁻²</td>
</tr>
<tr>
<td>Carrier density (cm⁻³)</td>
<td>1.3 × 10¹⁷</td>
<td>1.7 × 10¹⁸</td>
<td>6.1 × 10¹⁷</td>
</tr>
<tr>
<td>Hall mobility (cm² V⁻¹ s⁻¹)</td>
<td>10.4</td>
<td>0.23</td>
<td>0.46</td>
</tr>
<tr>
<td>Hall coefficients (cm³ C⁻¹)</td>
<td>+48.6</td>
<td>+3.7</td>
<td>+12</td>
</tr>
<tr>
<td>Seebeck coefficients (µV K⁻¹)</td>
<td>+183</td>
<td>+560</td>
<td>+260</td>
</tr>
</tbody>
</table>
The optical-absorption spectra of the thin films are displayed in fig. 2.14. The average transmission was 80% in the visible range. The optical bandgap for direct allowed transitions was estimated to be ~3.5 eV for CuAlO$_2$ and ~3.6 eV for CuGaO$_2$. The roughly estimated carrier activation energy was 0.2 eV for CuAlO$_2$, which is far smaller than one-half of the bandgap. Electrical conductivity at room temperature was $9.5 \times 10^{-1}$ S cm$^{-1}$ for CuAlO$_2$ and $6.3 \times 10^{-2}$ S cm$^{-1}$ for CuGaO$_2$. The temperature dependence of resistivity suggested the presence of gap states close to the Fermi level and the dominance of a variable range hopping mechanism at lower temperatures. Normal spinel ZnRh$_2$O$_4$ is another p-type wide-gap semiconductor with bandgap energy of 2.1 eV. The electrical conductivity of the sputtered film was 0.7 S cm$^{-1}$ at 300 K without intentional doping [62]. LaCuOS has also been reported as a transparent p-type semiconductor. The electrical conductivity of this material is controllable from $<10^{-6}$ to $10^{2}$ S cm$^{-1}$ by doping of divalent ions (Sr$^{2+}$ or Mg$^{2+}$), which act as acceptors by substituting La$^{3+}$ ions.
The energy gap of LaCuOS$_{1-x}$Se$_x$ systematically varies from $E_g = 3.1$ to 2.8 eV with an increase in $x$ from $x = 0.0$ to 1.0[63]. The complexity of these p-type structures has led the attention towards NiO, which exhibit interesting TCO characteristics with p-type nature. Nature and structure of NiO is discussed in section 2.5.3.

2.4. Device application

2.4.1. Organic Photovoltaics

Organic solar cells (OSCs) have attracted considerable attention due to their potential for low-cost solar energy conversion and the chemical flexibility for modifications on organic semiconductors via chemical synthesis methods. The power conversion efficiency has improved steadily through the use of new materials and novel structures. Organic semiconductors have poorer charge carrier mobility than the inorganic materials but, have relatively strong absorption coefficient ($> 10^5$ cm$^{-1}$), which gives high absorption even in very thin devices. The solar power conversion in an organic photovoltaic cell goes through the following consecutive steps: (i) absorption of photon in the active layer forming an excited state, the electron-hole pair (exciton). (ii) diffusion of exciton (iii) the charge separation occurs. (iv) transportation of charge to the anode (holes) and cathode (electrons) results in the direct current for the consumer load.

The difference in quasi-Fermi levels of separated positive and negative charges results in the potential energy stored. The electric current that a photovoltaic solar cell delivers corresponds to the number of created charges that are collected at the electrodes.
This number depends on the fraction of photons absorbed ($\eta_{\text{abs}}$), the fraction of electron-hole pairs that are dissociated ($\eta_{\text{diss}}$), and finally the fraction of (separated) charges that reach the electrodes ($\eta_{\text{out}}$) determining the overall photocurrent efficiency ($\eta_{\text{PE}}$) [64].

$$\eta_{\text{PE}} = \eta_{\text{abs}} \times \eta_{\text{diss}} \times \eta_{\text{out}}$$

(2.16)

The current-voltage characteristics for a solar cell in the dark and under illumination are shown in fig.2.15. In the dark, there is almost no current flowing, until the contacts start to inject heavily at forward bias for voltages larger than the open circuit voltage. Under illumination, the current flows in the opposite direction than the injected currents. At (a) the maximum generated photocurrent flows under short-circuit conditions; at (b) the photogenerated current is balanced to zero (flat band condition). Between (a) and (b), in the fourth quadrant, the device generates power (i.e., current $\times$ voltage). At a certain point, denoted as maximum power point (MPP), the product between current and voltage and hence the power output is largest.
Figure 2.15. Current-voltage (IV) curves of an organic solar cell (dark, dashed; illuminated, full line). [65].

\[ P_{\text{Max}} = V_{\text{MPP}} \times I_{\text{MPP}} \]

Figure 2.16. Power conversion efficiency limits as a function of the semiconductor bandgap [66].
It has been shown that the maximum power conversion efficiency for a semiconductor varies with bandgap assuming only radiative recombination and the solar radiation of earth as shown in fig. 2.16. AM0 is the solar spectrum above earth’s atmosphere while AM1.5 is the standard spectrum at sea level. The graphs show that for both the terrestrial and the space solar spectrum a semiconductor bandgap between 1.3 and 1.5 eV allows reaching power conversion efficiencies around 30%.

For an ideal case, the current through a solar cell is given by

$$I_d = I_o \left( e^{\frac{qV}{nkT}} - 1 \right) \quad (2.17)$$

Upon illumination the light generates a photo current $I_L$ that is simply superimposed (added) upon the normal rectifying IV characteristics of the diode D:

$$I_d = I_o \left( e^{\frac{qV}{nkT}} - 1 \right) - I_L \quad (2.18)$$

The highest voltage in this quadrant develops at the electrodes when $I_L$ just manages to cancel the dark current. Canceling of $I_d$ by means of $I_L$ can be considered in Eq. (2.21) by setting $I = 0$. $V_{oc}$ can then be derived quantitatively using:

$$V_{oc} = \frac{nkT}{q} \ln \left( \frac{I_L}{I_o} + 1 \right) \quad (2.19)$$

The open-circuit voltage, $V_{oc}$, is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current.
The short-circuit current is the current through the solar cell when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited). For an ideal solar cell at most moderate resistive loss mechanisms, the short-circuit current and the light-generated current are identical. The "fill factor" or "FF", is a parameter which, in conjunction with $V_{OC}$ and $I_{sc}$, determines the maximum power from a solar cell. It is determined by the fraction of the photogenerated charge carriers that actually reach the electrodes, when the built-in field is lowered toward the open circuit voltage. It is defined as the ratio of the maximum power from the solar cell to the product of $V_{OC}$ and $I_{sc}$.

$$FF = \frac{(IV)_{max}}{V_{OC}I_{sc}}$$  \hspace{1cm} (2.20)

So, the maximum power can be given by

$$P_{max} = FF \times V_{OC} \times I_{sc}$$  \hspace{1cm} (2.21)

This can give us power conversion efficiency of a solar cell at specific wavelength (Eq.)

$$\eta(\lambda) = \frac{FF(\lambda) \times V_{OC}(\lambda) \times I_{sc}(\lambda)}{P_{in}}$$  \hspace{1cm} (2.22)

Polymer solar cells have received increasing interest since 1992 when Sariciftci et al.[67] observed efficient photoinduced electron transfer from polymer semiconductors (conjugated polymers) to an electron acceptor, C60. A power conversion efficiency of 6–7.9% was within reach using conducting polymers as electron donor materials (fig. 2.17).
There has been constant progress in increasing the overall power conversion efficiency either by different architectures of the photoactive layer itself or by the introduction of transport/blocking layers for an improvement of the contacts. The bulk heterojunction solar cells provides the advantage of maximizing the $I_{sc}$ as absorption takes place throughout the whole photoactive layer, which can contribute to the photocurrent due to the efficient exciton dissociation everywhere in the bulk [65]. Forrest and coworkers have shown that $\eta$ exceeding 6.5% can be achieved without antireflection coatings to the substrates by using optimized tandem structures[69, 70]. In the tandem structure, the basic cell consists of glass/TCO/Copper Phthalocyanine (CuPC)/$C_{60}$/Ag or Al (electrode) with light incidence on glass side.

Figure 2.17. Efficiency evolution of state of the art polymer solar cells from 2001 to 2009 [68].
Use of C₆₀ leads to improved performance owing to the longer exciton diffusion length of C₆₀ (~77Å) compared to PTCBI (~30 Å) (perylenetetracarboxylic bisbenzimidazole)[71]. Even better performance can be achieved for a solar cell with a hybrid planar – mixed heterojunction (PM-HJ), which consists of a mixed Donor (D) – Acceptor (A) layer sandwiched between two homogeneous donor and acceptor layers [72]. Thus in the tandem structure individual bilayers or PMHJ cells can be stacked with a thin (~5 Å) discontinuous layer of Ag that acts as efficient recombination sites for the photogenerated carriers [69]. The open circuit voltage for such substrates is n times that of a single cell, where n is the number of cells in the stack. Another approach is to increase the absorption of the fullerene, which was recently demonstrated upon replacing C₆₀-PCBM with C₇₀-PCBM [73]. Due to the increased absorption of the C₇₀ methano-fullerene in the visible, the external quantum efficiency (EQE) was increased when compared to the same blend prepared from C₆₀ based PCBM. As Vₒc is the major component of the power conversion efficiency, special focus has been given to its upper limit. For inorganic solar cells, it has found that maximum Vₒc never exceeded the band gap of active material. However, in case of organic solar cells, the Vₒc is also found to depend on the difference in the work functions of both side electrode materials (Δϕ). Larger Δϕ creates a strong band bending near the semiconductor electrode interface and aids in the photo carriers extraction resulting in higher Vₒc.

So, for D-A type solar cells, if Δϕ > EₒDA(combined bandgap), the built in field due to the offset of LUMOs (ΔLUMO) and HOMOs (ΔHOMO) between the two components has to be large enough to provide the extra driving force.
Hence, the maximum $V_{oc}$ can be written as:

$$V_{OC} \leq |LUMO_A - HOMO_D| + \Delta LUMO + \Delta HOMO$$  \hspace{1cm} (2.23)

However, there have been reports for the case of gold cathodes, where the $V_{OC}$ exceeded largely the expected difference between the electrode work functions[74]. Fermi level pinning between the fullerene and the gold electrode has been forwarded to account for this result. However, this behavior was not found to be universal for all metal cathodes [75]. Hence, the individual energy level alignments between organic–metal interfaces are of high interest. For example interfacial dipoles at the electrodes can significantly change the apparent work function of a metal [76-80] and this has been exploited to modify the injection behavior of both electrodes. Furthermore, the dependence of the charge transport levels on temperature[81-83] and light intensity [69, 82-86] are reflected in the observed $V_{OCs}$. In the following section, electrode semiconductor interfaces are discussed.

### 2.4.2. Electrode/ Semiconductor interface

Charge injection across the metal/semiconductor interface has been studied a lot in inorganic semiconductor, but it is not clear to what extent these developed models are applicable to organic semiconductor. Figure 2.18 shows the band energy diagram of the D-A double heterojunction OSC. Photoexcited electrons from the CB of the electron acceptor (A) encounter a barrier before they can reach the Ag electrode. The same is true for holes from the VB near the Ga:ZnO or ITO contact.
These types of contacts are referred to as blocking contacts as Ag forms a blocking contact with the CB of the n-type semiconductor and semiconductor/GZO or semiconductor/ITO interface has similar situation. Since charge separation at the D/A interface leads to an excess of electrons in the CB of A (n-type) and holes in the VB of D (p-type), both charge carriers find barriers if they want to get out of the semiconductor. Thus, currents through this device are decreased by the contact barriers. Charge carriers can overcome the interface barrier either by thermionic emission or quantum mechanical tunneling (field emission) [87].

For high mobility semiconductors, current density for thermionic emission over a triangular barrier height of $\phi$ at metal semiconductor interface is given by

$$ J = A \phi T^2 e^{\frac{-\phi}{kT}} $$

(2.24)
Where $A\phi$ is the effective Richardson constant, and $T$ is the absolute temperature.

And the barrier height is dependent on the applied Electric field “E”. $q$ is the charge and $\varepsilon_0$ is the dielectric constant of vacuum.

$$\Delta \phi = \frac{q^2E}{4n\varepsilon_0}$$  \hspace{1cm} (2.25)

For low mobility semiconductor, current density is due to field emission across the barrier. For Schottky barrier the current can then be written as

$$J = J_o e^{qV/(nKT)}$$ \hspace{1cm} (2.26)

where $J_o$ is essentially a constant for low doping levels and $n\sim 1$ at high temperatures [88].

In this section, the factors which affect the charge collection across the semiconductor/electrode interface are discussed. The work function of the electrode determines together with the LUMO/HOMO and Fermi-level of the semiconductor whether the electrode forms an ohmic or a blocking (Schottky) contact for the respective charge carrier (holes in VB, electrons in CB).

Moreover, there are some other factors such as clean interface between the semiconductor and the electrode used for carrier collection. Interface states might be in the form of adsorbed species, impurity atoms, defects or simply discontinuities at the film surface. The interface states usually exhibit energy levels throughout the bandgap and can act as both acceptor and donor states depending on the Fermi level of the semiconductor [89].
Due to the difference in energy levels for the interface states and the semiconductor, there is transfer of charges, which results in redistribution of the potential and the electric field at the interface. Moreover, if the density of these states is high, it tends to pin the Fermi level, i.e. the built-in potential is no longer a function of the difference in work function of the two contacting materials. The pinning of the Fermi level is particularly critical for the junction between the transparent electrode and the semiconductor layer, because it can lead to formation of a Schottky barrier even if the work function of the TCO is well matched with the semiconductor.

To achieve maximum transfer of the carriers across the junction it is mandatory to have an ohmic contact with minimum resistance. In this case, maximum theoretical open circuit voltage Voc is determined by the difference between the work function of the electrode materials. Therefore, increasing the work function of the electrode would result in an efficient hole injection/collection contact with the active layer reducing the barrier at the interface. Hence, this would increase the Voc considerably (fig. 2.19). Thus, control of surface and interface states is of prime importance during the fabrication of high quality solar cells.
There have been several reports of pre-treating the ITO surface including the wet treatment [90], the low pressure plasma treatment [91], and the UV ozone treatment [92]. These pretreatment procedures increases the work function of ITO, but still the work function is not high enough to match the highest occupied molecular orbital (HOMO) level of the most commonly used hole transporting materials in OLEDs. Another commonly applied modification of the cathode is the deposition of a very thin LiF layer between the metal electrode and the organic semiconductor. This was found to improve charge injection in LEDs [93] [94], and also resulted in some cases in a higher $V_{OC}$ for organic solar cells [95].
Table 2.7. Physical properties of TCO anode films on glass substrates [96].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga_{0.12}In_{0.88}O_x [28]</td>
<td>1020</td>
<td>14</td>
<td>700</td>
<td>1100</td>
<td>5.2</td>
</tr>
<tr>
<td>Ga_{0.20}In_{0.80}Sn_{0.04}O_x [26]</td>
<td>170</td>
<td>18</td>
<td>3280</td>
<td>2000</td>
<td>5.4</td>
</tr>
<tr>
<td>Zn_{0.2}In_{0.8}O_x [23,29]</td>
<td>250</td>
<td>39</td>
<td>1010</td>
<td>800</td>
<td>5.2</td>
</tr>
<tr>
<td>Zn_{0.45}In_{0.55}Sn_{0.05}O_x [26]</td>
<td>360</td>
<td>12</td>
<td>2290</td>
<td>2700</td>
<td>6.1</td>
</tr>
<tr>
<td>ITO [a]</td>
<td>180</td>
<td>20</td>
<td>3500</td>
<td>8075</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Some non-ITO multi-component TCO materials, ZIO, GIO, GITO, and ZITO, have been reported as effective OLED anodes with higher work function than ITO (Table 2.7). OLED devices fabricated with these materials as anodes exhibit electroluminescence performance comparable or superior to ITO-based devices [96].

Another approach that has been applied to reduce the hole injection barrier and enhance the power conversion efficiency, is to coat the TCO layer with a thin overlayer of metal/oxide having higher work function [97]. The primary focus of this work is work function modification approach with novel overlayer materials, MoO_x and NiO_{1+y}. The incorporation of very thin overlayers ensures ohmic contact between the GZO and overlayers (fig. 2.19).
2.5. Material systems

2.5.1. ZnO

ZnO based TCOs have recently gained importance because it is a relatively inexpensive material and compared with In$_2$O$_3$, its cost is $\sim$1/6th that of In$_2$O$_3$. ZnO is also benign, which further lowers the cost of manufacturing. One of the most important features of ZnO is that it grows oriented along the [0001] at relatively low temperatures, which is attributed to the lowest energy associated with the (0001) basal plane [98, 99]. The textured growth of ZnO on temperature sensitive substrates (e.g. glass, polymer) at relatively low temperatures is of particular importance for the display and solar cell applications. Moreover, the hexagonal structure of ZnO can be grown epitaxially on technologically important substrates such as sapphire and is the key for its integration with the optoelectronic devices.

2.5.1.1. Crystal structure of ZnO

Zinc oxide crystallizes in the hexagonal wurtzite-type structure, which is the most stable phase. This structure belongs to the space group P63mc. This structure is composed of two interpenetrating hexagonal-close-packed (hcp) sublattices of Zn and O atoms (fig.2.20). These two sublattices are displaced from each other by 0.375 c along c-axis. This displacement of Zn and O sublattices makes this structure non-centrosymmetric and makes ZnO polar material along the c-axis. In this structure each zinc ion is surrounded tetrahedrally by four oxygen ions and vice versa. Though the tetrahedral coordination is indicative of sp$^3$ covalent bonding, ZnO has substantial ionic character. The ionicity of ZnO is at the borderline between covalent and ionic semiconductors.
The lattice constants of ZnO hexagonal unit cell are \( a = 3.2499 \, \text{Å} \) and \( c = 5.2066 \, \text{Å} \). The ratio \( c/a \) of the elementary translation vectors, with values around 1.602, deviates slightly from the ideal value of \( c/a = 1.633(\sqrt{8/3}) \) for hexagonal close packed structure. Though wurtzite structure is the most favorable structure of ZnO, under certain conditions cubic ZnO may take cubic rock salt and zinc blende-type structures. The zinc-blende ZnO structure is metastable and can be stabilized only by heteroepitaxial growth on cubic substrates, such as ZnS. The rock salt structure of ZnO is stable at high pressures.

2.5.1.2. Electronic structure of ZnO

ZnO is a direct-gap semiconductor with the global maxima of the valence band (VB) and the minima of the conduction band (CB) at the same point in the Brillouin zone, namely at \( k = 0 \). The lowest unoccupied orbital (LUMO), or the bottom of the conduction band is formed
from the 4s levels of Zn$^{2+}$. The top of the valence band, or highest occupied molecular orbital (HOMO), is formed from the 2p levels of O$^{2-}$. The band gap is \(~3.37\) eV at room temperature. The band structure of ZnO in the vicinity of the fundamental band gap is shown in fig.2.21. The effective electron mass is quite isotropic, with a value around $m_e = 0.28m_o$ [100]. The hole masses are similar for the A, B and C valence bands, with typical values of $m_{h_{\perp A,B}} = 0.59m_o$, $m_{h_{\parallel C}} = 0.31m_o$, and $m_{h_{\perp C}} = 0.55m_o$.

![Band structure of ZnO in the vicinity of the fundamental band gap.]

**Figure 2.21.** Band structure of ZnO in the vicinity of the fundamental band gap.

**2.5.1.3. Native defects in ZnO**

The understanding of the behavior of native point defects is essential for successful application of any semiconductor [101]. They affect the electrical and optical properties of ZnO. Possible native point defects in ZnO are: oxygen and zinc vacancies ($V_O$ and $V_{Zn}$),
interstitials ($O_i$ and $Zn_i$), and antisites ($O_{Zn}$ and $Zn_O$) [102]. These defects can exist in neutral as well as in single or double ionized states and can give rise to various mid-gap states in ZnO. The estimated defect levels in ZnO are shown in fig.2.22. Zinc interstitials and oxygen vacancies are believed to be the predominant defects in ZnO.

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

Figure 2.22. Energy level diagram of native defects in ZnO [102].

As-deposited oxygen deficient ZnO films always exhibit n-type conductivity even without any intentional dopants. The donor concentration in intrinsic ZnO films is strongly dependent on the processing conditions and varies in the range $10^{17}$-$10^{19}$ cm$^{-3}$. This intrinsic n-type conductivity in ZnO is generally attributed to native point defects. The defects responsible for n-type conductivity in ZnO have been the debatable issue to date. Oxygen vacancies ($V_O$), zinc interstitials ($Zn_i$), and hydrogen impurity have been often mentioned as sources of n-type conductivity in ZnO. $Zn_i$ are shallow donors but have high formation energy, whereas $V_O$ are most stable but deep donor like defect[103]. Hydrogen was said to be trapped by $V_O$ giving a shallow-donor state[104]. But even after the minimization of H contamination, the
carrier concentration was found to be still high [105]. Due to high concentration of defects, a strong defect-defect attractive interaction takes place between deep donor $V_o$ and shallow donor $Zn_i$. This lowers the overall system energy and $Zn_i$ can give rise to high concentration of electron carriers[103].

2.5.2. Molybdenum oxide

2.5.2.1. Crystal structure

Molybdenum oxide is very interesting material as it can exists in several phases [106-108]. It can be seen from the figure that the solubility of oxygen in solid Mo is extremely low. The pure Mo forms an eutectic with MoO$_2$, a stable phase with 67 at% of O in Mo. With oxygen concentration exceeding 75 at%, another stable phase, MoO$_3$ is obtained. There are various other phases reported namely, Mo$_6$O$_{23}$, Mo$_9$O$_{26}$, Mo$_4$O$_{11}$ and mixture of a MoO$_2$ + MoO$_3$ [107, 109]. Here, MoO$_2$ and MoO$_3$ will be emphasized. The crystal structure of monoclinic MoO$_2$ is shown in fig. 2.23. This monoclinic structure can be described as a distorted rutile type with the $P21/c$ symmetry group.

![Figure 2.23. Unit cell of monoclinic MoO$_2$ crystal [110].](image)
MoO$_3$ exhibits two different phases, namely $\alpha$–MoO$_3$ and $\beta$–MoO$_3$, of which $\alpha$–MoO$_3$ is found to be more stable thermodynamically\cite{111}. $\alpha$–MoO$_3$ has an orthorhombic structure with the symmetry group $Pbnm$. It has a unique layered structure, where the layers are parallel to (010) plane and are bound together by van der Waals interactions. Each layer is composed of MoO$_6$ octahedra that are connected at two levels in the [001] direction by the common edges which leads to the formation of zig-zag rows in the (100) plane. Along the [100] direction the octahedra are connected only by the corners. Schematic of $\alpha$–MoO$_3$ crystals composed of layered structure is shown in fig. 2.24.

![Figure 2.24. (a) Layered structure of $\alpha$–MoO$_3$\cite{112}.

The intermediate oxide structures with compositions between MoO$_2$ and MoO$_3$ are thought to be formed by the combination of Mo-O tetrahedra and octahedra. The formation of Mo suboxides has been explained by shear plane formation during the reduction / oxidation of molybdenum oxides.
2.5.2.2. Electronic structure

The band gap of $\alpha$–MoO$_3$ and $\beta$–MoO$_3$ are 3.1 eV and 2.9 eV, respectively. $\alpha$–MoO$_3$ is mostly transparent throughout the visible region, whereas, the $\beta$–MoO$_3$ has a yellowish appearance and is also less transmissive to the visible light [111]. The difference in the optical response of the two phases is attributed to the difference in their bandgaps. These films are very resistive, exhibiting either insulating or semiconducting behavior. However, non–stoichiometric MoO$_3$ films show reasonably good conductivity due to excess cations and oxygen vacancies that act as donors as well as color centers [113]. The excess cations and/or reduced state species have energy levels closer to the conduction band ($\Phi = 0.27$ eV), whereas the structural defects have energy levels deeper in the bandgap ($\Phi = 1 – 2$ eV), which act as trap centers and cause strong coloration of the films. In contrast, MoO$_2$ films are highly conducting with resistivities on the order of 8x10$^{-5}$ $\Omega$-cm at 300 K [114, 115]. Moreover, MoO$_2$ films exhibit metal like conductivity behavior in temperature dependent measurements of resistivity [32]. The properties of some of the additional molybdenum oxide compounds are listed in table 2.8.

The metallic conductivity in MoO$_2$ can be explained on the basis of the outer electronic configuration and the nature of cationic $d$ bands [116, 117]. The $d_{||}$ band in MoO$_2$ is split into metal – metal doublets, however, one $d$ electron contributes to the metal – metal $\sigma$ bonding, whereas the other $d$ electron is responsible for partially filling the metal – oxygen $\pi^*$ band. The distribution of partial and total density of states in monoclinic MoO$_2$ is shown in fig. 2.25.
Table 2.8. Summary of structure and physical properties of different phases of Molybdenum oxides.

<table>
<thead>
<tr>
<th>Molybdenum oxide</th>
<th>Structure</th>
<th>Mo oxidation state</th>
<th>Electrical Characteristics</th>
<th>Optical characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₂</td>
<td>Monoclinic</td>
<td>Mo⁴⁺</td>
<td>Metallic ( (\rho=8\times10^{-5},\Omega\text{-cm}) )</td>
<td>Opaque</td>
</tr>
<tr>
<td>Mo₄O₁₁</td>
<td>Monoclinic</td>
<td>Mo⁴⁺ and Mo⁶⁺</td>
<td>Metallic ( (\rho \sim 10^{-5},\Omega\text{-cm}) )</td>
<td></td>
</tr>
<tr>
<td>Mo₉O₂₆</td>
<td>Monoclinic</td>
<td>Mo⁴⁺ and Mo⁶⁺</td>
<td>Semiconducting ( (\rho \sim 10,\Omega\text{-cm}) )</td>
<td></td>
</tr>
<tr>
<td>MoO₃</td>
<td>Monoclinic</td>
<td>Mainly Mo⁶⁺ and Mo⁵⁺ (in reduced state)</td>
<td>Insulating ( (\rho \sim 10^{10},\Omega\text{-cm}) )</td>
<td>Transparent</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Orthorhombic</td>
<td>Mainly Mo⁶⁺ and Mo⁵⁺ (in reduced state)</td>
<td>Insulating ( (\rho \sim 10^{7},\Omega\text{-cm}) )</td>
<td>Transparent</td>
</tr>
</tbody>
</table>
Figure 2.25. Distribution of total and partial DOS in monoclinic MoO$_2$ [118].

For the intermediate / suboxides the properties are also intermediary as can be expected. MoO$_3$ is used in various application such as a cathode material solid-state microbatteries [119, 120], sensors [121, 122]. It is a chromogenic material and is used in the development of electrochromic display devices, optical switching coatings, display devices, and smart window technology [123-125].

**2.5.2.3. Molybdenum oxide (MoO$_x$) as a TCO**

The proper combination of some of the phases of molybdenum oxide or a proper distribution of molybdenum ions with different oxidation states may lead to materials with superior electronic and optical properties. It is well known that MoO$_3$, (Mo as Mo$^{6+}$) is insulating and transparent [126], whereas MoO$_2$ (Mo as Mo$^{4+}$) [116] is a metallic conductor. Therefore, an
appropriate mixture of these phases or these ions can form a material, which is transparent as well as conducting. There have been some reports about the growth of MoO$_x$ films consisting of mixed phases and mixed molybdenum oxidation states by various deposition techniques [115, 127, 128]. These compounds have shown interesting physical properties. Nonstoichiometric MoO$_x$ films are an excellent candidate to study the effect of composition on the structure and properties of such films. Recently, MoO$_x$ has been reported as a suitable n-type TCO material [40]. The structural characterization revealed that films had (100) orientation and a monoclinic structure, where molybdenum exists in different oxidation states (i.e., Mo$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$). It was established that the properties were dependent on the concentration of oxygen vacancies, and relative concentrations of Mo$^{4+}$, Mo$^{5+}$, and Mo$^{6+}$ states in the film, which are changed during annealing. The tunability of electrical and optical properties, however, without altering the structure could be an attractive feature for the application of MoO$_x$ films in solid-state devices.

2.5.3. Nickel oxide

2.5.3.1. Crystal structure

Nickel oxide has a cubic rock salt (NaCl) structure (fig. 2.26). This structure belongs to the space group $Fmar{3}m$. The lattice constants of NiO cubic unit cell is $a= 4.178$ Å. Its lattice constant is close to MgO (4.212 Å). There have been several reports of growth of NiO on MgO substrates [129].
2.5.3.2. Electronic structure

NiO is an insulator with an optically measured band gap of 4 eV [131]. Initially, NiO was considered to be a Mott-Hubbard system [132, 133]. Later, it was established to be charge transfer insulator. In this model, it was claimed that the optical gap forms between the ligand p electron and metal 3d electron exchange states. It has been said that d electrons are localized and conduction takes place in O 2p bands. The smallest ionization energy which accounts for the optical gap is not a single hole picture, rather it leads to a many body hole state $d^8L^{-1}$ [134]. The schematic of density of states in NiO is shown in fig. 2.27. In NiO, the Fermi energy level is said to be at 0.4 eV above the valence band.
Figure 2.27. Energy diagram of density of states (pseudoparticle) in NiO. Conducting states are shown to the left of vertical line. Right side shows non-conducting states. Shaded states are full, whereas unshaded states are empty.

The single-particle spectrum of the prototypical charge-transfer insulator NiO has been studied by the theoretical calculation using a combination of \textit{ab initio} band-structure methods and dynamical mean-field theory\cite{135}. The theoretical modeling is in good agreement with photoemission and inverse-photoemission spectra, obtained for both stoichiometric and hole-doped systems. For hole doping, the Hamiltonian of the undoped system was used. Replacement of \( x \text{Ni}^{2+} \) ions by \( \text{Li}^{+} \) ions introduces on average \( n_h = x/1-x \) hole per Ni site. In spite of a large Ni \( d \) spectral weight at the top of the valence band, the doped holes are found to occupy mainly the ligand \( p \) orbitals. A high hole doping leads to the filling of the correlation gap and a significant transfer of the \( d \) spectral weight which forms the incoherent part of the spectrum. Figure 2.28(a,b) shows single particle spectral density in undoped and hole doped NiO.
Figure 2.28. Ni  \textit{d} and O  \textit{p} resolved spectral densities for a) stochiometric NiO and b) hole concentration \( n_h = 0.6 \). The inset shows a comparison of \( eg \) spectral densities for hole concentrations \( n_h = 0.6 \) and 1.2[135].

2.5.3.3. Native defects in NiO

NiO, having wide band gap energy from 3.5 to 4.0 eV [136], is an insulator with resistivity of the order of \( 10^{13} \) \( \Omega \)-cm at room temperature. The p-type semiconducting behavior is believed can be produced via the creation of native defects such as Ni vacancies, which should lead to the formation of Ni\(^{3+} \) states to introduce uncompensated charge. Charge compensation is however, correctly said to occur by creation of O\(^{-1} \) ions instead of Ni\(^{3+} \) due to the energetic involved. Similarly, Li doping can produce hole conduction, where Li\(^+ \) goes to Ni\(^{2+} \) positions and O\(^{-1} \) ions are created for the charge compensation. The holes produce hopping conductivity and mechanism is explained in chapter 7 and 9.
2.6. Synthesis and processing

2.6.1. Pulsed laser deposition overview

Pulsed laser deposition (PLD) is a versatile non-equilibrium thin film growth technique based on physical vapor deposition. It involves the use of a high-powered laser to vaporize the target material required for thin film deposition. Laser-assisted growth was first demonstrated by Smith et. al. [137] in 1965 using a high power ruby laser. In 1983, Cheung et. al. [138] successfully synthesized epitaxial Hg$_{0.7}$Cd$_{0.3}$Te/CdTe and CdTe/GaAs using PLD. Later in the decade, in 1987 Dijkkamp et. al. [139] and Narayan et.al. [140] demonstrated the growth of YBa$_2$Cu$_3$O$_7$ superconducting thin films on sapphire. Since then PLD has been widely used to synthesize a variety of high quality thin films of metals, oxides and nitrides.

The PLD system consists of three main components; the laser, the vacuum chamber and the optics that control the laser. Due to this simplicity, the start-up cost for a PLD system is extremely low [141]. In fact, a PLD system can be set up at 1/10 the cost of a MBE system. Some lasers that can be used for PLD are; ruby laser, CO$_2$ laser, Nd-YAG laser and excimer lasers. The excimer laser is the most widely used, due to its unique characteristics (discussed in the next section). During PLD, the laser is directed into the vacuum chamber and focused onto the target by a set of lenses and mirrors. The vacuum chamber houses the target holder, the substrate holder and the vacuum gauges. The focused laser beam interacts with the target surface creating a luminous plasma plume. Laser-solid interaction and creation/expansion of the plasma is a complicated process and will be discussed in detail in the next section. The ejected species comprising the plume consists of high-energy atoms, electrons, molecules,
free radicals and sometimes clusters, particulates and molten globules [141]. These species then deposit on the substrate forming the thin film.

2.6.2. Advantages and disadvantages of PLD

There are several advantages associated with PLD that make it a popular thin film deposition technique. Most advantages arise due to the high energy of the ablated species [142, 143]. The energy of the ablated species can be as high as 10 to 100 eV (i.e. about 100-1000 kT). In comparison, the energy of the ejected species in an evaporation technique (thermal or e-beam) is about 0.1 eV at 1200 K [142, 143]. Listed below are some advantages and salient features of the PLD technique.

1. The high energy of the plume makes PLD a highly non-equilibrium processing technique.
   Using PLD complex metastable phases can be formed that would otherwise be difficult to form by equilibrium synthesizing routes.

2. In case of a multi-component system (like YBCO) the high energy of the plume helps to reproduce the stoichiometry of the target in the film [140]. The forward directed nature of the plume in PLD is responsible for maintaining stoichiometry [142, 143]. Due to the high energy density of the laser, the material removal from the target is so fast that vapor pressures of the individual components do not play a role.

3. The high energy of the plume can reduce processing temperatures. For example, epitaxial TiN can be grown on Si (100) at 600 °C by PLD [144]. On the other hand CVD growth of TiN requires temperatures as high as 900 °C.

4. Multi-layered heterostructure thin films can easily be synthesized using PLD. The target
carousel can be suitably manipulated to hold multiple targets (4 to 6 targets). This means multi-layered films can be deposited without breaking the vacuum. For example, using PLD epitaxial growth of PZT/YBCO/STO/MgO/TiN/Si(100) was demonstrated by Sharma et. al [145]. Here, the idea was to integrate PZT with Si (100). The rest of the layers act as template buffer layers.

5. Conceptually, any material can be ablated to form a thin film as long as it has a large enough absorption coefficient for the laser used [141].

6. Depending on the repetition rate of the laser the deposition rate of the film can be controlled. In fact, in PLD the number of nucleation sites can be controlled such that they are much higher than those formed in MBE or sputter deposition. By controlling the impingement rate and increasing nucleation site density the smoothness of the film can be improved [141-143].

7. It is important to realize that in the PLD system the energy source, which is the laser, is placed externally. The vacuum chamber in itself is devoid of filaments and other sources of contamination, thereby resulting in a clean process environment. The interaction between the laser and gas species in the vacuum chamber is minimal. This means that the dynamic range of deposition pressures could be high, resulting in less stringent vacuum requirements. Also, the spatial confinement of laser-solid interaction and the subsequent plume render PLD a clean process. The deposited films are thus relatively contamination free [141].

On the other hand, PLD also suffers from some disadvantages. The area of deposited material
obtained by PLD is relatively low (typically 1 cm x cm). In the case of large substrates, non-uniformity in film thickness is observed due to the forward directed nature of the plume [141]. Deposition on larger substrates and uniformity of film thickness can be achieved to some extent by rastering the laser beam over a large target and/or rotation and translation of the substrate [146]. The other important drawback of PLD is the formation of chunks during ablation, which can prove to be detrimental to the quality of the film [147]. Chunks are nothing but large (few microns) particulates or globules of molten material. These undesirable chunks are formed due to improper ablation that involve various mechanisms such as subsurface boiling, expulsion of the liquid layer by shock wave recoil and exfoliation [141-143, 147]. By careful manipulation of the laser parameters, the size and number of chunks can be minimized to some extent [141, 147]. Chunk control is also possible by increasing the absorption coefficient and thermal conductivity of the target material. A compact target with better cohesion of the grains also reduces the emission of chunks.

2.6.3. Types of lasers used for PLD

The term LASER stands for light amplification by stimulated emission of radiation. A laser emits coherent light, with a well-defined wavelength, in a narrow low divergent beam. The most important lasers used for PLD are the Nd:YAG [148, 149] and the excimer laser [150, 151]. Nd:YAG is a solid state neodymium doped yttrium aluminum garnet laser. The fundamental frequency for this laser is 1064 nm. But these lasers can be doubled, tripled or quadrupled to produce 532 nm, 355 nm and 262 nm wavelengths. The more popular laser used for PLD is the excimer laser, which uses a combination of an inert gas and a reactive
gas. Typically the inert gases used are Argon, Krypton and Xenon. The reactive gases typically used are fluorine and chlorine. The excimer lasers are pulsed and operate in the ultra-violet range. They typically operate with pulse duration in the nanosecond regime and repetition rates up to 100 Hz. They can have output energy as high as 1 J/pulse. Various excimer lasers with their corresponding wavelengths are listed in table 2.9. The term excimer is a short form of excited dimer. The excited state is formed from the inert gas (Kr) that forms temporarily bound molecules either with themselves or the halide (KrF). The excited state is usually induced by an electric discharge. The excited state then gives up its energy via stimulated emission to form the dissociated ground state molecules. This happens very rapidly (within picoseconds), resulting in a population inversion between the excited and ground state molecules. The lasing equations for a KrF excimer laser are shown below [152].

\[ \begin{align*}
2\text{Kr}(g) + F_2(g) & \xrightarrow{\text{electric discharge}} 2\text{KrF}(g) \quad \text{(excited state)} \\
2\text{KrF}(g) & \rightarrow 2\text{Kr}(g) + F_2(g) + \text{energy} \quad \text{(dissociated state)}
\end{align*} \]
Table 2.9. Various excimer lasers with operating wavelengths.

<table>
<thead>
<tr>
<th>Excimer laser</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂</td>
<td>157</td>
</tr>
<tr>
<td>ArF</td>
<td>193</td>
</tr>
<tr>
<td>KrCl</td>
<td>222</td>
</tr>
<tr>
<td>KrF</td>
<td>248</td>
</tr>
<tr>
<td>Cl₂</td>
<td>259</td>
</tr>
<tr>
<td>XeCl</td>
<td>308</td>
</tr>
<tr>
<td>XeF</td>
<td>351</td>
</tr>
</tbody>
</table>

2.6.4. Physics of the laser-solid interaction

Although the PLD system in itself is easy to build and operate, the underlying physics involving the laser-solid interaction is quite complex. At energy densities above the threshold for vaporization the laser solid interaction was analyzed and modeled by Singh et. al. [142, 143]. Depending upon the interaction of the laser with the target material, Singh et. al. [142, 143] divided the laser ablation process into three important regimes:

1. Interaction of the laser beam with the bulk target resulting in evaporation of the surface layers. This regime can be termed as the evaporation regime.

2. The interaction of the laser beam with the evaporated material resulting in the formation of a high-temperature isothermal expanding plasma. This regime prevails when the target starts to evaporate and continues until the end of the pulse.
3. The anisotropic three-dimensional adiabatic expansion of the plume giving rise to the characteristic forward directed nature of the deposition. It is important to realize that this regime starts after the termination of the laser pulse.

Each of these regimes is discussed below in brief.

*Laser target interaction:*

When a laser beam strikes the target, the electromagnetic energy is used to excite free electrons in the target material. The thermal energy generated by the electron-phonon coupling then evaporates the target material. It is important to realize that the reaction time for this process to occur is on the order of picoseconds [141-143]. In order to have better laser-solid coupling the target must be suitably prepared. A target with high roughness, low reflectivity (R) and high absorption coefficient (αᵣ) allows for efficient laser-solid coupling and thus provides low threshold energy for vaporization. Depending on the laser wavelength and the porosity and surface roughness of the target, typical values of threshold energy vary from 0.11 to 0.40 J/cm² [143]. It is important to realize that the energy deposited by the laser beam comprises, the energy required to evaporate the target material, conduction heat loss in the target and energy loss due to laser absorption by the expanding plasma. Using these concepts of energy balance, the thickness of the target for which evaporation (ΔXₜ) takes place can be calculated as [142, 143],

\[
ΔXₜ = (1-R) \frac{(E-E_{th})}{(ΔH + C_v ΔT)}
\]  

(2.27)
Where $R$ is the reflectivity, $E_{\text{th}}$ is the threshold energy, $\Delta H$ is the latent heat, $C_v$ is the volume heat capacity and $\Delta T$ is the maximum rise in temperature. It is important to realize that this equation is valid when the thermal diffusion length $(2Dt)^{0.5}$ is larger than the light penetration depth $(L = 1/\alpha_t)$ [143]. Here $D$ is the thermal diffusion constant and $t$ is the pulse duration of the laser. This validation is true for most metallic and semiconducting targets. However, for low thermal diffusivity materials (non-metallic targets), i.e. $(2Dt)^{0.5} < 1/\alpha_t$ a second regime is relevant. Here, thermal diffusivity does not play an important role and evaporation depth mainly depends on the attenuation distance of the laser beam [142, 143].

Plasma formation and initial isothermal expansion:

The laser interaction with the target material yields surface temperatures in the range of 2000-3200 K [142, 143]. This results in the emission of positive ions and electrons from the free surface. Generally, the ablation of the target is accompanied by the formation of a plasma (bright glow) extending normal to the target surface. The plasma contains charged and neutral species of atoms and molecules. The plasma also interacts with the incoming laser; this produces temperatures higher than the vaporization temperature in the plasma. The absorption of laser energy by the plasma occurs due to electron-ion collisions. This absorption primarily occurs by an inverse Bremsstrahlung process that involves absorption of a photon by a free electron [142, 143, 153]. The absorption coefficient ($\alpha_p$) of the plasma is given as [142, 143],

$$\alpha_p = 3.69 \times 10^8 \left( \frac{Z^3 n_i^2}{T^{0.5} \nu^3} \right) \left[ 1 - \exp(-h\nu/KT) \right] \quad (2.28)$$
Where, $Z$ is the average charge, $n_i$ is the ion density, $T$ is the temperature of the plasma, $h$ is Plank's constant, $K$ is the Boltzmann constant and $\nu$ is the free energy of the laser light. Since the absorption coefficient ($\alpha_p$) is proportional to $n_i^2$, the laser light is heavily absorbed close to the target surface, where the density of the ionized species is high. In comparison, the leading edge of the plume, is associated with high expansion velocities and low electron and ion densities. Hence, the outer edge of the plasma is transparent to the laser beam. The $[1 - \exp(-h\nu/ KT)]$ term takes into account the losses that occur due to stimulated emission depending upon the plasma temperature and laser wavelength [142, 143]. A variety of

Figure 2.29. Schematic illustration showing different regimes during laser irradiation of the target: (A) Bulk target that remains unaffected, (B) Thickness of the target material that evaporates, (C) region in which the plasma absorbs the laser heavily and (D) the expanding plasma region that is transparent to the laser [142, 153].
processes such as impact ionization, photo ionization, thermal ionization and electronic ionization effect the extent of ionization of the laser generated species. Figure 2.29 is a schematic that shows the different regimes that are present during the laser-solid interaction [143]. Region A is the unaffected bulk target and B is the thickness of the target material that is evaporated. Region C is the plasma region close to the target that absorbs the laser heavily. In this region, evaporated particles are continuously injected into the plasma. Region D depicts the outer region of the plasma that expands rapidly. In the region near the target surface, a dynamic self-regulating equilibrium exists between the plasma absorption coefficient and the rapid transfer of thermal energy into kinetic energy (due to injection of evaporated particles of the target into the plume). These compensating mechanisms govern the isothermal temperature attained by the plasma near the target surface [142, 143].

Singh et. al.[142, 143] have come up with expressions that determine the variation of density, pressure and velocity along the direction perpendicular to the target surface. Figure 2.30 is a summary of their results. It should be noted that the direction perpendicular to the target surface is the x direction. It is clear from the figure that the density of particles is a maximum in the near-target regions, whereas the velocity is minimum. The particle density in the plasma in the near surface regions can be approximated as a Gaussian. It has also been observed that the initial dimensions of the plasma are larger in the transverse direction when compared to the longitudinal direction. During the initial stages the velocity is low and acceleration is relatively high. After a while, when the expansion velocity increases, the acceleration decreases and eventually reaches zero.
This aspect governs the elongated shape of the plasma.

![Diagram](image)

Figure 2.30. Schematic illustration showing the variation of the pressure (P), velocity (V) and density (n) with the distance (moving out of the plasma) [143].

**Adiabatic expansion of the plasma:**

After the plasma formation and isothermal regime, the plasma plume expands adiabatically into the vacuum. The adiabatic expansion regime initiates after the termination of the laser pulse [143]. It is important to realize that in this regime, there is no injection of particles from the target into the plume and also the laser is no longer being absorbed by the plume. Singh et. al. [142, 143] have developed equations that explain the adiabatic expansion in relation to the dimensions of the plume. In this regime, the expanding plasma is associated with very high velocities arising from the thermal energy being converted to kinetic energy. The loss in thermal energy leads to a drop in temperature determined by a balance between cooling due to expansion and energy gain due to recombination of ions in the plasma. Figure 2.31 shows a schematic of the developing shape of the plume in the adiabatic regime. The initial dimensions of the plasma are larger in the transverse directions, i.e. in the y and z direction.
(see fig. 2.31). In the longitudinal x direction the expansion is minimal. It is also important to note that the plasma is elliptically shaped with y axis being the major axis (see fig. 2.31(a)). During the adiabatic expansion regime, the longitudinal x dimension expands rapidly resulting in the characteristic PLD plume. The plasma pressure drops rapidly until most of the thermal energy is converted to kinetic energy. Then the plume has no more energy for expansion and the plasma elongates in the shorter dimension. Eventually, an elliptical shape is retained but with the z dimension being the major axis (see fig. 2.31(b)). This theory was confirmed from the shape of the deposited YBCO film on Si, as shown in fig. 2.31(c).

Figure 2.31. (a) Schematic illustration showing the initial elliptical shape of the plasma just after the laser pulse is terminated. (b) Final shape of the plasma when it hits the substrate. (c) Shape of a YBCO film deposited on a Si substrate [143].
2.7. Growth

Thermodynamic understanding of thin film growth identifies three basic modes of growth [154]. The surface energy of the substrate ($\gamma_s$), the surface energy of the film ($\gamma_f$) and the interfacial energy ($\gamma_{sf}$) govern the growth mode for a given system. The three growth modes are illustrated in fig. 2.32.

1. Frank-van der Merwe (FM):

In this mode, deposition proceeds by two dimensional layer-by-layer growth. Complete wetting of the substrate surface occurs, i.e. the first set of atoms condense to form a monolayer on the substrate, after which the second layer comes in and builds on the first layer to form the film [154]. For this reason the FM growth mode is also referred to as the 2D growth mode. The FM growth mode is illustrated schematically in Fig. 2.32(a). The following condition favors FM growth;

$$\gamma_f + \gamma_{sf} < \gamma_s$$  \hspace{1cm} (2.29)

This equation suggests that the system gains energy when totally covered by the thin-film layer. Equality in equation (6) explains FM growth mode in the case of homoepitaxy, i.e. the substrate and the film material is the same. It is also important to realize that for FM growth to occur $\gamma_f$ should be much less than $\gamma_s$ and the interfacial energy ($\gamma_{sf}$) should be low. Most metal on metal and semiconductor on semiconductor systems follow the FM mode of growth. In the context of this study, TiN grows on Si (100) by FM growth.
2. Volmer-Weber (VW):

The VW growth mode is associated with the formation of 3D islands. Instead of wetting the surface, individual cluster-like islands are formed. This type of growth is illustrated in fig. 2.32(b). VW growth happens when the following equation is valid,

$$\gamma_f + \gamma_{sf} > \gamma_s$$  \hspace{1cm} (2.30)

i.e. the surface energy of the substrate is less than sum of the surface energy of the film and the interfacial energy [154]. Here, as shown in the Fig. 2.32(b), the interfacial energy is high and the surface energies of the film and substrate are low. So the system adjusts itself so that the high-energy interface formed is minimal and in doing so 3D islands are formed instead of a continuous wetting layer. It is important to realize that for longer growth times, the islands keep growing in size and finally neighboring islands coalesce to form a continuous thin film. This type of growth can be observed in systems where metals are grown on insulators, example Ni on amorphous Al$_2$O$_3$.

3. Stranski-Krastanov (SK):

This mode combines the 2D and the 3D growth modes as illustrated in fig. 2.32(c). Initially, a continuous wetting layer is formed over the substrate. Due to the lattice mismatch, strain accumulates in the 2D film and in order to relieve this strain 3D islands are formed [155, 156]. It is important to note that the islands grown in the SK mode are coherently strained and dislocation free, i.e., the accumulated strain that switches the growth mode from 2D to
3D is relieved by forming coherently strained islands rather than by introducing dislocations [156, 157]. This type of strain relaxation is called the volume elastic relaxation and it competes with the formation of dislocations [158]. SK growth also follows equation (6). But in this case the interfacial energy and the surface energy of the substrate are high and the surface energy of the film is low.

2.8. Domain matching epitaxy

Epitaxial growth of thin films with minimal defects is the key for the optimized performance of modern day microelectronic, optical and magnetic devices [160-162]. Epitaxy is the growth of a single crystal film on top of a single crystal substrate [163]. Traditionally, it was
understood that both the film and the substrate would have the same crystal structure and orientation. Homoepitaxy refers to the case where the grown film is made up of the same material as the substrate. In this case the lattice parameters of the film and the substrate are the same, i.e. no misfit strain exists and there are no missing interfacial bonds. Heteroepitaxy refers to the case where the film and the substrate are composed of different materials. In this case film properties largely depend on the mismatch between the film and substrate lattice parameter, the difference in the film and substrate chemistry and the difference in the thermal expansion coefficient of the film and the substrate. Thin-film growth in the case of heteroepitaxial systems can occur via the formation of a coherently strained lattice [163]. Due to the mismatch in lattice constants, the epilayer tries to assume the lattice constant of the substrate and in doing so the epilayer becomes strained [164-166]. With increase in thickness the strain energy in the system keeps increasing. Finally, dislocations or missing half planes are formed to relieve the built-in strain in the system.

Figure 2.33. Schematic illustration of lattice matching epitaxy (a) film and substrate shown individually before growth, (b) pseudomorphic or coherent growth below critical thickness, (c) formation of dislocation or missing half plane beyond the critical thickness [167].
The conventional lattice matching epitaxy explains heteroepitaxial growth for lattice misfit strains less than 7-8 %. The misfit strain in this case is calculated from the following expression,

\[ \varepsilon = \frac{a_f}{a_s} - 1 \]  

(2.31)

This misfit strain is accommodated by the coherently strained layer below a critical film thickness. Thus as shown in fig. 2.33(b), the film grows pseudomorphically until the critical thickness is reached. Beyond the critical thickness it becomes energetically favorable to form dislocations (see Fig. 2.33(c)) \[164-166\]. These dislocations relieve the remaining strain in the system. The dislocations that are formed at the film surface glide to the interface. The burgers vector and planes of the dislocation are governed by the active slip systems and glide planes are determined by the crystal structure of the film \[160, 164, 168\]. In the case of VW or 3D growth, the edge of the islands that are associated with dislocations have Burgers vectors dictated by geometrical constraints \[166\]. As an example, 90° dislocations at the edge of Ge islands on Si have \(a/2<110>\) as the Burgers vector and lie in the (001) film-substrate interface \[169\]. It is important to note that smaller misfits are associated with smaller interfacial energy and coherent epitaxy conditions \[160, 164\]. Above the 7-8 % misfit regime, it was understood that textured or poly-crystalline films would form. This notion was changed when Narayan et. al. \[164\] proposed the concept of domain matching epitaxy (DME).

DME is a new paradigm of thin film growth, where integral multiples of lattice planes match
across the film-substrate interface and the size of the domain equals integral multiples of planar spacing [164, 170]. This idea is fundamentally different from the conventional lattice matching epitaxy where lattice constants are matched one-to-one across the film-substrate interface to grow epitaxial films with less the 7-8 % misfit. By invoking the concept of DME, epitaxy can be explained in systems with high misfit, i.e. beyond the 7-8 % misfit regime [164]. It is important to realize that when the film and the substrate have similar crystal structure the matching of planes is the same as matching of lattice constants. Hence for low misfit systems (less than 7-8 %) with the same crystal structure, DME reduces to the conventional lattice matching epitaxy.

In DME, the large misfit between the film and the substrate is accommodated by a series of interface dislocations. Due to the large misfit, the dislocations are introduced within the first few monolayers and the rest of the film can be grown defect free. It is important to note that at misfit strains greater than 8 % we are looking at critical thicknesses less than a monolayer [164]. The atomic steps formed within the second monolayer provide nucleation sites for the dislocations. The dislocations have to travel only a monolayer before they reach the interface.

If the growth mode is FM or 2D, then the dislocations propagate to the sides of the wafer and in doing so they are confined to the interface. In this case the formation of undesirable threading dislocations is minimal [164]. On the other hand, if initial growth of the monolayer is a mixture of 2D and 3D growth (VW growth) then the dislocation segments may not propagate throughout the entire length and threading dislocations form. So using DME one can control the dislocation density and confine dislocations to the interface depending on the growth characteristics and number density of surface steps [164].
By invoking the concept of DME, one can get strain-free oxide films by growing them on high-misfit substrates like MgO [14]. In a large misfit condition, the critical thickness is less than a monolayer. Additionally, during the initial stages of growth there are a lot of steps formed that make dislocation nucleation easy. In this condition once the dislocation nucleates it does not have to propagate far (only a monolayer) to reach the interface. So for oxide growth via DME, the dislocations are set at the interface and the entire strain is relieved within a monolayer. The rest of the film then grows strain free.

The conventional lattice matching epitaxy for low misfit systems suffers from some critical disadvantages. Firstly, complete strain relief can be difficult to achieve via the conventional lattice matching epitaxy. This is particularly true in systems where nucleation and propagation of dislocations is difficult. Secondly, there is a high probability of forming threading dislocations that ruin the device. For low misfit systems the critical thickness is large. The dislocations nucleate only after the critical thickness is reached and must then glide across the film thickness to the interface. This process results in the formation of half-loops that are composed of two threading segments and a straight segment along the interface.

In the following section mathematical concepts governing the DME framework will be described. Domain matching epitaxy, as the name suggests is based on the idea of matching lattice planes of the film and the substrate [164]. Within a domain integral planes of the film and substrate match and the domains themselves are separated by missing half-planes (dislocation). The film and the substrate can have either a fixed or same orientation depending on the kind of misfit [164]. The planes that are matched in DME can be different
as long as they maintain similar crystal symmetry. In comparison, in the case of conventional lattice matching epitaxy for low misfit systems (< 7-8 %) only the same planes of the film and substrate are matched. In DME the initial misfit strain ($\varepsilon$) can be very large and it is given as [164],

$$\varepsilon = \frac{d_f}{d_s} - 1$$  \hspace{1cm} (2.32)

Where $d_f$ and $d_s$ are the planar spacing of the film and substrate, respectively. This misfit can be relaxed by matching $m$ planes of the substrate with $n$ planes of the film. So the residual misfit ($\varepsilon_r$) can be calculated as [164],

$$\varepsilon_r = \frac{md_f}{nd_s} - 1$$  \hspace{1cm} (2.33)

If $md_f = nd_s$ and $\varepsilon_r = 0$, then perfect matching occurs. This means a single $m/n$ domain repeats itself throughout the system to relax the misfit strain. On the other hand if $\varepsilon_r$ is non-zero and has a finite value, then two domains exist that alternate with a certain frequency to provide for a perfect matching. So by introducing the frequency factor $\alpha$ we arrive at the following equation [164],

$$(m + \alpha) d_f = (n + \alpha) d_s$$  \hspace{1cm} (2.34)

To understand this concept let us proceed with an example where $\alpha = 0.5$. In this case there exist two domains $m/n$ and $m+1/n+1$, that alternate with equal frequency to relieve the misfit
strain in the system. If we assume that \( d_f > d_s \), then it implies that \( n > m \). Hence,

\[
-n-m = 1 \text{ or } f(m) \tag{2.35}
\]

where \( f(m) \) is a function of \( m \). From the above equations we arrive at

\[
(m + \alpha) \varepsilon = 1 \text{ or } f(m) \tag{2.36}
\]

This equation governs the concept of DME and is plotted in fig. 2.34 [164]. In this figure the misfit strain is plotted versus the inverse of the integral multiple of planes matching across the interface. It provides a unified framework encompassing both the LME and DME with misfit strains ranging from 2 – 50 %. In this plot, \( n-m = 1 \) for \( \varepsilon = 0 \) to 50 % and \( n-m = f(m) \) for \( \varepsilon = 50 \) to 100. An example of growth of epitaxial ZnO film on Sapphire will now be discussed as it is relevant to the present work involving TCOs based on ZnO. ZnO with wurtzite structure has lattice parameters, \( a = 3.252 \) Å and \( c = 5.213 \) Å, whereas sapphire \((\alpha \text{Al}_2\text{O}_3)\) has lattice parameters \( a = 4.758 \) Å and \( c = 12.991 \) Å. This results in a large misfit \( (\varepsilon = 17\%) \). However, it has been shown by Narayan et.al that growth of high quality epitaxial ZnO films on sapphire is possible by DME despite the large misfit [171]. Figure 2.35 clearly illustrates the matching of 5 or 6 (2110) planes of ZnO with 6 or 7 (0110) planes of sapphire. This is in good agreement with the values predicted by the DME model (fig. 2.34).
Figure 2.34. Unified plot of misfit strain vs film-substrate planar spacing ratio showing both the LME ($< 7\%$ strain) and DME regions [164].

Figure 2.35. Fourier filtered image of DME between (2110) planes of ZnO and (0110) planes of sapphire [171].
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Chapter 3

Experimental Techniques

3.1 Substrate preparation

In this present work, mainly glass substrates of 0.15-0.17 mm thickness and sapphire substrates of 300-500 μm thickness were used. It is very essential to remove the dust particles and organics from the substrate surface as they can hamper the nucleation and epitaxial growth of the films on substrate. The glass substrates were first cleaned in trichloroethylene bath by ultrasonication for 5 minutes followed by heat treatment in acetone bath to 220°C. This process was repeated in acetone and methanol, respectively. Finally, the substrates were cleaned in hydrochloric acid, washed in DI water and blow dried in high purity nitrogen. For sapphire substrates, the same process was followed with the exception of hydrochloric acid cleaning step. After cleaning, substrates were immediately loaded into the pulsed laser deposition chamber.

3.2 Growth by PLD

Thin film and nanostructure growth in this study was performed by pulsed laser deposition. The theory and principle involved in this process has been discussed in detail in the previous chapter. This section will deal with the experimental parameters involved during thin film growth by pulsed laser deposition. The experimental setup of the PLD system is illustrated schematically in fig. 3.1. The KrF excimer laser source used was the LPX 210 from Lambda Physik. The laser wavelength was 248 nm and pulse duration was 25 ns. The laser can
operate at a maximum energy of 674 mJ at 24 KV. The laser beam is directed into the vacuum chamber using an aperture, mirror and a lens. The mirror is used to control the position at which the laser strikes the target inside the chamber. The lens is used to focus the laser beam on the target. Essentially, the lens offers control over the spot size. The laser beam enters into the vacuum chamber through the laser window. A quartz laser window with a CaF$_2$ antireflection coating is used to minimize losses due to reflection. The laser beam is directed such that it strikes the target at an incident angle of 45°. Due to laser-solid interaction a plume is formed and deposition occurs onto the substrate.

![Figure 3.1. Schematic illustration of the PLD setup.](image)

The PLD chamber holds a target assembly that can be mounted and detached from the top.
The target carrousel is designed to hold up to four targets. The target carousel is connected to a hand-driven motion controller in order to position any required target in the path of the laser beam. The multi-target assembly enables easy growth of multi-layered thin films. The individual targets themselves are designed to rotate by using a small driving motor. By rotating the target we ensure that the laser beam strikes the target at different locations. Thus uniform ablation of the target occurs and exfoliation is reduced.

The substrate assembly is located parallel to the target surface at a distance of 4.0 cm. It has been found that with increase in substrate target distance, the maximum thickness at the center of the film decreases rapidly [1, 2]. However, the uniformity of film in terms of its thickness improves with increase in substrate target distance. Singh et. al. [1, 2] have reported the variation of the maximum thickness of the film with the substrate-target distance (d) as \( d^{-p} \). Here \( p \) is the expansion coefficient, with a value of 3 for three dimensional spherical expansions and a value of 1 for linear expansion in one dimension. The value of \( p \) is also a function of spot size. Larger spot sizes make the plume more forward directed, i.e. a more linear type of expansion. For smaller spot size the plume is spherical. This can be explained in terms of a \((\cos \theta)^n\) type of dependence [1, 2]. For a forward directed plume \( n = 8-12 \). For a point source, like in the case of e-beam evaporation, \( n \) will be equal to 1. In such a case the plume will be largely spherical with minimal forward directedness.

In our study, the spot size for ZnO and NiO growth is usually large (0.1 cm\(^2\)) and hence the plume is relatively more forward directed. For MoO\(_x\) growth, a smaller spot size (0.06 cm\(^2\)) is used, mainly to increase the energy density. Generally, laser ablation of metals requires a larger energy density [3]. In the case of metals, laser-solid coupling may be difficult when
the surface is shiny. A smooth shiny surface causes losses due to reflection. In this study, a complex target geometry of Mo metal mounted on MoO₂ target was used for MoOₓ growth. Hence, higher energy density (3-4 J/cm²) was used for the ablation. The pulse frequency in the range of 5-10 Hz was used in all cases. The PLD chamber was evacuated to ~1x 10⁻⁶ Torr before heating the substrate for thin film deposition. Mostly, oxygen was introduced into the PLD chamber during film deposition.

### 3.3 X-Ray diffraction

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

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (3.1)

Where \( n \) is an integer indicating the order of reflection, \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the inter-planar spacing and \( \theta \) is the incident angle. X-ray diffraction is carried out
using a diffractometer. For this study we used a Rigaku Geigerflex diffractometer with Cu Kα radiation ($\lambda = 1.54$ Å). Essentially, a diffractometer consists of an X-ray source, a monochromator, a slit, a sample holder and a detector. The schematic of an XRD system is shown in fig. 3.2. The X-ray source is a tube consisting of a tungsten filament (cathode) and a Cu target (anode). A huge potential difference (~30 KV) causes the filament to emit electrons, which are accelerated to collide with the cathode in order to produce X-rays. Slits are used to adjust the shape and size of the beam. The detector measures the intensity of the diffracted beam through an angle of $\theta$. Generally in a $\theta$-2$\theta$ scan, the sample moves by $\theta$ and the detector moves by 2$\theta$.

![Figure 3.2. Schematic illustration of the XRD $\theta$-2$\theta$ scan.](image)

The X-ray diffraction technique provides crystal information from a relatively large area of the sample. It is a non-destructive technique and requires minimal sample preparation.
The sample is mounted onto the holder using clay. Care needs to be taken to mount the sample such that it is in the plane of the sample holder with no tilt. The sample surface should be relatively clean. It is important to realize that in the XRD technique only the planes parallel to sample surface contribute to the signal. For a single crystalline sample only one set of planes are parallel to the surface. So an XRD scan of a single crystal should have only one peak and higher order peaks of the same family. In the case of a poly crystalline film, several planes belonging to different grains will be parallel to the sample surface. Hence the XRD scan of a poly sample will have numerous peaks representing various planes. An amorphous sample will have a wide diffused peak at about 20°.

Although, the XRD technique provides easy and quick information about crystal orientation and phase composition it suffers from its own disadvantages. Importantly, it gives information about texturing only in the growth direction. If the amount of material is less than 10 % by weight, detection by X-ray becomes difficult. Particles or precipitates with sizes in the nano-regime may not be detected.

Though two-circle diffractometer gives information about the growth orientation, it does not give any information on in-plane orientation of thin film. Knowing in-plane orientation is important to establish epitaxy. The in-plane orientation of thin films can be accessed by four-circle diffractometer. In addition to rotation along θ-axis and 2θ-axis, in four-circle diffractometer the sample can be tilted with respect to the incident beam (ψ-axis) and also rotated 360 degrees around the surface normal (φ-axis). A schematic diagram of four-circle diffractometer is shown in fig. 3.3.
The in-plane epitaxial details can be established by $\varphi$-scans. To perform a $\varphi$-scan an appropriate crystallographic plane (hkl), which is inclined to the growth plane (sample surface) is identified. The $\theta$ and $2\theta$ angles are set to corresponding to Bragg angle for the identified plane. The sample tilt, $\psi$ is set equal to the crystallographic angle between the growth plane (sample surface) and the (hkl) plane identified for the $\varphi$-scan. The diffraction intensity is then recorded as a function of sample rotation along $\varphi$-axis. If the film is epitaxial, the $\varphi$-scan exhibits sharp peaks at certain $\varphi$-angles. On the other hand if the in-plane orientation of the film is random, there is no appreciable variation in the diffraction intensity in the $\varphi$-scan.

![Figure 3.3 A schematic diagram of the Philips X’Pert diffractometer used for $\varphi$-scans. IBO: Incident beam optics, DBO: Diffracted beam optics](image)

### 3.4 Transmission electron microscopy (TEM)

For atomic scale characterization and exact orientation relationship TEM is the most effective and direct technique available. TEM can also be used to investigate defects such as dislocations and their Burgers vectors, stacking faults, twins and precipitates.
Chemical composition and subsequent qualitative analysis can be done using electron energy loss and X-ray spectroscopy. High resolution cross section imaging was used to study domain matching epitaxy at the LiNiO/ MgZnO interface. For this purpose we used a JEOL 2010F transmission electron microscope with a point-to-point resolution of 1.8 Å. A Gatan imaging filtering system was used for HRTEM.

The TEM uses an electron beam as a probe. Typically, a TEM operating at 200 KV generates an electron beam with wavelength $\lambda = 0.03 \, \text{Å}$ [5]. According to the Raleigh criterion (shown below) resolution is directly proportional to wavelength.

$$\delta = \frac{0.61 \lambda}{\beta}$$  \hspace{1cm} (3.2)

Here $\delta$ is the resolution, $\lambda$ is the wavelength and $\beta$ is the semi-angle of collection of the magnifying lens. The smaller the wavelength the better the resolution. Hence resolution obtained in a TEM is in the order of few angstroms, i.e. atomic level resolution. Essentially, a TEM consists of two main components; the illumination system and the imaging system. The illumination system consists of the electron gun and electromagnetic lenses that focus the beam onto the sample [5, 6]. The electron beam interacts with the specimen. The imaging system detects the scattered electrons to form the image/diffraction pattern. The important TEM techniques used in this study were; diffraction, bright field and dark field imaging and high resolution TEM.

**Diffraction:** The TEM operates in two modes; the diffraction mode and the image mode. Diffraction patterns can be formed on the screen by placing the back focal plane on the objective plane of the intermediate and projector lens [5, 6].

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For thin samples information obtained in the diffraction mode is mainly from elastically scattered electrons. Since the electron wavelength is small, the Ewald sphere will have a large radius. Consequently, almost a plane section of the reciprocal lattice (zero order Laue zone) is observed during electron diffraction. Generally, a parallel beam of electrons is used for diffraction (selected area diffraction). If information from a smaller area is required, then a convergent beam of electrons can be used (convergent beam electron diffraction) [5]. Single crystal samples scatter the electron coherently and thus produce a spot diffraction pattern. Polycrystalline samples produce ring-like patterns. Sample with nano-sized grains produce spotty discontinuous rings. The diffraction pattern of an amorphous sample will show a diffused ring.

**Imaging:** Bright field imaging is done using the transmitted beam of electrons. This is done by inserting the objective aperture in the back focal plane (the plane where the diffracted image is formed) [5, 6]. The objective aperture then allows only the transmitted beam through for bright field imaging. The dark field imaging is done when the diffracted beam is allowed to pass and the transmitted beam is blocked. The best contrast is obtained in a two beam condition [5, 6]. In this condition the sample is titled such that only one diffracted beam is strong enough to remain. Essentially, two spots remain in the diffraction pattern the central transmitted spot and another strong diffraction spot with a known g-vector. If the objective aperture is placed on the central spot we obtain a bright field image. If the sample is tilted such that the diffracted beam passes through the aperture, then we obtain a dark field image.
**HRTEM:** This technique allows lattice imaging of the sample. Here, atomic level resolution is obtained by allowing many beams to pass through the objective aperture. The diffracted beams interfere with the direct beam resulting in a phase contrast [5, 6]. This phase contrast contributes to a high resolution TEM image. For proper analysis of a HRTEM image the sample should tilted to an exact zone. Choosing the proper defocus condition (based on the contrast transfer condition) is also of prime importance for good resolution of a HRTEM image. A first Scherzer defocus condition with minimal objective lens astigmatism is used to obtain a good HRTEM image.

**TEM sample preparation**

The cross section TEM samples were prepared by a series of steps including mechanical polishing, dimpling and ion-milling. To begin with, two small sample pieces (about 4 x 4 mm) were stuck together with the film side facing each other. An M-Bond 610 adhesive was used to stick the samples together. The sample was then mounted onto a pyrex stub. Then the sample was mechanically polished until a mirror like surface was obtained. For this purpose, a series of emery papers with reducing grit sizes were used. Final polishing was done on diamond papers for sapphire substrates. The sample was then flipped over. Now the sample was thinned down to a thickness of about 100 microns from the rough side. A smooth grit paper (1200-4000) was then used to bring down the thickness of the sample from 100 to 40 microns. The sample was then dimpled using a Gatan dimpling machine. Dimpling involved grinding with a Cu wheel and further polishing with a cloth wheel. Diamond pastes of 6, 3 and 1 micron sizes were used during dimpling.
After dimpling up to a thickness of 15-20 microns, ion-milling was performed. For this purpose a precision Gatan 691 PIPS ion milling machine was used. A small hole at the interface was formed by sputtering the sample with Ar ions. The energy of the Ar ion beam was maintained at ~ 5 KeV with a tilt angle of 5°. For plane view TEM samples, the sample was stuck onto the stub with film side facing down. The sample was then mechanically thinned, dimpled and ion milled until electron transparency was achieved.

3.5 Hall Effect Measurement

Hall measurement is a very simple and quick method to determine the carrier density, the carrier type and mobility. This measurement is based on the Lorentz force acting on the moving electrons in the presence of a magnetic field [7]. Lorentz force results in Hall voltage in a direction perpendicular to both the applied electric and the magnetic fields. In order to determine both the mobility (μ) and the sheet density (nS), a combination of a resistivity measurement and a Hall measurement is done. We have used van der Pauw technique to do these measurements. The thin film samples were cut in the shape of a ~1cm x 1cm squares. Electrical contacts were made on the four corners using indium pads and gold wires. First the resistances RA and RB were measured as shown schematically in fig. 3.4 (a) and (b). Subsequently a magnetic field was applied perpendicular to the substrate surface and Hall voltage VH was measured (fig. 3.4(c)). From these measurements sheet resistance (Rs), carrier density (nS) and mobility (μ) were calculated [8].
While carrying out Hall measurements, it should be ensured that contacts to the sample are ohmic and small in size. The lateral dimensions of the sample should be large compared to film thickness and contact size. The sample should be uniform and the thickness should be known accurately to estimate the carrier concentration. Also, the sample should be enclosed in dark space to minimize photoconductive and photovoltaic effects. [8]

3.6 Four-Point Resistivity Measurement

Figure 3.5 A schematic diagram showing four probe measurement setup in linear configuration.
For the electrical resistivity measurements, a four-probe technique was employed. Resistivity of a material is defined as and given by [7]:

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

(3.3)

In the four-probe measurement the probes are collinear with uniform spacing between them. The outer two probes carry the current (I) and the resultant voltage (V) is measured across the inner pair. The schematic of the resistivity measurement set-up is shown in fig. 3.5. For thin films grown on insulating substrates it is common to measure sheet resistance \((Rs)\); the corresponding resistivity \((\rho)\) is then given by \(Rs.t\), where \(t\) is the film thickness.

In the present study, contacts were made with gold wire attached to the top of sample by indium dots. The electrical measurements were performed using an Agilent HP8545 semiconductor parameter analyzer. The room temperature value of resistivity is an important criterion for selection of a TCO, however, to understand the electrical conduction mechanisms in the film requires the study of resistivity as a function of temperature. Therefore, temperature dependent resistivity measurements have also been performed in the temperature range 15 – 300 K. The samples were cooled down to 15 K using a cold-stage. The stage is cooled using a He cryostat which recycles compressed He. The temperature coefficient of resistivity (TCR) is a direct indication of the conductivity type of the sample, e.g. positive TCR corresponds to metal-like behavior, whereas negative TCR suggests semiconductor behavior. The investigation of conduction mechanisms, both carrier generation and transport, is part of this work. This is done by detailed analysis of resistivity plots as a function of measurement temperature.
3.7 X-ray photoelectron spectroscopy

XPS (also referred to as Electron Spectroscopy for Chemical Analysis, ESCA), which employs X-rays for the excitation of the solid and the detection of emitted photoelectrons with characteristic energies, can provide chemical information about the material. In general, the kinetic energy of the photoelectron depends on the photon energy $h \nu$ (in this case, X-ray) following the Einstein photoelectric relation

$$KE = h \nu - \varphi_s - BE$$  \hspace{1cm} (3.4)

where $h \nu$ is the energy of the incident radiation, KE is the kinetic energy of the photoelectron, $\varphi_s$ is the work function of the instrument and BE is the binding energy of the orbital from which the electron is ejected.

The binding energy is a measure of the energy required to just remove an electron from its initial level to the vacuum level; since the electron binding energies in solids are typically measured relative to the Fermi level, rather than the vacuum level, a small correction to the above equation is made to account for the work function of the solid. The photoelectrons that have sufficient kinetic energy can escape from the surface of the sample by overcoming its work function. Thus, from the measurement of the photoelectron kinetic energy, one can determine the electron binding energy, which is characteristic to the particular atom, and thus the corresponding atom can be identified. Due to quantized energy levels in atoms, the photoelectron kinetic energy distribution is comprised of a series of discrete bands. Since the energies of photoelectrons are much less than 1 keV, the escape depth, and thus the depth resolution, is within about 20 Å of the surface. Thus, in this technique, the energy spectrum
of the photoelectrons, which are emitted from the sample, provides nondestructive elemental and chemical analysis of the surface. The photoelectrons emitted during the ESCA experiment are energy separated and detected using a complex energy analyzer. The number of electrons detected reflects the intensity (relative concentration in the sample), and the position of the electron at the exit represents its spectral energy. Figure 3.6 shows a schematic of the different processes that occur and the instrumentation used in a typical XPS measurement.

Figure 3.6 Schematic of the experimental set-up of the XPS instrument [9].

3.8 Ultraviolet photoelectron spectroscopy

Only photoelectrons whose kinetic energy is higher than the work function $\Phi$ of a sample can escape from the surface, consequently $\Phi$ can be determined in photoemission by the
difference between the photon energy and the width of the spectrum. To guarantee that electrons with the lowest kinetic energies can be analyzed an additional bias voltage of 3 to 10 V is usually applied to the sample. The width of the photoemission spectrum is given by the energetic separation of the high binding energy (secondary electron) cutoff and the Fermi energy. In this context, possible shifts of the cutoff and thus of the vacuum level suggest the formation of an interfacial dipole layer \( \Delta \).

In photoemission spectroscopy, electrons from occupied states are excited above the vacuum level and can thus escape from the sample. In a first approximation, the measured kinetic energy \( E_{\text{kin}} \) allows the determination of the binding energy \( E_B \) of the photoelectron via a simple equation:

\[
E_B = h\nu - E_{\text{kin}} - \varphi_{\text{SP}}
\]  

(3.5)

where \( h\nu \) is the photon energy and \( \varphi_{\text{SP}} \) is a spectrometer specific constant, the work function of the spectrometer.

The spectrum is calibrated in a way that the Fermi level is located at 0 eV binding energy. The Fermi level (or “edge”) manifests itself as a step, since it separates occupied and empty states (PES works only with occupied states, since there need to be electrons that can be photoemitted, i.e. states above the Fermi level do not emit electrons). Then there is the high binding energy cutoff (or “secondary edge”), where the spectrum ends. Electrons close to the edge are the slowest electrons of the spectrum (right at the edge they have a kinetic energy of zero after leaving the sample surface, i.e. they had barely enough energy to overcome the work function of the material). The electrons responsible for the secondary edge and the sloping up tail before the edge are inelastically scattered electrons, which were initially
emitted from the valence bands states, but lost energy through scattering processes on their way to the sample surface. Since we know the binding energy of the electrons right at the secondary edge, we can determine the work function, which is just the difference between the energy of the UV photons (21.2 eV for He I radiation) and the binding energy of the secondary edge.

3.9 Optical characterization

For semiconductor thin films, the absorption/transmission spectroscopy is the most fundamental technique to determine the material properties such as the absorption coefficient, transmission, bandgap, as well as thin film thickness.

In general, when a light beam travels through a medium, absorption, transmission and reflection can occur, as is shown in fig 3.7. The absorbed, transmitted and reflected lights satisfy Eq. 3.6:

\[ \%A + \%T + \%R = 1 \]  

3.6

The absorption coefficient \( \alpha \) is defined by the following differential equation:

\[ \frac{dI(\lambda)}{dx} = -\alpha(\lambda) \cdot I(\lambda) \]  

3.7

where \( I(\lambda) \) is the intensity of light and \( x \) is the distance that the light propagates. This equation yields another equation, known as Beer-Lambert law:

\[ I(\lambda) = I_o(\lambda) \cdot e^{-\alpha(\lambda) \cdot x} \]  

3.8

The absorption coefficient \( \alpha \) can be calculated as following:

\[ \alpha(\lambda) = -\frac{1}{d} \ln \left( \frac{I(\lambda)}{I_o} \right) \]  

3.9
This equation is convenient to determine the absorption coefficient with a given thickness.

An absorption spectrometer (or transmission spectrometer) is generally composed of one or two monochromators, light sources, and a photomultiplier. Figure 3.7 illustrates the absorption/transmission spectrometer used in this thesis work.

Figure 3.7 Schematic layout of Hitachi U-3010 UV-Visible spectrometer.
References


Chapter 4

Results and Discussion:

MoO$_x$ Modified ZnGaO based Transparent Conducting Oxides for Organic Photovoltaic cells.

We report here the growth of a high work function bilayered structure of a composed thin MoO$_x$ ($2.0 < x < 2.75$) layer (few nanometers) deposited on a Zn$_{0.95}$Ga$_{0.05}$O film by pulsed laser deposition (PLD) on glass and sapphire substrates for transparent electrode applications. It was found that the films were highly textured along the [0001] direction. The crystalline quality of the films deposited at different substrate temperatures was investigated by X-ray diffraction, transmission electron microscopy (TEM) imaging, and selected area diffraction pattern (SAED). In the MoO$_x$ layer, molybdenum exists in Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$ oxidation states and the ratio of (Mo$^{4+}$ + Mo$^{5+}$) to Mo$^{6+}$ was determined to be $\sim$ 2:1. The bilayer films showed good optical transparency ($\geq$ 80%) and low resistivity of $\sim$ 10$^{-4}$ $\Omega$-cm. Different transport behavior of the MoO$_x$ / ZnGa$_{0.05}$O films grown at different $T_s$ (substrate temperature) was observed in temperature-dependent resistivity measurements. The bilayer film deposited at higher $T_s$ showed metallic conductivity behavior down to 113K. Moreover, a blue shift of the absorption edge in the transmission spectrum was observed with the increase in $T_s$, indicating an increase in the carrier concentration. It was observed that the ZnGa$_{0.05}$O films with an ultra-thin MoO$_x$ ($\sim$ 1-2 nanometers) overlayer showed a higher work function (varying from 4.7 eV to 5.1 eV) as compared to the single layer ZnGa$_{0.05}$O film work function ($\sim$ 4.4 eV). A correlation between the surface work function and MoO$_x$ layer thickness is observed. The higher
work function of the MoO₃ overlayer is envisaged to improve the transport of the carriers across the heterojunction in a solid state device, thus resulting in the increase in device efficiency. Some preliminary test device results of GZO based OPVs are presented.

4.1 Introduction

Research on transparent conducting oxides (TCOs), as an alternative to indium tin oxide (ITO), has attracted considerable attention due to the serious concern related to the increased cost and chemical stability in a reduced ambient [1]. ZnO doped with group III elements (Al, Ga) is a promising candidate because of its superior stability in hydrogen environment, benign nature and relatively inexpensive supply. These materials have shown promising results when used as an anode in organic solar cells (OSC), organic light emitting diodes (OLED) and other optoelectronic devices [2-4].

We have demonstrated in our earlier work that highly conducting and transparent Ga:ZnO can be deposited on single crystalline sapphire substrates as well as on glass substrates using pulsed laser deposition (PLD) [5,6]. It was found that the electrical properties of the TCO films are determined by the details of microstructure, stoichiometry and defects, which could in turn be controlled by the processing and substrate parameters. The formation of textured <0001> films on amorphous glass substrates poses a major technical challenge in terms of our ability to control the grain size in nanometer range, texture and grain boundary characteristics in these films to achieve superior properties and cell performance. In a recent report from our group, the
suitability of these nanocrystalline ZnGa$_{0.05}$O films deposited on a glass substrate as the anode of a double heterojunction OPV cell has been demonstrated with power conversion efficiencies > 1% [7]. The power conversion efficiencies of ZnGa$_{0.05}$O based cell were comparable to ITO based OPV cell, even though it showed relatively higher contact resistance. The higher contact resistance was attributed to the film surface and interface characteristics of ZnGa$_{0.05}$O with the organic layer owing to the lower work function of ZnO based TCOs. This suggests that although, low resistivity and high %T are prerequisites for superior device performance, surface work function is also a critical parameter. The lower work function of the TCOs makes it difficult to achieve ohmic contacts at the interface, which increases the series resistance and limits the realization of maximum theoretical open-circuit voltage ($V_{oc}$) in OSCs [8]. In the case of OLED, the surface work function affects the energy barrier height at the interface of the TCO with the organic semiconductor layer, playing a role in enhancing the hole injection efficiency and reducing the operating voltages of the device [9, 10]. Another important issue is the interface stability between TCO and organic layer in the device, which is critical for achieving reliability and long-term performance. Therefore diffusion barrier characteristics of TCO play an important role in determining reliability and performance of these devices.

In this study, we report on the growth of novel alternative TCO consisting of thin buffer layer of MoO$_x$ (2.0 < x < 2.75) on Ga doped ZnO (GZO) prepared by PLD to solve both the issues of surface characteristics and interface stability. MoO$_x$ has superior diffusion
barrier properties [11], provides higher work function, and is envisaged to improve the transport of the carriers across the heterojunction in the device, thus resulting in increased device efficiency. MoO\textsubscript{x} is an interesting material as it can exist as combination of different phases or single phase with different oxidation states, leading to superior electronic and optical properties [12]. The electronic structure of molybdenum oxide (MoO\textsubscript{x}) suggests that this material can be used as a TCO. The band gap of MoO\textsubscript{x} also varies between 0.7 and 3.1 eV, depending on the fraction of different oxidation states. It has been shown in our earlier report that epitaxial MoO\textsubscript{x} films can be successfully grown on sapphire (0001) substrates using Pulsed Laser Deposition (PLD) [12]. The MoO\textsubscript{x} films grew epitaxially on sapphire single crystalline substrates via domain matching epitaxy where integral multiples of lattice planes match across the film-substrate interface [13]. From the (electron and X-ray) diffraction patterns, MoO\textsubscript{2} phase of the film with a monoclinic structure was identified and the lattice parameters were determined as, \(a = 5.61\pm0.01\ \text{Å},\ b = 4.856\pm0.01\ \text{Å},\ c = 5.628\pm0.01\ \text{Å}\) and \(\beta = 120.6^\circ\pm0.1^\circ\). It was found that the variation of electrical and optical properties was governed by the fraction of different oxidation states of molybdenum, namely (Mo\textsuperscript{4+}, Mo\textsuperscript{5+} and Mo\textsuperscript{6+}) in the monoclinic phase. The non-stoichiometry of MoO\textsubscript{x} could be tuned (2.0 < x < 2.75) by optimal target configuration and deposition parameters (PO\textsubscript{2}, annealing conditions) [12].

In this paper, experimental results involving optical, structural, chemical and electrical property measurements of MoO\textsubscript{x} / ZnGa\textsubscript{0.05}O bilayers on sapphire and glass substrates are presented. An attempt has been made to establish correlations between the processing
parameters, the structure and properties of the bilayer films (MoO\textsubscript{x} / ZnGa\textsubscript{0.05}O) for transparent electrode applications. It is shown that by growing a thin MoO\textsubscript{x} buffer layer on ZnGa\textsubscript{0.05}O, higher work function can be achieved without affecting the overall transmittance and sheet resistance. It is further shown that the work function of this composite TCO can be tuned by changing the deposition parameters and/or thickness of MoO\textsubscript{x} layer.

4.2 Experimental Details:

Ga doped ZnO (GZO) and MoO\textsubscript{x} films were grown on c-plane (0001) sapphire substrates as well as amorphous glass substrates. A pulsed KrF excimer laser of wavelength (248 nm) and pulse duration (25 ns) was used for the deposition. An optimized target for 5 at. % of Gallium doped ZnO was prepared by conventional solid state reaction technique. For the case of MoO\textsubscript{x}, a compound target assembly (metal Mo strip mounted on the MoO\textsubscript{2} target) was used to achieve layer by layer film growth with controlled composition. The chamber was evacuated to a base pressure of 10\textsuperscript{-6} Torr prior to growth and deposition was carried out at an oxygen pressure of ~ (1.0 – 4.0 x 10\textsuperscript{-3}) Torr, in order to control the defects which further influence the electrical and optical properties of the film. The laser energy density was varied from 2.0 - 5.0 J/cm\textsuperscript{2} with repetition rate of 10 Hz was used for GZO and 4.0 - 7.0 J/cm\textsuperscript{2} for MoO\textsubscript{x}. The deposition was carried out at 200\textdegree{}C and 400\textdegree{}C for the glass and sapphire substrate, respectively. By depositing the GZO layer for 20 min, a thickness of ~ 600 ± 50 nm was obtained. The thickness of the MoO\textsubscript{x} layer was carefully controlled by controlling the repetition rate and the number of
pulses. X-ray diffraction (XRD) was used to determine the growth orientation and texture of the films. A Rigaku Geigerflex diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) and a Ni filter. The XPS analysis of the films was carried out in a Riber LAS-3000 X-ray photoelectron spectrometer Al K$_\alpha$ X-ray source. The oxidation states of the elements present in the film were analyzed by deconvolution using a Shirley routine and Casa software [14]. The values corresponding to the C 1s peak were used as a reference for the curve fitting analysis. Microstructural and growth characteristics of the as deposited films were investigated in detail by using a JEOL-2010 field emission transmission electron microscope (TEM), operating at 200kV with a point- to –point resolution of 0.18 nm. For the TEM observations, cross-section samples were prepared by mechanical polishing, followed by dimpling and Ar-ion milling. The main aim for TEM experiments was to determine the grain size and characteristics of grain boundaries of GZO layer on glass and to determine the thickness of thin MoO$_x$ layer. Optical transmittance measurements were carried out as a function of wavelength in the range 200 – 900 nm using a Hitachi U-3010 Spectrophotometer. To understand the affect of microstructure and MoO$_x$ layer on electrical properties of films, electrical resistivity of the films was measured using a four–probe technique in the temperature range of 15 K - 300 K. The contacts on the films were made by using indium dots on the top layer for the electrical measurements. Hall measurements were also performed on these samples using Van der Pauw method. The UPS measurements were conducted with a Kratos Axis Ultra DLD Ultraviolet Photoelectron Spectrometer equipped with a monochromatic He ultraviolet source He I (21.2 eV). A 5 V bias was applied to enhance the extraction of low kinetic energy, K.E.
electrons and to successfully determine the energy of the low KE edge [15]. The Fermi edge for these samples was determined after sputter cleaning of the surface of the samples with Ar\(^+\) ions for 2 min in UHV. The samples were mounted with Cu clips grounding the film surface to reduce the possibility of charging effect. All the samples were referenced with a clean gold sample. Proper connection of the samples on the same stub ensured that the samples are in electronic equilibrium with the spectrometer.

4.3 Results and Discussion

4.3.1 Structural characterization

Figure 4.1(a) and 4.1(b) show the XRD patterns (θ-2θ scan) of the bilayer film (MoO\(_x\) / ZnGa\(_{0.05}\)O) grown at 200°C and 1.0 x 10\(^{-3}\) Torr of oxygen pressure on c-plane sapphire and amorphous glass substrates, respectively. The FWHM of the (0002) diffraction peaks corresponding to ZnGa\(_{0.05}\)O obtained from the XRD spectra on sapphire and glass substrates are 0.29° and 0.36°, respectively. The sharp (0002) ZnGa\(_{0.05}\)O peak suggests good crystalline growth both on sapphire and amorphous glass substrates at a lower temperature of 200°C. The absence of additional peaks excludes the possibility of any extra phases.
Figure 4.1. XRD of MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films deposited at 200°C and $1 \times 10^{-3}$ Torr of oxygen pressure on (a) sapphire and (b) glass.

However, the MoO$_x$ peak in the film could not be detected in the XRD pattern due to its very small thickness. So, the detailed analysis of Molybdenum oxide phase was performed by XPS measurements. The XPS results shown here are from bilayer films (MoO$_x$ / ZnGa$_{0.05}$O) at different growth parameters and substrates, although the deposition time for both the layers was kept constant. The films surfaces were cleaned with Ar$^+$ ions for 2 min in UHV before the measurement. Figure 4.2(a) and 4.2(b) show the XPS survey spectrum acquired from the surface of bilayer film (MoO$_x$ / ZnGa$_{0.05}$O) grown at 200°C on glass and c-plane sapphire, respectively. From fig. 4.2(a), the Ga 2p$_{3/2}$
and Ga 2p₁/₂ peaks are found to be at 1116.7 eV and 1143.6 eV, respectively, which suggests the presence of Ga³⁺ [6]. Thus, Ga³⁺ can act as a donor and effectively increase the carrier concentration. The peaks corresponding to Mo-3d, Mo3p and O1s in fig. 4.2(a) and 4.2(b) clearly indicate the growth of Molybdenum oxide layer on ZnGa₀.₀₅O layer. There is no indication of any extra element present in the film from the XPS data. The multiple oxidation states of molybdenum (Mo⁴⁺, Mo⁵⁺ and Mo⁶⁺) in the MoOₓ layer have been verified by the high-resolution Mo 3d core level spectrum as shown in fig. 4.2(c). The spectrum consists of complex mixture of Mo 3d₅/₂,₃/₂ spin-doublets of molybdenum in its multiple oxidation state of +4, +5 and +6 [12]. The Mo oxidation states have been resolved by using a non-linear curve fitting technique. The Mo⁴⁺ (3d₅/₂), Mo⁵⁺ (3d₃/₂) and Mo⁶⁺ (3d₅/₂) peak are present at 229.2 eV, 230.3 eV and 232.1 eV, respectively, and is in accordance with the values reported in our earlier work [12]. The corresponding fraction of different oxidation states of Molybdenum in MoOₓ layer was found to be Mo⁴⁺ - 58.1%, Mo⁵⁺-9.3% and Mo⁶⁺-32.8%. The relative concentration of multiple oxidation states of Mo has been determined by calculating the area under the resolved peaks and the ratio of (Mo⁴⁺, Mo⁵⁺) to Mo⁶⁺ was calculated to be ~2:1. This ratio corresponds to x = 2.3 for the MoOₓ film.
Figure 4.2. (a) Survey XPS spectrum from the surface of \( \text{MoO}_x/\text{Zn}_{0.95}\text{Ga}_{0.05}\text{O} \) film deposited at 200°C and \( 1 \times 10^{-3} \) Torr of oxygen pressure on glass and (b) XPS spectrum of \( \text{MoO}_x/\text{Zn}_{0.95}\text{Ga}_{0.05}\text{O} \) film deposited at 200°C and \( 1 \times 10^{-3} \) Torr of oxygen pressure on sapphire (c) High-resolution spectrum of Mo 3d peak from the surface of \( \text{MoO}_x/\text{Zn}_{0.95}\text{Ga}_{0.05}\text{O} \) on sapphire (d) \( \text{MoO}_x/\text{Zn}_{0.95}\text{Ga}_{0.05}\text{O} \) film deposited at 400°C and \( 1 \times 10^{-3} \) Torr of oxygen pressure on glass.
Figure 4.2(d) shows the XPS survey spectrum acquired from the surface of the bilayer film (MoO$_x$ / ZnGa$_{0.05}$O) grown at 400$^\circ$C on glass. It is interesting to note that the relative intensity of Mo 3p, Mo 3d and O1s peaks to Zn 2p peaks has increased when compared to XPS survey spectrum at 200$^\circ$C $T_s$. In XPS, the X-ray source interacts with the first few monolayers of the film. This gives an indication that relatively thicker MoO$_x$ has been grown on ZnGa$_{0.05}$O at a higher substrate temperature as the volume interaction with the underlying ZnGa$_{0.05}$O layer has decreased.

Detailed TEM analysis was performed on cross-section samples to analyze the film microstructure. The bilayer film was capped with alumina post deposition at 100$^\circ$C to preserve the thin MoO$_x$ layer from ion milling damage during the TEM sample preparation. A representative bright field TEM micrograph corresponding to a cross-section of the as grown bilayer film (MoO$_x$ / ZnGa$_{0.05}$O) at 200$^\circ$C on amorphous Si-SiO$_2$ substrate is presented in fig. 4.3(a). This micrograph shows the presence of small angle grain boundaries referred as sub-grain boundaries. The inset in fig. 4.3(b) shows the selected area diffraction pattern (SAED) of ZnGaO layer at 200$^\circ$C. The spotty patterns indicate a crystalline structure with a small amount of misorientation (depicted by the small arcs). These results suggest that the grain size is greater than 1μm and the subgrains within one grain are contributing to the SAED pattern. These results along with X-ray diffraction pattern confirm that the films grown at these temperatures are highly textured along the [0001] orientation.
Figure 4.3. (a) Bright field image of MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O film at $T_s = 200^\circ$C on Si-SiO$_2$ showing the interface of the film and SiO$_2$ (b) Low magnification image of MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O film at $T_s = 200^\circ$C showing the embedded MoO$_x$ between Zn$_{0.95}$Ga$_{0.05}$O and Al$_2$O$_3$. The film was capped with alumina (Al$_2$O$_3$) to protect the MoO$_x$ layer from any damage during TEM sample preparation. The inset shows the SAED of Zn$_{0.95}$Ga$_{0.05}$O. As MoO$_x$ is very thin, its spots could not be seen in the SAED pattern.

The overall thickness of the film was estimated to be $\sim$ 600 nm. Figure 4.3(b) and 4.4(a) show a thin MoO$_x$ layer sandwiched between ZnGa$_{0.05}$O and Al$_2$O$_3$ at 200$^\circ$C and 400$^\circ$C, respectively. The thickness of MoO$_x$ at 200$^\circ$C substrate temperature is determined to be $\sim$0.9 nm (few monolayers), as shown in fig. 4.3(b). For the film deposited at $T_s$ of 400$^\circ$C, the thickness of MoO$_x$ is determined to be $\sim$1.5 nm (fig. 4.4(a)). This data clearly indicates that the thickness of MoO$_x$ layer increases with increasing $T_s$ when grown for
the same amount of time. This finding is consistent with the XPS data and may be related to wettability (sticking coefficient) of the MoO\(_x\) plasma to the growth surface.

Figure 4.4. (a) Low magnification image of MoO\(_x\)/Zn\(_{0.95}\)Ga\(_{0.05}\)O film at \(T_s = 400^\circ\text{C}\) showing the embedded MoO\(_x\) between Zn\(_{0.95}\)Ga\(_{0.05}\)O and alumina (Al\(_2\)O\(_3\)). (b) HR-TEM of MoO\(_x\)/Zn\(_{0.95}\)Ga\(_{0.05}\)O film at \(T_s = 400^\circ\text{C}\) showing the Zn\(_{0.95}\)Ga\(_{0.05}\)O layer. The arrow is indicating the grain boundary.

It can be further observed from these micrographs that the growth of MoO\(_x\) takes place via a 2-D (two dimensional) growth mode at 200\(^\circ\text{C}\) and 400\(^\circ\text{C}\) substrate temperature. The 2-D growth of MoO\(_x\) on ZnGa\(_{0.05}\)O template leads to a uniform coverage, which is envisaged to be conducive to improving the device performance. A typical high resolution TEM (HRTEM) image of ZnGaO layer at 400\(^\circ\text{C}\) is presented in fig. 4.4 (b), which reveals the crystalline nature of the grains. A low angle grain boundary can be
observed in the film with the tilt angle of $\sim 1.5^\circ$. This is indicative of good crystalline nature of growth which is a critical parameter for superior electrical properties. It should be noted that the growth parameters like substrate temperature and forward-directedness of plume are important factors governing the quality and microstructure of film. It can also be observed that the film is free of any nano-sized clusters or precipitates.

4.3.2 Electrical and optical characterization

Preliminary optimization of the MoO$_x$ for the top layer was done by varying the film thickness, temperature and in-growth O$_2$ partial pressure in separate MoO$_x$ depositions on c-sapphire and glass. Series resistance and the optical transmittance, which determine the incident photon absorption, are the dominant factors affecting the device performance. Hence, the films were optimized taking these factors. It was found that on increasing the MoO$_x$ thickness in a few nanometers range ($\sim 1$ to $\sim 3$ nm), the transmittance of MoO$_x$/sapphire (Ts = 400$^\circ$C) in visible region decreased from 80% to 70% and the sheet resistance decreased by one order of magnitude. Moreover, the films at lower temperature showed higher sheet resistance. The same trend was found for glass substrates with higher transmittance and higher sheet resistance values.

The (MoO$_x$/ZnGa$_{0.05}$O) bilayer films were characterized with an optimum range of MoO$_x$ layer thickness. Figure 4.5(a) illustrates the transmission spectra of the bilayer film (MoO$_x$/ZnGa$_{0.05}$O) at different temperatures on glass and sapphire substrates, with the inset showing the transmission spectra of the ZnGa$_{0.05}$O/glass at 200$^\circ$C.
Table 4.1 presents the average transmittance values for films at different growth conditions. It can be observed that all the films show an average transmittance $\geq 80\%$ in the visible region. There is not much reduction in transmittance of MoO$_x$/ZnGa$_{0.05}$O compared to ZnGa$_{0.05}$O/glass. The slightly lower transmittance of MoO$_x$/ZnGa$_{0.05}$O at 400°C can be attributed to an increase in carrier concentration.

Figure 4.5. UV-Vis transmission spectra of the MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films (a) $T_s$ of 200°C and 1 x $10^{-3}$ Torr of oxygen pressure on sapphire (b) $T_s$ of 200°C and 1 x $10^{-3}$ Torr of oxygen pressure on glass (c) $T_s$ of 400°C and 1 x $10^{-3}$ Torr of oxygen pressure on glass. The inset shows the transmission spectra of Zn$_{0.95}$Ga$_{0.05}$O film at $T_s$ of 200°C and 1 x $10^{-3}$ Torr of oxygen pressure on glass.

Moreover, the bilayer film deposited at 400°C shows a blue shift of the absorption edge as compared to the bilayer films deposited at lower substrate temperature ($T_s$). The
optical band gap \((E_g)\) can be calculated by assuming a direct transition between valence and conduction bands. The absorption coefficient \(\alpha\) obeys the following relationship with \(E_g\) near the band gap

\[
(\alpha h \nu)^2 \propto A(h \nu - E_g),
\]

Where \(A\) is a constant, \(h\) is Planck’s constant, and \(\nu\) is the incident photon’s frequency.

The absorption coefficient \(\alpha\) was obtained by using the relation \(\alpha = -\frac{1}{d} \ln(T)\), where \(T\) is the transmittance and \(d\) is the thickness of the bilayer film. The band gap was obtained by extrapolating the linear part of the plot \((\alpha h \nu)^2\) vs \(h \nu\) to the energy axis as shown in fig. 4.6. As \(T_s\) is increased from 200°C to 400°C, \(E_g\) increased slightly from 3.46 eV to 3.6 eV. This widening of band-gap is attributed to the Burstein-Moss effect, since the absorption edge of a degenerate semiconductor is shifted to the smaller wavelength with increasing carrier concentration [16,17].

The ZnGa_{0.05}O/glass film showed room temperature resistivity of \(2.4 \times 10^{-4} \ \Omega\)-cm, Hall mobility of 13.2 cm²V⁻¹s⁻¹ and carrier concentration of \(2.2 \times 10^{21} \ \text{cm}^{-3}\). The sheet resistance was measured to be 3Ω/□. The film thickness was kept around 600 nm to get a lower sheet resistance without degrading the transmittance. The MoO\(_x\) / ZnGa\(_{0.05}\)O bilayer films had n-type conductivity and the values of resistivity, carrier concentration and Hall mobility of these films are summarized in table 4.2. The Hall measurement data (from table 4.1) depicts that though the carrier concentration did not change much from single layer to bilayer, the Hall mobility decreased from 13.2 to 7 cm²V⁻¹s⁻¹. This may be related to the grain structure of the thin MoO\(_x\) layer and the interface scattering effect.
between the MoO$_x$ and ZnGa$_{0.05}$O layer. The grain barriers or other structural defects affect significantly the carrier transport in thin films.

As the deposition temperature was increased to 400°C, the MoO$_x$/ZnGa$_{0.05}$O bilayer film showed lower resistivity value. The resistivity is inversely proportional to the product of the carrier concentration and mobility. The decrease in resistivity may be attributed to the effective increase in the carrier concentration at higher deposition temperature (table 4.1).

Figure 4.6. $(\alpha h \nu)^2$ vs $h \nu$ plot for (a) Zn$_{0.95}$Ga$_{0.05}$O film at $T_s$ of 200°C (b) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films at $T_s$ of 200°C on glass (c) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films at $T_s$ of 200°C on sapphire (d) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films at $T_s$ of 400°C on glass.
Table 4.1. Summary of electrical and optical properties for films at different growth conditions. T(K) shows the transition temperature in the resistivity behavior of the samples with temperature.

<table>
<thead>
<tr>
<th></th>
<th>Sheet Resistance $\Omega/\square$</th>
<th>Transmittance (%T)</th>
<th>Carrier Concentration (cm$^{-3}$)</th>
<th>Hall mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Room temp resistivity $\rho$ (Ω-cm)</th>
<th>T(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$<em>{0.95}$Ga$</em>{0.05}$O ($T_s$-200$^\circ$C)</td>
<td>3</td>
<td>$\sim$87</td>
<td>$2.2 \times 10^{21}$</td>
<td>13.2</td>
<td>$2.4 \times 10^{-4}$</td>
<td>168</td>
</tr>
<tr>
<td>MoO$<em>x$/Zn$</em>{0.95}$Ga$_{0.05}$O ($T_s$-200$^\circ$C)</td>
<td>4</td>
<td>$\sim$85</td>
<td>$2.4 \times 10^{21}$</td>
<td>7</td>
<td>$2.8 \times 10^{-4}$</td>
<td>_</td>
</tr>
<tr>
<td>MoO$<em>x$/Zn$</em>{0.95}$Ga$_{0.05}$O ($T_s$-400$^\circ$C)</td>
<td>2.5</td>
<td>$\sim$80</td>
<td>$2.9 \times 10^{21}$</td>
<td>8</td>
<td>$2.2 \times 10^{-4}$</td>
<td>113</td>
</tr>
</tbody>
</table>

This high carrier concentration of the film is in agreement with the optical transmittance data, which show a blue shift in the absorption edge. At higher temperatures, more impurities will be ionized leading to an increase in carrier concentration [18]. However, the mobility remained almost the same ($8$ cm$^2$V$^{-1}$s$^{-1}$) with the increase in deposition temperature.
Figure 4.7. Resistivity vs temperature for (a) Zn$_{0.95}$Ga$_{0.05}$O films deposited at 200°C (b) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films deposited at 400°C (c) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O films deposited at 200°C.

Figure 4.7 shows temperature dependence of resistivity for the ZnGa$_{0.05}$O and MoO$_x$/ZnGa$_{0.05}$O bilayer films. The ZnGa$_{0.05}$O/glass showed metal like behavior above 168K as shown in fig. 4.6 (a). The metallic conductivity can be explained by the formation of a degenerate band appearing in heavily doped semiconductors as suggested, by Mott [19]. Similar behavior was observed and reported in earlier work [20]. This mixed behavior of negative TCR up to a certain temperature, followed by positive TCR, is governed by two competing phenomena of mobility and carrier concentration variation with temperature. The MoO$_x$/ZnGa$_{0.05}$O bilayer film grown at 400 °C also showed a
similar metallic behavior above 113K as shown in fig. 4.6 (b). Surprisingly, MoO$_x$/ZnGa$_{0.05}$O bilayer film deposited at 200°C showed semiconducting behavior till room temperature as shown in fig. 4.7(c). This behavior can be attributed to MoO$_x$ layer contribution to the effective resistivity.

![Resistivity vs temperature plot of MoO$_x$ on glass substrate at $T_s$ of 200°C and 1 x $10^{-3}$ Torr of oxygen pressure.](image)

Figure 4.8 shows temperature dependence of resistivity for the thin MoO$_x$ film on glass deposited at 200°C. This film was deposited for the same time as the bilayer film. It can be observed that this film showed semiconducting behavior with room temperature resistivity of $2 \times 10^{-3}$ $\Omega$-cm, which is an order of magnitude higher than ZnGa$_{0.05}$O. The
effective sheet resistance and resistivity is assumed to result from the resistivities of single layers coupled in parallel. Though the sheet resistance and effective resistivity of the bilayer will be dominated by the thicker layer of ZnGa$_{0.05}$O and the most of the current should pass through it, some series combinational effect does occur because of the electrical contact configuration, which affect the overall resistivity as well as effective mobility.

4.3.3 Surface characterization (Work function measurement)

The effective work functions of these modified surfaces of ZnGa$_{0.05}$O/glass are determined by UV-photoelectron spectroscopy, using He (I) excitation source (21.2 eV). Figure 4.9 compares UPS spectra of ZnGa$_{0.05}$O/glass and surface modified ZnGa$_{0.05}$O (MoO$_x$ (x = 2.3) / ZnGa$_{0.05}$O) at two different conditions. The work function ($\Phi_{zgo}$) of all the samples is determined by the difference between the width of the photoemission spectrum, and the source energy:

$$\Phi_{zgo} = 21.2 \text{ eV} - t,$$

where $t$ is the difference between the Fermi edge energy, $E_f$ and the lowest kinetic energy edge of the UPS spectra [21]. The Fermi energy cutoff for the ZnGa$_{0.05}$O film is shown in the inset of fig. 4.9.
Figure 4.9. (a) UPS spectra of Zn$_{0.95}$Ga$_{0.05}$O film on glass at T$_s$ 200°C (b) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O film on glass at T$_s$ 200°C (c) MoO$_x$/Zn$_{0.95}$Ga$_{0.05}$O film on glass at T$_s$ 400°C.

It is revealed from the UPS spectra that the lowest kinetic energy edge for the bilayer films of MoO$_x$/ZnGa$_{0.05}$O/glass shift towards higher energy, resulting in the higher effective work functions than the ZnGa$_{0.05}$O/glass films. The work function values with the effective MoO$_x$ layer thickness on ZnGa$_{0.05}$O layer is summarized in table 4.2. The highest work function of 5.1 eV is achieved for the bilayer film grown at 400°C. The corresponding XPS spectra of the bilayer films MoO$_x$ (x = 2.3)/ ZnGa$_{0.05}$O/glass at deposition temperature of 200°C and 400°C are shown in fig. 4.2(a) and 4.2(d), respectively. This work function data is consistent with our XPS and TEM data. It is evident from the XPS data (fig. 4.2(a), 4.2(d)) as well as cross-section TEM that thicker
MoOₓ layer is grown at higher temperature (400°C). So, the higher work function from the bilayer surface may be attributed to the grain structure of MoOₓ layer. This UPS data suggests that the work function of the ZnGa₀.₀₅O/glass can be improved by coating it with thin MoOₓ layer and this work function can be further tuned by changing the growth parameters.

Table 4.2. Values of work function determined from UPS spectra for different growth conditions.

<table>
<thead>
<tr>
<th>MoOₓ layer thickness</th>
<th>MoOₓ layer thickness</th>
<th>Work function (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn₀.₉₅Ga₀.₀₅O (Tₓ-200°C)</td>
<td>0 nm</td>
<td>4.4</td>
</tr>
<tr>
<td>MoOₓ/Zn₀.₉₅Ga₀.₀₅O (Tₓ-200°C)</td>
<td>~0.9 nm</td>
<td>4.7</td>
</tr>
<tr>
<td>MoOₓ/Zn₀.₉₅Ga₀.₀₅O (Tₓ-400°C)</td>
<td>~1.5 nm</td>
<td>5.1</td>
</tr>
</tbody>
</table>

In this work, it was found that the bilayer film (MoOₓ/ZnGa₀.₀₅O) on glass at deposition temperature of 400°C and 1 x 10⁻³ Torr of oxygen pressure showed the lowest resistivity of 2.2×10⁻⁴ Ω-cm, with optimum transmittance of 80% and sheet resistance of 2.5Ω/□. The resistivity measurements from the films showed a metallic behavior with higher carrier concentration of 2.9×10²¹ cm⁻³. In addition to this, this film showed a higher work function of 5.1 eV. The thickness of the ZnGa₀.₀₅O (~600 nm) seems to be optimum for the desired value of sheet resistance and transmittance. However, the MoOₓ layer
thickness can be varied further to study in depth the affect of thickness on the surface work function and a correlation between its mixed valence states and its work function property can be established. It has been shown in our earlier work that the properties of MoO$_x$ can be altered by annealing in air as the corresponding ratio of (Mo$^{4+}$, Mo$^{5+}$) to Mo$^{6+}$ can be varied [12]. So the bilayer films can be optimized further by changing the processing conditions and annealing the films in different ambient to get higher mobilities without degrading other desirable properties.

4.3.4 Device Results

4.3.4.1 Organic Photovoltaic cell (OPV)(I)

To evaluate the suitability of Zn$_{0.95}$Ga$_{0.05}$O (GZO) films for OPV application, OPVs of nearly identical structures were compared directly, one utilizing a conventional ITO anode, Zn$_{0.95}$Ga$_{0.05}$O anode and MoO$_x$/ Zn$_{0.95}$Ga$_{0.05}$O anode. These devices were fabricated in collaboration with Prof. S.R. Forrest research group [22]. OPVs were fabricated using copper phthalocyanine (CuPc) as the donor, and the fullerene C60 as the acceptor grown on top of the TCO by organic vapor phase deposition (OPVD) [23,24]. The schematic of device structure is shown in (fig. 4.10). Prior to loading in the deposition chamber, Zn$_{0.95}$Ga$_{0.05}$O (GZO) based electrodes were cleaned using deionized (DI) water, acetone and iso-propanol, and then were treated in UV –ozone for 10 min. The OPV was completed by deposition of the exciton blocking layer 2,9-dimethyl-4,7-diphenyl-1,10- phenanthroline (BCP) and a Ag cathode through a shadow mask with 1 mm diameter openings. The base pressure in the OPVD growth chamber was maintained
at < 90 mTorr, whereas the BCP and Ag layers were grown in a chamber with a base pressure less than $2 \times 10^{-7}$ Torr. BCP has been found to transport electrons to the cathode from the adjoining acceptor layer while effectively blocking excitons in the lower-energy-gap acceptor layer from recombining at the cathode [25]. The thicknesses of the CuPc and C60 layers are 30 nm and 45 nm, respectively. Device current densities versus voltage ($J - V$) characteristics were measured under simulated AM1.5G solar illumination using an HP4155B semiconductor parameter analyzer. The external quantum efficiency (EQE) was measured according to the ASTM standard [26] from which the spectral-calibrated power conversion efficiency is calculated.

Figure 4.10. Schematic of double layer heterojunction OPV (CuPC/C60) using GZO electrode with MoO$_x$ interfacial layer.
Figure 4.11. Current density vs. voltage characteristics of a) (Control) ITO/CuPc/C60/BCP/Ag, b) GZO /CuPc/C60/BCP/Ag and MoOx/ GZO /CuPc/C60/BCP/Ag OPV devices at 1 sun (100 mW/cm²) simulated AM 1.5G irradiance.
Figure 4.12. a) Log plot I-V Curve showing open circuit voltage (Voc), b) External quantum efficiency spectra comparison of the ITO/CuPc/C60/BCP/Ag, GZO/CuPc/C60/BCP/Ag and MoOx/GZO/CuPc/C60/BCP/Ag OPV.
Figure 4.11 (a) shows the J–V characteristics under illumination for the OPV with the ITO anode, and with GZO based anode (fig. 4.11 (b)). At 100 mW/cm$^2$, AM1.5G, of simulated illumination the GZO based OPV has a fill factor (FF) of 0.42 and power conversion efficiency ($\eta$) of 0.52% at 1 sun. The lower values of OPV parameters for GZO-based OPV compared to ITO based OPV (FF = 0.56, $\eta$ = 1.3%) may be attributed to the lower work function values of GZO. With MoO$_x$/GZO electrode, OPV showed FF of 0.5 and corresponding $\eta$ of 1.0 % at 1 sun. It can be clearly seen from (fig. 4.12 (a)) that Voc is higher for MoO$_x$/GZO based OPV (0.41V) than the Voc for GZO-based OPV (0.32V). As anticipated in the earlier discussion, MoO$_x$/GZO based OPV shows improved current injection into the CuPc layer because of the smaller barrier to hole injection. This increases the charge-separating built-in electrostatic potential ($V_{bi}$), leading to improved collection of the photogenerated carriers at higher positive voltages (Voc), and hence, an increased power conversion efficiency ($\eta$). These MoO$_x$/GZO based OPV show results comparable to the control device (ITO anode). However, this value of efficiency can be further increased by optimizing the thickness and the structure of the organic layers so as to accommodate the differences in the surface characteristics.

Figure 4.12(b) shows the comparative EQE of the OPVs. The peaks at wavelengths of $\lambda$=450, 620 and 690 nm correspond to the absorption maxima of C60 and CuPc. The photocurrent contribution of C60 is generated between 400 and 550 nm, while the CuPc layer contributes from 550 to 750 nm, such that the solar spectrum is completely covered [25]. It should be noted that, in this device configuration, CuPc is in contact with GZO or
ITO based anode. Our results show that MoO$_x$/GZO based OPV shows an increase in EQE compared to the GZO based one in the corresponding region of CuPc. This clearly suggests better collection of photo-generated carriers by employing the high work function anode.

**4.3.4.2 OPVs (II)**

Bulk heterojunction organic OPVs provide the advantage of a largely increased interfacial area where charge separation occurs. Due to the interface being dispersed throughout the bulk, no loss due to very small exciton diffusion lengths is expected, because ideally all excitons will be dissociated within their lifetime.

To evaluate the suitability of GZO films for bulk heterojunction OPV application, patterned GZO anodes were prepared on glass substrates. These devices were fabricated in collaboration with Prof. Veena Mishra’s research group [27]. Figure 4.13 shows schematics of the OPV structure discussed here. The pre-patterned substrates were cleaned by ultrasonic treatment in acetone and methanol followed by a UV–ozone treatment. These substrates were then spun coated with poly-3,4-ethylenedioxythiophene–poly-styrenesulphonate (PEDOT:PSS, Aldrich) at 4000 rpm for 40 s and annealed at 120°C for 1 h. For the active layer, 1 wt% of poly-3-hexylthiophene-2,5-diyl (P3HT, Rieke Metals) was blended with 0.8 wt% of 6,6-phenyl-C61-butyric acid methyl ester (PCBM, Nano-C) in 1,2-dichlorobenzene for 12 h inside a N$_2$-filled glove box. The PEDOT-coated ITO substrates were transferred into the glove box and
spun coated with the P3HT/PCBM blend at 600 rpm for 60 s [28]. Immediately after spin casting, these films were dried in a covered Petri dish for 20 min to yield 100 nm of the active layer. The samples were then briefly exposed to ambient air while being transferred into the thermal evaporator. Al was deposited through a shadow mask to define an active device area of 10 mm². No post metal anneal was done for the samples.

Figure 4.13. Schematics of the bulk heterojunction OPV structure. BHJ signifies the P3HT–PCBM bulk heterojunction layer.
Figure 4.14. Current density vs. voltage characteristics of a) GZO / P3HT–PCBM /Al with anneal after spinning polymer at 110°C for 10 minutes (preanneal) b) (Control) ITO/ P3HT–PCBM /Al, with anneal after spinning polymer at 110°C for 10 minutes, c) GZO/NiO_{1+x}/ P3HT–PCBM /Al, with anneal after spinning polymer at 110°C for 10 minutes. The OPVs have been measured at 1 sun (100 mW/cm²) simulated AM 1.5G irradiance. No post metal annealing was done for all cases.
Figure 4.14. shows the J–V characteristics under illumination for a GZO based OPV with annealing (fig. 4.14 (a)), without annealing (fig. 4.14 (b)), ITO based control OPV (fig. 4.14 (c)) and NiO/GZO based OPV. The open circuit voltage ($V_{OC}$), short circuit current ($J_{SC}$), efficiency ($\eta$), and the fill factor (FF) for both the devices are listed in table 4.3.

Table 4.3. The performance characteristics of OPVs

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/PEDOT (pre anneal)</td>
<td>6.92</td>
<td>0.53</td>
<td>33</td>
<td>1.2</td>
</tr>
<tr>
<td>GZO/PEDOT (no anneal)</td>
<td>4.02</td>
<td>0.35</td>
<td>28</td>
<td>0.39</td>
</tr>
<tr>
<td>GZO/PEDOT (pre anneal)</td>
<td>7.17</td>
<td>0.53</td>
<td>32</td>
<td>1.2</td>
</tr>
<tr>
<td>GZO/NiO (pre anneal)</td>
<td>7.00</td>
<td>0.44</td>
<td>50%</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The performance of the OPV devices based on GZO anode was optimized by changing the thickness of GZO film and annealing process of active layers. The optimized GZO thickness was about ~400 nm. It was observed that performance parameters including $\eta$ increased by annealing (preanneal) the device after spinning the polymer at 110°C for 10 minutes (table 4.3). The OPV performance with GZO anode at this condition was similar to the control device (ITO) and power conversion efficiency ($\eta$) of 1.2% was obtained. $V_{OC}$ up to 0.53 V was obtained. Further PEDOT was replaced by unoptimized NiO and the FF was found to increase by 17%. The efficiency increased to 1.6%. Increase in FF is attributed to the p-type nature and wide band gap of NiO, which reduces the recombination losses at the electrode interface. This act as a hole transporting layer while
effectively blocking the electrons. However, the \( V_{oc} \) has to be further improved by varying NiO thickness and doping. Moreover, S. Sarkar et al. has reported that the efficiency of a polymer OPV is enhanced by doing a post metal deposition anneal at 150\(^\circ\)C [29]. They have found \( \eta \) increased upto 2.8% by this post metal anneal approach. Moreover, the control device shows efficiency (\( \eta \)) lower than the typically reported values [29] because these devices were exposed to ambient conditions while being transferred into thermal evaporator. Hence, the efficiencies could be further improved by using a single glove box for the whole process.

With our GZO based devices also, the \( \eta \) is expected to show such an improvement, however, the post metal annealing process has to be optimized. These optimized GZO anode substrates should then be modified with optimized MoO\(_x\) and NiO\(_{1+x}\) layers to test their suitability for higher power conversion efficiency (\( \eta \)) of the OPV.

### 4.4 Conclusions

In summary, we have grown ZnGa\(_{0.05}\)O films with very thin MoO\(_x\) (~ 1-2 nanometers) top layer on glass and sapphire substrates at different conditions by PLD technique and investigated the effect of MoO\(_x\) layer on the physical properties of the bilayer film. All the films deposited on glass were highly oriented. This preferred [0001] orientation was due to the lowest surface energy of the basal plane and high energy of the ablated species. Excellent crystalline quality was found in the growth temperature range of 200\(^\circ\)C to 400\(^\circ\)C. From TEM results, 2-D (2-dimensional) growth mode of MoO\(_x\) on ZnGa\(_{0.05}\)O was observed. Different transport behavior of the MoO\(_x\)/ZnGa\(_{0.05}\)O films on glass was
observed at different $T_s$. The film at lower temperature $T_s \sim 200^\circ$C showed semiconducting behavior, whereas the film at $T_s \sim 400^\circ$C showed a metallic behavior beyond 113K. The bilayer films possess good transparency ($\geq 80\%$) and showed resistivity of ($\sim 2 \times 10^{-4}$ Ω-cm). It was found as $T_s$ increases, there is a slight increase in carrier concentration and the film showed their lowest resistivity and lower sheet resistance values ($\sim 2.5$ Ω/□). A significant observation was that the ZnGa$_{0.05}$O films with ultra thin MoO$_x$ ($\sim 1$-2 nanometers) overlayer showed higher work function as compared to the single layer ZnGa$_{0.05}$O film. The highest work function of 5.1 eV was achieved for the bilayer film grown at 400$^\circ$C. A correlation between the surface work function and MoO$_x$ layer thickness was observed. On the basis of these results, it is suggested that the work function of this composite TCO can be tuned by changing the deposition parameters and/or thickness of MoO$_x$ layer. Thus, by using a thin overlayer of MoO$_x$ on ZnGa$_{0.05}$O, a higher work function can be achieved without affecting the overall transmittance and sheet resistance. Results of test device structures of OPV with GZO based anode have demonstrated that MoO$_x$ (2-3 nm)/Zn$_{1-x}$Ga$_x$O anode results in higher open circuit voltage (Voc) and hence improved power conversion efficiency compared to GZO based OPVs. It has also been shown that by optimizing the film and active layer processing conditions, power conversion efficiencies comparable to ITO based OPVs (bulk heterojunction) can be achieved in GZO based OPVs. NiO$_{1+x}$/GZO based OPV showed enhancement of FF by 17%. Preliminary results show that Zn$_{1-x}$Ga$_x$O films have a potential to substitute ITO for transparent electrode applications.
Acknowledgments

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27. Prof. Veena Mishra research group, Department of electrical and computer engineering, North Carolina State university.


Chapter 5

High Work function (p-type NiO$_{1+x}$) / Zn$_{0.95}$Ga$_{0.05}$O heterostructure

Transparent Conducting Oxides

We report on the growth and properties of heterostructure thin films consisting of thin overlayers of p-NiO$_{1+x}$ on Zn$_{0.95}$Ga$_{0.05}$O (GZO) prepared by pulsed laser deposition (PLD) for transparent electrode applications. The GZO films with a thin p-type NiO$_{1+x}$ overlayer exhibited a higher work function that will facilitate hole injection across the heterojunction in a solid state device resulting in device efficiency improvement. Crystalline quality of the bilayer films were investigated by X-ray diffraction. The NiO$_{1+x}$ overlayers showed a preferred orientation along the NiO [111] direction on Zn$_{0.95}$Ga$_{0.05}$O (0001) deposited on the glass substrates while they were found to be epitaxial when the substrate used was sapphire (0001). Effects of the NiO$_{1+x}$ overlayer thickness variation and Li doping on the electrical and optical properties of NiO$_{1+x}$/Zn$_{0.95}$Ga$_{0.05}$O bilayer films were also investigated. Bilayer films with an optimized overlayer thickness showed good optical transparency ($\geq 85\%$) and low resistivity of $\sim 10^{-4} \, \Omega\text{-cm}$ to the temperatures as low as 100 K. Using X-ray photoelectron spectroscopy results, it has been established that nickel in the NiO$_{1+x}$ overlayer exists in multiple oxidation states of Ni$^{2+}$ and Ni$^{3+}$. The presence of Ni$^{3+}$ gives rise to p-type conductivity in non-stoichiometric NiO$_{1+x}$. The bilayer films also exhibited high work function values ranging from 5.2 to 5.3 eV in the ultraviolet photoelectron spectroscopy (UPS) studies. A correlation between the surface work function and Ni$^{3+}$/Ni$^{2+}$ ratio in NiO$_{1-x}$ layer has been established.
5.1. Introduction

Research on alternative transparent conducting oxides (TCOs) has attracted considerable attention due to serious concerns related to increased cost of indium tin oxide (ITO) and its chemical instability in a reducing ambient [1]. ZnO doped with group III elements (Al, Ga) have shown promising results when used as anode in organic solar cells (OSC), organic light emitting diodes (OLED) and other optoelectronic devices [2-4]. In our earlier work, we demonstrated that highly conducting and transparent Zn_{0.95}Ga_{0.05}O (GZO) can be deposited on single crystalline sapphire substrates as well as on glass substrates using pulsed laser deposition (PLD) technique [5,6]. It was found that the electrical properties of the TCO films are determined by the details of microstructure, stoichiometry and defects, which can in turn be controlled by the processing and substrate parameters. The formation of textured \(<0001>\) films on amorphous glass substrates poses a major technical challenge in terms of our ability to control the grain size (in nanometer range), texture, and grain boundary characteristics in these films for achieving superior properties and performance in devices such as solar cell. These nanocrystalline GZO films, deposited on glass substrate, were also tested for suitability as an anode of a double heterojunction OSC cell [7]. The power conversion efficiencies of GZO based cells were found to be comparable to those based on ITO, however, GZO based cells showed relatively higher contact resistance. Higher contact resistance was attributed to the energy level misalignment at the anode/organic layer interface which happens because of the lower work function of GZO anode layer. This suggests that, although low resistivity and high transmittance (\%T) are prerequisites for superior device performance, another critical parameter is the surface work function of the
Lower work function of the TCO anode layer makes it difficult to achieve ohmic contacts at the interface, which increases the series resistance and limits the realization of maximum theoretical open-circuit voltage ($V_{oc}$) in OSCs [8]. In case of OLEDs, lower work function of the TCO leads to a higher energy barrier for the hole injection into organic semiconducting layer, thereby increasing the operating voltage of the device [9, 10]. There have been several reports of pre-treating the ITO surface including the wet treatment [11], the low pressure plasma treatment [9], and the UV ozone treatment [12]. These pretreatment procedures increases the work function of ITO, but still the work function is not high enough to match the highest occupied molecular orbital (HOMO) level of the most commonly used hole transporting materials in OLEDs. Another approach that has been applied to reduce the hole injection barrier and enhance the power conversion efficiency, is to coat the TCO layer with a thin overlayer of metal/oxide having higher work function [13]. In a recent article, we have reported the growth of an alternative TCO consisting of a thin overlayer of n-type MoO$_x$ ($2.0 < x < 2.75$) on GZO by PLD which will lead to a higher work function ($\sim 5.1$ eV), without affecting the overall transmittance and sheet resistance [14].

Nickel oxide is a p-type semiconductor with band gap energy from 3.6 to 4.0 eV, which exhibits a high work function [15]. Although stoichiometric Nickel Oxide is an insulator with a resistivity of $10^{13}$ $\Omega$-cm at room temperature, its resistivity can be decreased by an increase in concentration of Ni$^{3+}$ ions or by doping Nickel Oxide with monovalent atoms like Li [16]. It has been reported that inserting a p-type NiO$_{1+x}$ interfacial layer on ITO can result in increased power conversion efficiencies in bulk-heterojunction (BHJ) solar cells [8], but ITO grows polycrystalline on glass. This same polycrystallinity is also observed in the NiO
overlayer. As the workfunction in NiO possesses crystallographic anisotropy [17], this may lead to surface fluctuations in the work-function of a NiO/ITO heterostructure configuration. In this study, we report the growth of thin-films heterostructure consisting of thin [111] oriented overlayer of p-NiO$_{1+x}$ on Zn$_{0.95}$Ga$_{0.05}$O (GZO) films prepared by PLD. Due to the non-equilibrium nature of the PLD growth technique, the defect concentration and non-stoichiometry of NiO$_{1+x}$ could be tuned by optimizing the deposition parameters such as oxygen gas pressure (P$_{O_2}$), substrate temperature (T$_s$) and O$_2$ nozzle placement with respect to the laser plume. We have also grown p-type Li$_{0.05}$Ni$_{0.95}$O as an overlayer to further decrease the resistivity of the NiO$_{1+x}$ so that the interfacial power losses can be minimized. The experimental results involving optical, structural, chemical (bonding state), electrical characterization and work-function measurements of NiO$_{1+x}$ / GZO and Li$_{0.05}$Ni$_{0.95}$O / GZO bilayers are presented. An attempt has been made to establish correlations between the processing parameters, structure and properties of the bilayer films for transparent electrode applications. The effect of varying the NiO$_{1+x}$ thickness on the electrical and optical properties of (NiO$_{1+x}$ / GZO) bilayer films has also been investigated.

5.2 Experimental Details:

GZO films with a thin NiO$_{1+x}$ overlayer were grown on c-plane (0001) sapphire as well as amorphous glass substrates. To enhance the overall room temperature conductivity, TCO films with Li (5 at%) doped NiO$_{1+x}$ overlayer were also deposited. A pulsed KrF excimer laser of wavelength 248 nm and pulse duration of 25 ns was used for the depositions. GZO, NiO$_{1+x}$ and Li$_{0.05}$Ni$_{0.95}$O targets used for deposition were prepared by conventional solid state
reaction technique. The deposition chamber was evacuated to a base pressure of $10^{-6}$ Torr. Subsequently, thin film growth was performed in O$_2$ with pressure in the range of $1.0-4.0 \times 10^{-3}$ Torr in order to vary the concentration of the defects which further influences the electrical and optical properties of the film. A laser energy density of 2-3 J/cm$^2$ and a pulse rate of 10 Hz and 5 Hz was used for GZO and NiO$_{1+x}$, respectively. The substrate temperature was varied between (200$^\circ$C – 400$^\circ$C). By depositing the GZO layer for 20 min, a thickness of ~600 nm was obtained. The thickness of the NiO$_{1+x}$ layer was carefully controlled in the range of (4- 25 nm) by adjusting the repetition rate and the number of pulses. A Rigaku Geigerflex diffractometer with Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) and a Ni filter was used for x-ray diffraction (XRD) ($\theta$-2$\theta$ scan). The x-ray phi scan measurements were carried out by using high-resolution XRD (Philips X’Pert PRO MRD HR). The surface morphology was determined using atomic force microscope (AFM) (Dimension 3100). The XPS analysis of the films was carried out in a Kratos Axis-Ultra DLD X-ray photoelectron spectrometer using Al K$_\alpha$ X-ray source. The oxidation states of the elements present in the film were analyzed by deconvolution using a Shirley routine and CASA software [18]. The values corresponding to the C 1s peak were used as a reference for the curve fitting analysis. Optical transmittance measurements were carried out as a function of wavelength in the range 200 –900 nm using a Hitachi U-3010 Spectrophotometer. The electrical resistivity of the films was measured using a four–probe technique in the temperature range of 15 K - 300 K. The contacts on the films were made using indium dots on the top layer for the electrical measurements. Hall measurement was also performed on these samples. The ultraviolet Photoelectron Spectroscopy (UPS) measurements were conducted with a Kratos Axis Ultra
DLD Ultraviolet Photoelectron Spectrometer equipped with a monochromatic He ultraviolet source He I (21.2 eV). A 5.0 V bias was applied to enhance the extraction of low kinetic energy (K.E.) electrons and to successfully determine the energy level of the low KE edge [19]. The Fermi edge for these samples was determined after sputter cleaning the surface of the samples with Ar⁺ ions for 2 min in Ultra high vacuum (UHV). The samples were mounted with Cu clips grounding the film surface to reduce the possibility of charging. A clean gold sample was used as a reference and proper connection of the samples on the same stub ensured that all the samples were in electronic equilibrium with the spectrometer.

5.3 Results and Discussion

5.3.1 Structural characterization

Figure 5.1 (a) and (b) show typical XRD patterns (θ-2θ scan) of the bilayer films (NiO₁₊ₓ (25 nm)/GZO) grown at 200°C on the c-plane sapphire and amorphous glass substrates, respectively. These XRD patterns indicate that the GZO and cubic NiO layers are singly oriented, normal to the film plane, in [0001] and [111] directions, respectively. The FWHM of the (0002) diffraction peaks corresponding to GZO obtained from the XRD spectra on sapphire and glass substrates is 0.23° and 0.27°, respectively. The sharp (0002) GZO peak suggests good crystalline growth both on sapphire and amorphous glass substrates at a lower temperature of 200°C. In our earlier work, it has been established using transmission electron microscopy studies that the GZO films grown at this temperature on glass substrates are highly textured along the [0001] direction [14]. It is concluded that NiO₁₊ₓ layers grown on textured GZO films would also be textured. The absence of additional peaks excludes the
possibility of any other phases of NiO\textsubscript{1+x} and suggests that NiO\textsubscript{1+x} layer has only one out of plane orientation on GZO layer on both the substrates. For the films with thin (~4nm) NiO\textsubscript{1+x} overlayer the intensity of the NiO\textsubscript{1+x} (111) peak was too small to observe in XRD scans although the presence of ultrathin NiO\textsubscript{1+x} overlayer was confirmed by the XPS measurements (discussed later). It should be noted that the work function of a material depends on the crystallographic orientation of the surface [17]. The resulting work-function difference between two surface orientations can be as high as 1eV [20]. Nickel oxide is known to have highest work-function in (111) orientation and here we are able to grow single orientation (111) NiO\textsubscript{1+x} on GZO layer.

![X-ray diffraction (θ-2θ scan) of NiO\textsubscript{1+x} (25 nm)/ GZO films on (a) sapphire and (b) glass substrates.](image)

Figure 5.1. X-ray diffraction (θ-2θ scan) of NiO\textsubscript{1+x} (25 nm)/ GZO films on (a) sapphire and (b) glass substrates.
Higher roughness of the anode layer can induce short-circuits in the device operation. We found lower surface roughness of GZO film at 200°C substrate temperature and for this reason this substrate temperature was chosen for the GZO layer in this work. The AFM images of the GZO and GZO with NiO\textsubscript{1+x} (8 nm) overlayer deposited on glass substrates at substrate temperature \( T_s = 200^\circ\text{C} \), are shown in Fig. 5.2 (a) and (b) respectively. The surface morphology of the GZO film shows smooth layer with average surface roughness (Ra) = 1.76 nm. The surface morphology of GZO film with NiO\textsubscript{1+x} (8 nm) overlayer did not show any appreciable change and the average surface roughness (Ra) was found to be 2.05 nm. The growth mode is envisaged to be two-dimensional. It is expected that smooth and uniform surfaces of TCO layer will give good interface properties with the organic layer of the device.

![AFM images](image)

**Figure 5.2.** AFM images (3 X 3 \( \mu \text{m}^2 \)) of (a) GZO film (b) NiO\textsubscript{1+x} (8nm)/ GZO bilayer film on glass substrates.
5.3.2 Electrical and optical characterization

Preliminary optimization of the NiO\(_{1+x}\) overlayer in terms of film conductivity and optical transparency was performed in separate NiO\(_{1+x}\) depositions on sapphire and glass substrates. The optimization was performed by varying the substrate temperature (\(T_s\)), O\(_2\) gas pressure (P\(_{O2}\)), and by directing the O\(_2\) nozzle towards the substrate holder near the substrate surface. These films were approximately 300 nm thick. The optimized NiO\(_{1+x}\) film showed a room temperature resistivity of 3 \(\Omega\)-cm and optical transparency of 70%. It was observed that with the increasing oxygen pressure during growth, resistivity of the NiO\(_{1+x}\) layer reduced. This decrease in the resistivity of non-stoichiometric NiO\(_{1+x}\) can be attributed to the increase in the concentration of Ni\(^{3+}\) ions due to the formation of Ni\(^{2+}\) vacancies and interstitial oxygen atoms, which contribute to the hole density in NiO\(_{1+x}\) [16]. The bilayer films (NiO\(_{1+x}\)/GZO) were characterized with NiO\(_{1+x}\) overlayers grown in varied oxygen pressure (P\(_{O2}\)). The quantification of Ni\(^{3+}\) present in NiO\(_{1+x}\) overlayers grown in different condition was done by XPS and is presented in the later section. To further increase the conductivity of the overlayer, NiO\(_{1+x}\) films were also doped with Li\(^{+}\). The room temperature resistivity of the Li\(_{0.05}\)Ni\(_{0.95}\)O films at optimized temperature and O\(_2\) pressure was found to be at least one order of magnitude lower than that of NiO\(_{1+x}\) films (2×10\(^{-1}\) \(\Omega\)-cm). The effect of NiO\(_{1+x}\) thickness variation on the electrical and optical properties of bilayer (NiO\(_{1+x}\)/GZO) films was also investigated. The electrical and optical characterizations of the films with three different thicknesses (4 nm, 8 nm and 25 nm) of NiO\(_{1+x}\) were performed.
Figure 5.3. Comparative UV-Vis transmission spectra of the GZO and the bilayer films on glass substrates. Sample description is below in table 5.1.

Figure 5.3 illustrates the transmission spectra of the bilayer (NiO_{1+x}/GZO) film with different NiO_{1+x} overlayer thicknesses and doping levels. Table 5.1 presents an average transmittance value for the films deposited under different conditions (details of these conditions along with sample description are listed in table 5.1 caption). It is observed that the GZO film (S1) shows an average ~ 87% transmittance in the visible region. Also, bilayer films with NiO_{1+x} overlayer showed no appreciable decrease in transmittance up to 8 nm thickness of NiO_{1+x} layer, which should allow the maximum photon flux to reach the active layer for photocurrent generation. As the thickness of the overlayer (NiO_{1+x} or Li_{0.05}Ni_{0.95}O) is further increased to 25 nm, the transmittance of the samples S5 and S6 reduces to 79% and 68%, respectively.
The GZO films showed measured sheet resistance of 1.8Ω/□, Hall mobility of 18 cm²V⁻¹s⁻¹ and carrier concentration of 1.1 × 10²¹ cm⁻³. The film thickness was kept around 600 nm to get a lower sheet resistance without degrading the transmittance. The GZO films have n-type conductivity with p-type NiO₁₊ₓ overlayers. The values of sheet resistance, carrier concentration and Hall mobility of these bilayer films are also summarized in table 5.1. It should be noted that the carrier concentration in GZO films with (NiO₁₊ₓ or Li₀.0₅Ni₀.₉₅O) overlayer thickness of 8 nm (S2, S3, S4, and S5) remained almost same as that of single layer GZO film. As the thickness of overlayer (NiO₁₊ₓ or Li₀.0₅Ni₀.₉₅O) was further increased to 25 nm, the effective carrier concentration of the films (S6 and S7) significantly reduced to the order of 10¹⁸ cm⁻³. This reduction in the overall carrier concentration can be attributed to the lower carrier concentration of p-NiO₁₊ₓ overlayer which might be affecting the overall carrier concentration measurement. Also, the Hall mobility decreased only marginally in the bilayer configurations when compared to the single layer GZO film as shown in table 5.1.

Figure 5.4 shows the temperature dependence of resistivity for the bilayer (NiO₁₊ₓ/ GZO) film (S6). The film showed metal like conductivity behavior above 100 K. The metal like conductivity can be explained on the basis of a degenerate band formation in heavily doped semiconductors as suggested, by Mott [21]. Similar behavior has been observed in our earlier work [5, 14]. The effective room temperature resistivity of the bilayer configuration sample (S6) estimated from the resistivity measurement (Fig.5.4) was 2.2 × 10⁻⁴ Ω-cm which is of the same order as that of GZO film.
Table 5.1. Summary of electrical and optical properties for NiO\(_{1+x}\)/GZO films at different growth conditions and different NiO\(_{1+x}\) thickness. Sample description as follows: S1: GZO ; S2: NiO\(_{1+x}\) (4 nm)/ GZO ; S3: NiO\(_{1+x}\) (8 nm)/ GZO (P\(_{O2(NiO)}\) = 10\(^{-3}\) Torr) ; S4: NiO\(_{1+x}\) (8 nm)/ GZO (P\(_{O2(NiO)}\) = 7\times 10\(^{-2}\) Torr) ; S5: Li\(_{0.05}\)Ni\(_{0.95}\)O (8 nm)/ GZO (P\(_{O2(NiO)}\) = 7\times 10\(^{-2}\) Torr); S6: NiO\(_{1+x}\) (25 nm)/ GZO; S7: Li\(_{0.05}\)Ni\(_{0.95}\)O (25 nm)/ GZO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO(_{1+x}) thickness</th>
<th>Sheet Resistance (\Omega/\square)</th>
<th>Hall mobility (\mu) (cm(^2)V(^{-1})s(^{-1}))</th>
<th>Carrier Concentration (N) (cm(^{-3}))</th>
<th>Transmittance (%)T</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 : GZO</td>
<td>0nm</td>
<td>1.8</td>
<td>18</td>
<td>1.1\times 10(^{21})</td>
<td>87</td>
</tr>
<tr>
<td>S2 : NiO(_{1+x})/ GZO</td>
<td>4nm</td>
<td>1.9</td>
<td>16.0</td>
<td>1.1\times 10(^{21})</td>
<td>87</td>
</tr>
<tr>
<td>S3 : NiO(_{1+x})/ GZO</td>
<td>8nm</td>
<td>1.8</td>
<td>16.9</td>
<td>1.2\times 10(^{21})</td>
<td>86</td>
</tr>
<tr>
<td>S4 : NiO(_{1+x})/ GZO</td>
<td>8nm</td>
<td>1.7</td>
<td>16.6</td>
<td>1.2\times 10(^{21})</td>
<td>87</td>
</tr>
<tr>
<td>S5 : LiNiO/ GZO</td>
<td>8nm</td>
<td>1.8</td>
<td>16.4</td>
<td>1.3 \times 10(^{21})</td>
<td>88</td>
</tr>
<tr>
<td>S6 : NiO(_{1+x})/ GZO</td>
<td>25nm</td>
<td>1.8</td>
<td>16.8</td>
<td>1.1 \times 10(^{18})</td>
<td>79</td>
</tr>
<tr>
<td>S7 : LiNiO/ GZO</td>
<td>25nm</td>
<td>1.7</td>
<td>16.7</td>
<td>2.1 \times 10(^{18})</td>
<td>68</td>
</tr>
</tbody>
</table>

The effective sheet resistivity measured by the four probe technique is assumed to result from the resistivity of individual layers coupled in parallel. It is, therefore, envisaged that the sheet resistance of the bilayer films will be limited by the sheet resistance of the thick GZO underlayer and that most of the current should pass through this layer during the four probe measurement. Our resistivity and carrier concentration values of the deposited films at 200\(^{\circ}\)C are similar to the values reported \((\rho = 2.2 \times 10^{-4} \ \Omega\text{-cm}, \ N_e = 1.3 \times 10^{21} \ \text{cm}^{-3}\)\) in case of Aluminium or Gallium doped ZnO [22,23]. Our mobility values are also similar to the reported value \((\mu = 18 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1})\) by Fortunato et al. [22] and comparable to the reported value \((\mu = 24.6 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1})\) with similar dopant concentration by Cornelius et al. [24].

It should be noted that the electron mobility is controlled by the dopant concentration and the
best mobility values are obtained with lower dopant concentrations [24]. We also found that improved crystallinity of the films grown at higher deposition temperature ($T_s = 400^\circ$C) led to an increase in mobility values to $21 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It is worth mentioning that the mobility values obtained for (NiO$_{1+x}$/ GZO) films are $\sim$50% higher than the (MoO$_x$/ GZO) bilayer films (the data shown in chapter 4). In terms of resistivity and optical transmittance behavior, films with NiO$_{1+x}$ overlayer thickness of (4-8 nm) showed the optimum results. Surface characterization results for this optimized overlayer thickness of the bilayer films are presented and discussed in the following section.

![Resistivity vs temperature for NiO$_{1+x}$ (25 nm)/ GZO heterostructure film.](image)

**Figure 5.4. Resistivity vs temperature for NiO$_{1+x}$ (25 nm)/ GZO heterostructure film.**

### 5.3.3 Surface characterization

The detailed analysis of thin NiO$_{1+x}$ overlayer was performed by the XPS measurements. The XPS results discussed here are from GZO and bilayer films (NiO$_{1+x}$ (8 nm)/ GZO) at
different growth parameters (S1, S3, S4 and S5). Figure 5.5(a–d) shows the XPS survey spectra of these films grown at 200°C on glass.

![Survey XPS spectrum from the surface of (a) S1: GZO film, (b) S3: NiO_{1+x} (8nm)/ GZO film, (c) S4: NiO_{1+x} (8nm)/ GZO film, (d) S5: Li_{0.05}Ni_{0.95}O (8nm)/ GZO film.](image)

Figure 5.5. Survey XPS spectrum from the surface of (a) S1: GZO film, (b) S3: NiO_{1+x} (8nm)/ GZO film, (c) S4: NiO_{1+x} (8nm)/ GZO film, (d) S5: Li_{0.05}Ni_{0.95}O (8nm)/ GZO film.

As shown in Fig. 5.5(a), the Ga 2p_{3/2} and Ga 2p_{1/2} peaks were found to be at 1116.7 eV and 1143.6 eV, respectively, which suggests the presence of Ga in +3 valence state [6]. Ga^{3+} in GZO films acts as donor and effectively increases the carrier concentration. The peak positions corresponding to Ni 2p, Ni 3p, Ni 3s and O 1s for sample S3, S4 and S5 (Fig. 5.5(b), (c), (d)) clearly indicate the growth of a nickel oxide layer on the GZO layer. XPS data also confirms the absence of any impurity elements.
From the XRD data, only the peaks associated with Ni$^{2+}$ bonding state (from NiO) were detected, indicating the presence of a single nickel oxide phase. However, the presence of Ni$^{3+}$ oxidation state has been verified in high-resolution Ni 2p core level spectrum (as shown in Fig. 5.6). The presence of Ni$^{3+}$ ions is known to give rise to p-type conductivity in non-stoichiometric NiO$_{1+x}$ [16]. The spectrum consists of complex mixture of Ni 2$p_{3/2,1/2}$ spin-doublets of Ni in its multiple oxidation state of +2 and +3. The Ni 2$p_{3/2}$ oxidation states have been resolved by using a non-linear curve fitting technique (Fig. 5.6). The Ni$^{2+}$ (2$p_{3/2}$) and Ni$^{3+}$ (2$p_{3/2}$) peaks are observed at 853.7 eV and 855.4 eV, respectively. The broad peak at 860.8 eV is designated to be electron loss peak [25]. The corresponding fraction of different oxidation states of Ni 2p in NiO$_{1+x}$ overlayer and the ratio of Ni$^{3+}$/Ni$^{2+}$ is summarized in table 5.2 for samples S3, S4 and S5. The relative concentration of the multiple oxidation states of Ni has been determined by calculating the area under the resolved peaks. There is no significant peak shift observed in Ni 2$p_{3/2}$ spectrum with the change in oxygen pressure (PO$_2$) during growth, but the relative concentration of Ni$^{2+}$ (2$p_{3/2}$) and Ni$^{3+}$ (2$p_{3/2}$) did change. As shown in table 5.2, the Ni$^{3+}$/Ni$^{2+}$ ratio increased with increase in Po$_2$ during the growth of NiO$_{1+x}$ layer. It should be noted here that the film with higher Ni$^{3+}$/Ni$^{2+}$ ratio would be more conductive. This behavior was confirmed in separate NiO$_{1+x}$ thin film depositions as mentioned in previous section.

The effective work functions of these modified surfaces of GZO /glass are determined by UV-photoelectron spectroscopy using He (I) excitation source (21.2 eV). Figure 5.7
compares UPS spectra of GZO and surface modified GZO, i.e., NiO$_{1+x}$/GZO at different growth conditions. The work function ($\Phi_{\text{GZO}}$) of all the samples is determined by the difference between the width of the photoemission spectrum and the source energy;

$$\Phi_{\text{GZO}} = 21.2 \text{ eV} - t$$ (5.1)

where $t$ is the difference between the Fermi edge energy ($E_f$) and the lowest kinetic energy edge ($E_{K,E}$) of the UPS spectra [26].

Figure 5.6. High-resolution XPS spectra of Ni 2p peak from the surface of S4: NiO$_{1+x}$ (8nm)/GZO film.
It is revealed from the UPS spectra that the lowest kinetic energy edge for the bilayer films shifts towards a higher energy value, resulting in the higher effective work functions than the GZO films. The work function values of the GZO and bilayer films are summarized in table 5.2. The work functions of the bilayer films were obtained in the narrow range from 5.2 to 5.3 eV. The work function values for these bilayer films are higher than those reported for nickel oxide (~ 5.0 eV) by Olivier et al. [27] and similar to those reported by Yun et al. [28].

Figure 5.7. Comparative UPS spectra of (a) S1: GZO film, (b) S3: NiO$_{1+x}$ (8nm)/ GZO film, (c) S4: NiO$_{1+x}$ (8nm)/ GZO film, (d) S5: Li$_{0.05}$Ni$_{0.95}$O (8nm)/ GZO film.

Moreover, the work function values are higher than the MoO$_x$ modified GZO films. In the present work, the film with higher Ni$^{3+}$/Ni$^{2+}$ ratio in NiO$_{1+x}$ layer showed higher work function (table 5.2). In comparison to NiO$_{1+x}$ the work function increase for the Li$_{0.05}$Ni$_{0.95}$O overlayer though marginal was too small to quantify assertively. The increase in the Ni$^{3+}$/Ni$^{2+}$ ratio resulting in higher hole concentration leads to lowering of the Fermi level and increase in work function.
Table 5.2. Values of work function determined from UPS spectra and Ni 2p bonding states from XPS spectra for different growth conditions. $E_F$ denotes the Fermi edge energy which was 25.5 eV and $E_{K,E}$ represents the lowest kinetic energy edge of the UPS spectra.

<table>
<thead>
<tr>
<th></th>
<th>$E_{K,E}$</th>
<th>WF (eV)</th>
<th>Ni$_{2+}$ (2p)</th>
<th>Ni$_{3+}$ (2p)</th>
<th>Ni$<em>{3+}$/Ni$</em>{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1: GZO</td>
<td>8.9</td>
<td>4.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S3: NiO$_{1+x}$/GZO</td>
<td>9.5</td>
<td>5.20</td>
<td>13.0%</td>
<td>31.9%</td>
<td>2.5</td>
</tr>
<tr>
<td>S4: NiO$_{1+x}$/GZO</td>
<td>9.6</td>
<td>5.30</td>
<td>12.8%</td>
<td>43.2%</td>
<td>3.4</td>
</tr>
<tr>
<td>S5: LiNiO/GZO</td>
<td>9.63</td>
<td>5.33</td>
<td>11.0%</td>
<td>44.0%</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The typical highest occupied molecular orbital (HOMO) level of the organic donor layer in case of OSCs is ~ (5.0 - 5.2 eV) [8,29]. The work function of the modified TCO (NiO$_{1+x}$/GZO) in the range of (5.2 eV – 5.3 eV) would align well with the HOMO level of the organic donor layer. This would result in an efficient hole injection/collection contact with the active layer reducing the barrier at the interface. This should increase the $V_{oc}$ and enhance the power conversion efficiency of the solar cell. NiO$_{1+x}$, being a wide band gap semiconductor, can also serve as an effective electron blocking layer in the present BHJ devices. Higher mobility and higher work function of (NiO$_{1+x}$/GZO) films compared to (MoO$_x$/GZO) films suggest that NiO$_{1+x}$ can be a suitable overlayer on GZO, and better device results could be obtained by tuning its physical properties.
5.3.4 Conclusions

We have grown GZO films with very thin NiO$_{1+x}$ overlayer on glass and sapphire substrates at different conditions by PLD process for transparent electrode application in the OSC cells and optoelectronic devices. The bilayer films have low roughness and have good crystalline quality at growth temperatures ($T_s$) as low as 200$^\circ$C. The GZO films deposited on glass were highly textured and oriented in the [0001] direction. NiO$_{1+x}$ layer shows preferred orientation along [111] direction on GZO (0001) and this crystallographic orientation possesses relatively higher work function with respect to the other orientations. The GZO films with very thin NiO$_{1+x}$ overlayer grown on sapphire substrates were found to be epitaxial. The effect of varying the NiO$_{1+x}$ thickness and doping (Li$_{0.05}$Ni$_{0.95}$O) on the electrical and optical properties of (NiO$_{1+x}$/GZO) bilayer films has also been investigated and optimum results were found for the thickness range of (4 -8 nm). The bilayer films with optimum overlayer thickness possess good transparency ($\geq$ 85%) and showed measured resistivity $\sim 2 \times 10^{-4}$ $\Omega$-cm. NiO$_{1+x}$ modified GZO films showed higher work function (5.2 -5.3 eV) as compared to the single layer GZO film (4.6 eV). The oxygen pressure during the growth of NiO$_{1+x}$ layer seems to affect the Ni$^{3+}$/Ni$^{2+}$ ratio. We have shown that a higher fraction of Ni$^{3+}$ in the film, which results in higher hole concentration, leads to higher conductivity of NiO$_{1+x}$ overlayer and higher work function of the bilayer film.

Acknowledgments

The authors are also grateful to Carrie Donley of CHANL facility (at UNC Chapel Hill) for her help in UPS measurements.
References


Chapter 6

P-type NiO thin films growth and characterization on c-sapphire and glass substrates.

In this chapter, the results of epitaxial growth of cubic NiO thin films on c-plane sapphire ($\alpha$-Al$_2$O$_3$) and glass substrates by pulsed laser deposition technique are presented. Epitaxial nature of the films on sapphire was determined by x-ray $\phi$ scan and electron diffraction data from high resolution transmission electron microscopy (HRTEM) technique. Growth of NiO occurs epitaxially in [111] direction with two types of crystalline grains rotated by 60° with respect to each other. Size of each of these crystalline domains is in the range of 30-60 nm and they are uniformly distributed throughout the film. Selected area diffraction pattern revealed the following epitaxial relationship: (a) [111]$_{\text{NiO}}$ || [0001]$_{\text{Al}_2\text{O}_3}$ (out of plane) (b) [110]$_{\text{NiO}}$ || [01\overline{1}0]$_{\text{Al}_2\text{O}_3}$ and [210]$_{\text{NiO}}$ || [21\overline{1}0]$_{\text{Al}_2\text{O}_3}$ (in plane). The films grown on glass substrates were polycrystalline. The films were optically transparent in UV-Vis region with maximum transmittance of ~83% and the films showed p-type conductivity with minimum resistivity of 3 $\Omega$-cm. Further optimization of these properties is expected to result in applications utilizing p-type transparent conductors.
6.1 Introduction

Nickel oxide (NiO) is a p-type semiconductor with band gap energy ranging from 3.6 to 4.0 eV [1, 2]. It exhibits interesting electrical, optical and magnetic properties and has excellent chemical stability and hence, it has been widely investigated for potential applications in spin-valve giant magneto resistance (GMR) sensor [2], gas sensors [3], electrochemical display devices [4] and p-type transparent conducting electrodes [1]. NiO films also exhibit large work function and have been widely studied as contact materials to $p$-GaN in LEDs [5].

Various deposition techniques have been employed for the thin film growth of NiO [6, 7]. Pulsed laser deposition (PLD) has an advantage of growing epitaxial films at lower substrate temperatures than other methods [8]. From this point of view, the present work investigates the epitaxial growth of cubic NiO thin films on c-plane sapphire ($\alpha$-Al$_2$O$_3$) using PLD. In case of heteroepitaxial growth, growth orientations are often explained in terms of lattice symmetry and lattice mismatch between the film and the substrate. NiO has a cubic rock salt crystalline structure with lattice constant of 0.417 nm. Epitaxial growth of NiO on c-plane sapphire (which is a rhombohedral system, with lattice parameters $a = 4.758$ nm, $c = 12.991$ nm) makes it an interesting system to study in terms of lattice symmetry.

In this paper, we report that NiO (111) planes align perpendicular to the c-axis of $\alpha$-Al$_2$O$_3$. Interestingly, it is found that in the film plane, NiO films have two possible
orientations with one orientation rotated by 60° from the other. Epitaxial relationship of NiO on c-plane sapphire has also been explained on the basis of domain matching epitaxy (DME) paradigm in this study [9]. The physical properties such as optical absorption and electrical resistivity were measured and the effect of deposition parameters on the variation of these properties was studied.

6.2 Experimental details

A pulsed KrF excimer laser of wavelength (248 nm) and pulse duration (25 ns) was used for the deposition. A laser energy density of 2 J/cm² with a pulse rate of 5 Hz was used. The target to substrate distance of ~4.1 cm was maintained. NiO target was prepared by conventional solid state reaction technique. Sapphire substrates were cleaned ultrasonically in acetone and methanol sequentially before being transferred to the deposition chamber. The chamber was evacuated to a base pressure of 10⁻⁶ Torr prior to the growth. Substrate temperature was raised to 350°C and oxygen gas was subsequently introduced to maintain a pressure of 1.0 x 10⁻⁴ Torr. Films were deposited by ablating the NiO target. Maintaining a proper oxygen pressure is essential to control defects in the NiO films. A Rigaku Geigerflex diffractometer with Cu Kα radiation (λ = 1.54 Å) was used to obtain x-ray diffraction (θ-2θ scan) data. X-ray φ scan measurements were carried out using high-resolution XRD instrument (Philips X’Pert PRO MRD HR). Cross-sectional samples of these films were characterized by a JEOL-2010 field emission transmission electron microscope (TEM) with Gatan image filtering. Optical
transmittance measurements were carried out as a function of wavelength in the range 200–900 nm using a Hitachi U-3010 Spectrophotometer.

6.3 Results and discussion

6.3.1 Structural Characterization

Figure 6.1 shows the x-ray θ-2θ scan of the NiO film grown on c-plane Al₂O₃ substrate. It is evident that the growth of cubic NiO films occurs in [111] direction normal to the film plane. The sharp NiO (111) peak suggests good crystalline quality of the films. In this scan, no additional peaks were observed which excludes the possibility of formation of any other phase.

Figure 6.1. X-ray diffraction (θ-2θ scan) of NiO films on [0001] α-Al₂O₃.
To further investigate the in-plane orientation and establish the epitaxial growth of the film, high resolution x-ray \( \phi \) scan and HRTEM studies were carried out. \( \phi \) scans were performed for the (200) reflection of NiO film and the (1\( \bar{1} \)02) reflection of Al\(_2\)O\(_3\) substrate which are inclined at \( \psi = 54.73^\circ \) and 57.61\(^\circ\) respectively from the growth plane. The substrate reflection exhibited threefold symmetry about the film normal \( <111> \) rotation axis. From fig.6.2, it can be observed that 6 diffraction peaks from NiO (200) reflection are present at discrete values of \( \Phi \), separated by 60\(^\circ\). Since (111) planes of cubic NiO have threefold symmetry, six fold symmetry of NiO (200) reflections about the film normal \( <111> \) suggests the following possibilities: (a) NiO film growth takes place epitaxially where two types of domains have 60\(^\circ\) in-plane rotation with respect to each other about the [111] growth direction or, (b) the presence of twins in NiO (111) planes where the twinned crystal is rotated by 60\(^\circ\) with respect to the original underlying crystal about the [111] growth direction. Both of these possibilities have been observed in our TEM results and discussed in the following section.
Figure 6.2. Azimuthal (Φ scan) of (111) oriented NiO films a) (102) sapphire, at 2θ = 25.58°, and Ψ = 57.61°, (b) (200) NiO, at 2θ = 43.28°, and Ψ = 54.73°.

The selected area electron diffraction (SAED) pattern from a large area cross-section of the film interface is shown in fig.6.3(a). Analysis of the diffraction pattern reveals that the zone axes of NiO and α-Al₂O₃ are [110] and [0110], respectively and (224) planes of NiO are aligned with (2110) planes of α-Al₂O₃ with [111]_{NiO} || [0001]_{Al₂O₃}. It should be noted here that there are two sets of spots that are indicated by different color line pattern in fig.6.3(a). These two sets of pattern belong to the same [110] zone axis of NiO, but they are mirror to each other in (111) plane.
Two dark field transmission electron micrographs of the same region in NiO/ [0001] α-Al₂O₃ film were acquired by selecting the individual sets of f.c.c electron diffraction spots as shown in fig.6.3(a). The image contrast inversion in these dark field micrographs (shown in fig.6.3 (b), (c)) confirms the presence of two domains. It can also be observed that the domain size varies from (30 – 60) nm. The two different regions have statistically uniform distribution due to random nucleation probability inherent to the growth process. It should be noted that the domain boundaries are not distinctly sharp owing to the fact that these boundaries can run in any direction leading to an overlap of neighboring domains in the projected TEM zone direction. From the TEM results, the thickness of the film is estimated to be ~ 80 nm.
Figure 6.3 (a) Selected area diffraction pattern of the interface of NiO on [0001] \( \alpha \)-Al\(_2\)O\(_3\). Red and green line pattern indicates the two sets of f.c.c spots from the same zone of NiO [110]. The two patterns are mirror image of each other about the plane indicated by blue dashed lines (b) and (c) Dark filed images of NiO on [0001] \( \alpha \)-Al\(_2\)O\(_3\) obtained by selecting neighboring spots from two individual sets of f.c.c pattern. The arrow indicates the contrast reversal of the same region by the reflection of the neighboring spots.
Figure 6.4.(a) High-resolution transmission electron micrograph of a cross-sectioned sample of NiO/ [0001]α-Al₂O₃ showing the interface, (b) Inverse fast Fourier transform image obtained by selecting NiO (200) and sapphire (21-10) diffraction spots indicating that twelve NiO planes match thirteen sapphire planes across the interface. (c) High-resolution transmission electron micrograph of a cross-sectioned sample of NiO/ [0001]α-Al₂O₃. The arrow indicates the twin lying in (111) plane.

A high resolution transmission electron micrograph presented in fig.6.4 (a) shows a sharp NiO/Al₂O₃ interface with no evidence of any interfacial reaction.
Figure 6.5(a). Schematic showing different f.c.c orientations. A, B, C are the lattice positions in a closed-packed plane. Blue color balls denotes 1st monolayer, green color balls denotes 2nd monolayer and red color balls denotes 3rd monolayer from the surface. m shows the crystallographic mirror plane (b) twin stacking configuration, (c) Schematic of the NiO(111) and the basal plane of α-Al2O3 showing the orientation relationship. The misfit values are calculated by considering the closest matching planes.

The occurrence of two in-plane orientations can be explained by possible stacking sequences in the [111] direction which make up an fcc structure. Any fcc on a hexagonal system (0001) or rhombohedral (001) when grows in [111] direction has two possible orientations. An fcc structure is described as having an ABCABC… type stacking in the closed packed direction. During the nucleation on the closed packed plane (cpp) of Al2O3, the first monolayer plane sets in one orientation which is the same everywhere if the substrate surface has no steps. Fixing this first monolayer cpp as reference and denoting it as A, the next cpp monolayer can settle in a B or a C type position. Upon further growth in [111] direction the fcc can orient itself either in ABCABC… or ACBACB… type stacking. These two possibilities are random in nature and manifest themselves in two different orientations of fcc structure which have 60° in-plane rotation with respect to each other (fig.6.5(a)). The crystallographic mirror plane ‘m’ in the fig.6.5(a) is equivalent to a 60° rotation of f.c.c about [111] direction. The grain boundary between two such oriented grains can run in any in-plane direction. Interestingly there is a
possibility that one of the orientation grows on top of the other as in the situation where a growing ABCABC… type stacking faults and it generates the twin and continues as ACBACB… type stacking (fig.6.5(b)). For better understanding, we have demonstrated the crystal projection of NiO and sapphire (0001) in NiO [110] zone (fig.6.6). This model shows the atomic arrangements of NiO (111), NiO (100) and Sapphire (0001) planes. It clearly shows that the (100) and (111) planes of NiO from both the domains have mirror symmetry about [111] direction.

Figure 6.6. Crystal projection of NiO and sapphire (0001) in NiO [110] zone, showing two twinned grains of NiO having mirror (180°) symmetry with respect to each other.

Our cross-section TEM micrograph taken in [110] zone direction shows this type of fault (fig.6.4 (c)). In this case the (111) growth plane is the twin plane and the corresponding
diffraction pattern obtained is shown in fig. (6.3(a). The twin boundary is indicated by an arrow in fig.6.4 (c). The original grain and the twinned region on top of it also have a 60° rotation with respect to each other about the growth direction.

It should be noted that the diffraction pattern obtained by a twinned structure is exactly the same as case where these two orientations are present in individual grains and their diffraction pattern is superimposed. The FFT diffraction patterns from the regions across the twin boundary are 180° mirror image of each other about (111) growth plane as shown in fig.5 (marked as 1 and 2). These two diffraction patterns upon superimposition will result in the same diffraction pattern as that shown in fig.6.3 (a). Figure 6.4(b) shows the presence of such two grains and following the growth up to (8-10) nm, one grain deforms the other and creates a fault in the other grain leading to a (111) plane deformation twin. The region where both of the grains are over each other in the cross-section sample we can see Moiré fringes because of the superposition of atomic columns.

From the analysis of φ scan and the SAED pattern, it can be concluded that NiO grows epitaxially on [0001] α-Al₂O₃ with the following orientation relationship: (a) [111]_{NiO} || [0001]_{Al₂O₃} (out of plane) (b) [110]_{NiO} || [01\bar{1}0]_{Al₂O₃} and [210]_{NiO} || [21\bar{1}0]_{Al₂O₃} (in plane). This epitaxial relationship is known as 30° or 90° rotation, where NiO rotates by 30° in the basal c-plane of α-Al₂O₃ [9]. These 30° and 90° directions are equivalent in hexagonal structure. The epitaxial growth of (111) NiO on (0001) α-Al₂O₃ can be explained in the
framework of DME, where matching of planes is taken into account instead of lattice matching [9]. The misfit between NiO and \(\alpha\)-Al\(_2\)O\(_3\) is 7.5\% in both the in-plane direction (fig.6.5(c)). Along the [21\(\bar{1}\)0] direction, twelve NiO (110) planes match with thirteen \(\alpha\)-Al\(_2\)O\(_3\) (30\(\bar{3}\)0) planes. Similarly, along the [01\(\bar{1}\)0] direction, twelve NiO 3-(224) planes match with thirteen \(\alpha\)-Al\(_2\)O\(_3\) 1/2(21\(\bar{1}\)0) planes. To observe matching of planes at the NiO/ [0001]\(\alpha\)-Al\(_2\)O\(_3\) interface, the diffraction spots from the NiO (200) and sapphire (21-10) planes were masked in the fast Fourier transform in order to form an inverse fast Fourier transform (IFFT) image (fig.6.4(b)). Twelve (200)\(_{\text{NiO}}\) planes matching thirteen (21\(\bar{1}\)0)\(_{\text{Sap}}\) planes between (200)\(_{\text{NiO}}\) and (21\(\bar{1}\)0)\(_{\text{Sap}}\) planes can be observed in this image. This result confirms domain matching epitaxial growth of the Nickel oxide film in the NiO/ [0001]\(\alpha\)-Al\(_2\)O\(_3\) heterostructure.

Nickel oxide films were also grown on glass substrates. X-ray diffraction patterns from films grown at different substrate temperature didn’t show any peak suggesting the possibility of either amorphous nature or random orientation of grains in the film. For detailed microstructural analysis, TEM was done on a plan view sample. Figure 6.7 (a) shows the indexed SAED pattern of the film. Continuous ring pattern indexed to (111), (200) and (220) planes shows polycrystalline nature of the film. Figure 6.7 (b) shows the plan view TEM micrograph of the film. The average grain size of the film varies from 50 to 150 nm.
6.3.2 Electrical and optical properties

The optical transmittance of NiO$_{1+x}$ thin films deposited at different substrate temperatures, $T_s$ in the wavelength range of 200-900 nm is shown in fig.6.8 (a). All the films were ~350 nm thick. The films showed blue shift in the absorption edge with increasing substrate temperatures, $T_s$. Transmittance of the film increased with increasing $T_s$ and the film deposited at $T_s = 450^\circ$C showed average transmittance as high as 83%. Fig.6.8(b) also shows the % transmittance dependence of the films at ($\lambda = 650$ nm) with respect to in-growth O$_2$ partial pressure (PO$_2$). As we can see, optical transmittance of NiO$_{1+x}$ films decreases with increasing oxygen pressure.
Figure 6.8. UV-Vis transmission spectra of NiO thin films at different a) substrate temperatures, b) oxygen pressures.
Corresponding blue shift in the absorption edge at elevated substrate temperatures can be attributed to improved crystallinity and less stoichiometric defects that cause band tailing. It is known that stoichiometric NiO film is an insulator with a room temperature resistivity value of about $10^{13} \, \Omega\cdot\text{cm}$ [10]. But if the sufficient concentration of Ni$^{2+}$ vacancies is present, nickel oxide (non-stoichiometric) can exhibit p-type extrinsic semiconductor. The resistivity of NiO thin films has been reported to be in the range of $10^1 - 10^6 \, \Omega\cdot\text{cm}$ [11]. The lowest room temperature resistivity of undoped NiO in our case is 3 $\Omega\cdot\text{cm}$. The carrier concentration type was confirmed to be p-type by Hall measurement. The optimized conductivity of NiO film was achieved by varying the substrate temperature ($T_s$) and in-growth $O_2$ partial pressure ($P_{O_2}$). The correlation between p-type conductivity and its chemical composition is discussed in chapter 4 and 9.

### 6.4 Conclusions

In summary, we have investigated the microstructural characteristics of NiO thin films grown by PLD on c-plane $\alpha$-Al$_2$O$_3$. Our $\phi$ scan and TEM results show that the growth of NiO is epitaxial in $[111]$ direction with two types of crystalline grains rotated by 60° with respect to each other. Our cross-sectional HRTEM results also show that deformation twinning takes place in (111) growth plane of NiO. Transmission electron microscopy showed the following epitaxial relationship: (a) $[111]_{\text{NiO}} \parallel [0001]_{\text{Al}_2\text{O}_3}$ (out of plane) (b) $[110]_{\text{NiO}} \parallel [0\overline{1}\overline{1}0]_{\text{Al}_2\text{O}_3}$ and $[210]_{\text{NiO}} \parallel [2\overline{1}\overline{1}0]_{\text{Al}_2\text{O}_3}$ (in plane). The films were optically transparent in UV-Vis region with maximum transmittance of $\sim$83% and the films showed p-type conductivity with minimum resistivity of 3 $\Omega\cdot\text{cm}$. 

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Chapter 7

Effect of Li doping in NiO thin films on its transparent and conducting properties

Li doped NiO (Li$_x$Ni$_{1-x}$O) thin films were epitaxially grown along [111] orientation on c-sapphire by pulsed laser deposition (PLD). The structural, electrical and optical properties of the films were investigated using X-ray diffraction (XRD), four probe technique and UV-visible spectra, respectively. The epitaxial growth of [111] NiO on [0001] sapphire was determined by using high resolution x-ray Φ scan. Effects of the deposition condition and Li doping concentration variations on the electrical and optical properties of Li doped NiO films were investigated. The analysis of the resistivity data show that doped Li ions occupy the substitutional sites in the films, enhancing the p-type conductivity. The minimum resistivity of 0.15 Ω-cm was obtained for Li$_{0.07}$Ni$_{0.93}$O film. The activation energy of Li doped NiO films were estimated to be in the range of 0.11-0.14 eV. Based upon these values, a possible electrical transport mechanism is discussed.
7.1. Introduction

Nickel oxide, a p-type semiconductor with band gap energy from 3.6 to 4.0 eV, is a promising candidate for transparent conducting oxide (TCO) applications\(^1\). Although, stoichiometric NiO is an insulator with a resistivity of \(10^{13} \Omega\text{-cm}\) at room temperature, its resistivity can be decreased by increasing the concentration of Ni\(^{3+}\) ions, which results from the introduction of nickel vacancies, or can be achieved by doping NiO with monovalent atoms like Li\(^2\). The Li doped NiO (Li\(_x\)Ni\(_{1-x}\)O) finds potential applications in smart windows and anti-dazzling devices for vehicles\(^3\,^4\). It can also be used for high-performance thermoelectric devices\(^5\), cathodes of molten carbon fuel cells\(^6\), and sensors for various gases such as hydrogen\(^7\). NiO\(_{1+x}\) has also been used as an interfacial layer at anode contact in organic solar cells\(^8\) and organic light emitting diodes (OLEDs)\(^9\). Chan et al.\(^9\) reported that the operation threshold voltage of OLED reduced significantly with the use of thin NiO\(_{1+x}\) as a hole-injecting layer. In a recent article, we reported the growth of high work function (p-type NiO\(_{1+x}\) / Zn\(_{0.95}\)Ga\(_{0.05}\)O composite layered structures for transparent conducting oxide applications\(^10\). Due to the widespread application of Li\(_x\)Ni\(_{1-x}\)O films, there is a considerable interest in understanding its electrical and transport properties, which is critical for further improvement of TCO characteristics.

Various techniques like sputtering\(^11\), electron beam evaporation\(^12\), spray pyrolysis\(^13\), chemical deposition\(^14\), and sol-gel processing\(^15\) have been employed to prepare undoped or Li doped NiO films. But, the pulsed laser deposition technique (PLD), adopted in this study has significant advantages: i) it allows the growth of epitaxial films at relatively lower
temperatures, ii) possibility of having higher dopant concentrations owing to the non-equilibrium nature of the PLD growth process. In this article, we report on the systematic growth of epitaxial Li$_x$Ni$_{1-x}$O (LNO) thin films on c-sapphire substrate with different doping concentrations using Pulsed laser deposition technique. We present results from structural, optical and electrical property measurements and their dependence on deposition conditions. The investigation of electrical transport in Li doped NiO gives an insight into the transport mechanism and the origin of its enhanced p-type nature. We have also investigated its suitability as a p-type layer by fabricating a p-n junction diode structure (discussed in next chapter).

7.2. Experimental Details:

A pulsed KrF excimer laser of wavelength (248 nm) with pulse duration (25 ns) was used for the deposition. A laser energy density of 2 J/cm$^2$ with a pulse rate of 5 Hz was used. The target to substrate distance of ~4.0 cm was maintained. The Li$_x$Ni$_{1-x}$O ($0 \leq x \leq 0.07$) targets were prepared by conventional solid state reaction technique. Sapphire substrates were cleaned ultrasonically in acetone and methanol sequentially before being transferred to the deposition chamber. The chamber was evacuated to a base pressure of $10^{-6}$ Torr prior to the growth. Subsequently, thin film growth was performed in O$_2$ at pressures in the range of ($10^{-4} – 10^{-1}$) Torr in order to vary the concentration of the defects which further influence the electrical and optical properties of the film. Moreover, the O$_2$ nozzle was directed towards the susbtrate holder near the substrate surface inside the chamber. The substrate temperature was varied between (25 – 400) °C. Films were deposited by ablating the Li$_x$Ni$_{1-x}$O target.
A Rigaku Geigerflex diffractometer with Cu Kα radiation (λ = 1.54 Å) was used to obtain x-ray diffraction (θ-2θ scan) data. X-ray Φ scan measurements were carried out using high-resolution XRD instrument (Philips X’Pert PRO MRD HR). Optical transmittance measurements were carried out as a function of wavelength in the range 200–900 nm using a Hitachi U-3010 Spectrophotometer. Electrical resistivity was measured using a four–probe technique in the temperature range of 15 K - 300 K. The contacts on the films were made using indium dots.

7.3. Results and Discussion.

7.3.1. Structural Characterization

Figure 7.1 (a) shows the x-ray θ-2θ scans of the LiₓNi₁₋ₓO (0≤x≤0.07), grown at substrate temperature (Tₛ) of 350°C. The peaks could be assigned to the cubic phase of nickel oxide. It is evident that the growth of the films occurs in [111] direction normal to the film plane. The sharp (111) peaks suggest good crystalline growth for both undoped and LiₓNi₁₋ₓO. No additional peaks were observed for LiₓNi₁₋ₓO (0≤x≤0.05) which excludes the possibility of formation of any other phase. However, an additional small intensity peak corresponding to some other phase of LiNiO₂ was observed when the Li doping was increased to x=0.07 (shown in fig. 7.1 inset). As shown in fig. 7.1 (b), the (111) peak shifted towards a higher angle as NiO is doped with 2 at% Li, (x=0.02). On increasing the doping concentration, the (111) peak shifted further towards a higher angle. This trend was observed for all LiₓNi₁₋ₓO (0.02 ≤ x ≤ 0.07).
Figure 7.1. (a) X-ray diffraction (θ-2θ scan) of NiO thin films with different Li+ dopant concentration. The inset shows Log plot of (θ-2θ scan) of Li_{0.07}Ni_{0.93}O showing extra phase peak marked by a circle. (b) Magnified view of (111) peak of LNO depicting the 2θ shift.
This suggests that due to Li\(^+\) doping, the lattice constant of NiO crystal reduced. The continuous lattice parameter reduction with increasing Li\(^+\) dopant concentration (0.02\(\leq x \leq 0.07\)) can be attributed to the substitutional sites being occupied by the Li\(^+\) ions. Figure 7.2 shows the X-ray diffraction patterns of Li\(_x\)Ni\(_{1-x}\)O (\(x=0.05\)) films that were prepared at different substrate temperatures (RT, 200\(^0\)C, 350\(^0\)C, 450\(^0\)C). It can be seen that the film deposited at room temperature (RT) had weak and broadened (111) diffraction peak which indicates poor crystallinity. The (111) peak became sharper and stronger at elevated substrate temperatures.

Figure 7.2. X-ray diffraction (\(\theta\)-2\(\theta\) scan) of Li\(_{0.05}\)Ni\(_{0.95}\)O thin films at different substrate temperatures.
The full width at half maximum, (FWHM) of the (111) reflection of the \( \text{Li}_x\text{Ni}_{1-x}\text{O} \) \((x=0.05)\) film follows a decreasing trend with increased substrate temperature as shown in fig. 7.3. This suggests improved microstructure and the crystallinity of the film at elevated temperatures.

![Graph showing FWHM vs. substrate temperature](image)

**Figure 7.3.** Full width half maxima (FWHM) plot of \( \text{Li}_{0.05}\text{Ni}_{0.95}\text{O} \) thin films at different substrate temperatures.

To further investigate the in-plane orientations and establish the epitaxial growth of the film, high resolution x-ray φ scans were performed for the (200) reflection of the \( \text{Li}_{0.05}\text{Ni}_{0.95}\text{O} \) film and the (1 1 02) reflection of the \( \text{Al}_2\text{O}_3 \) substrate. The \( \text{Li}_{0.05}\text{Ni}_{0.95}\text{O} \) (200) planes and \( \text{Al}_2\text{O}_3 \) (1 1 02) are inclined at \( \psi = 54.73^\circ \) and \( 57.61^\circ \) respectively, from the growth plane. The substrate
reflection exhibited threefold symmetry about the film normal <111> rotation axis. From fig. 7.4, it can be observed that 6 diffraction peaks from Li$_{0.05}$Ni$_{0.95}$O (200) reflections are present at discrete values of $\Phi$, separated by 60°. Since (111) planes of cubic NiO have threefold symmetry, six fold symmetry of Li$_{0.05}$Ni$_{0.95}$O (200) reflections about the film normal <111> depicts that Li$_{0.05}$Ni$_{0.95}$O film growth takes place biepitaxially where two types of domains have 60° in-plane rotation with respect to each other about the [111] growth direction. The epitaxial relationship can be written as: [111]$_{\text{NiO}}$ || [0001]$_{\text{Al}_2\text{O}_3}$ (out of plane) (b) [110]$_{\text{LNO}}$ || [10 $\bar{1}$0]$_{\text{Al}_2\text{O}_3}$ and [112]$_{\text{LNO}}$ || [21 $\bar{1}$0]$_{\text{Al}_2\text{O}_3}$ (in plane). This epitaxial relationship is known as 30° or 90° rotation, where Li$_{0.05}$Ni$_{0.95}$O rotates by 30° in the basal c-plane of $\alpha$-Al$_2$O$_3$. These 30° and 90° directions are equivalent in hexagonal structure. The epitaxial growth of (111) Li$_{0.05}$Ni$_{0.95}$O on (0001) $\alpha$-Al$_2$O$_3$ can be explained in the framework of DME, where matching of planes is taken into account instead of lattice matching. The misfit between NiO and $\alpha$-Al$_2$O$_3$ is 7.5% in both the in-plane direction. Along the [21 $\bar{1}$0] direction, twelve Li$_{0.05}$Ni$_{0.95}$O (110) planes match with thirteen $\alpha$-Al$_2$O$_3$ (30$\bar{3}$0) planes. Similarly, along the [01 $\bar{1}$0] direction, twelve Li$_{0.05}$Ni$_{0.95}$O 3-(224) planes match with thirteen $\alpha$-Al$_2$O$_3$ 1/2(21 $\bar{1}$0) planes.
Figure 7.4. Azimuthal (Φ scan) of (111) oriented Li$_{0.05}$Ni$_{0.95}$O films a) (1$ar{1}$02) sapphire, at $2\theta = 25.58^\circ$, and $\Psi = 57.61^\circ$, (b) (200) Li$_{0.05}$Ni$_{0.95}$O, at $2\theta = 43.28^\circ$, and $\Psi = 54.73^\circ$.

### 7.3.2. Electrical and optical characterization

The optical transmittance of the Li$_{0.05}$Ni$_{0.95}$O thin films deposited at different substrate temperatures, $T_s$ in the wavelength range of 200-900 nm is shown in fig.7.5. All the films were ~350 nm thick. It can be seen that the films were more transparent in the near-IR region than in the visible region. The films also showed blue shift in the absorption edge with increasing substrate temperatures, $T_s$. Figure 7.6 shows the optical transmittance of the
Li$_{0.05}$Ni$_{0.95}$O films at ($\lambda = 650$ nm) with varying substrate temperatures, $T_s$.

Figure 7.5. UV-Vis transmission spectra of Li$_{0.05}$Ni$_{0.95}$O thin films at different substrate temperatures.

Transmittance of the film increased with increasing $T_s$ and the film deposited at $T_s = 450^{\circ}$C showed average transmittance as high as 83%. Fig. 7.6 also shows the % transmittance dependence of the films at ($\lambda = 650$ nm) with respect to in-growth O$_2$ partial pressure (PO$_2$). As we can see, optical transmittance of Li$_{0.05}$Ni$_{0.95}$O films decreases with increasing oxygen pressure, however, the reduction in transmittance was only marginal for oxygen pressures above $10^{-2}$ Torr.
The optical band gap ($E_g$) can be calculated by assuming a direct transition between valence and conduction bands. The absorption coefficient $\alpha$ obeys the following relationship with $E_g$ near the band gap

$$ (\alpha h \nu)^2 \propto A(h \nu - E_g) $$(7.1)

Where $A$ is a constant, $h$ is Planck’s constant, and $\nu$ is the incident photon’s frequency. The absorption coefficient $\alpha$ was obtained by using the relation $\alpha = \frac{1}{d} \ln(T)$, where $T$ is the transmittance and $d$ is the thickness of the film. The band gap was obtained by extrapolating the linear part of the plot $(\alpha h \nu)^2$ vs $h \nu$ to the energy axis.

Figure 7.6. Variation of Li$_{0.05}$Ni$_{0.95}$O thin films transmittance w.r.t substrate temperature and oxygen pressure.
The estimated values of the direct band gap of Li$_{0.05}$Ni$_{0.95}$O films with different $T_s$ are shown in Fig.7.7. The corresponding $(\alpha h \nu)^2$ vs $h \nu$ plots for the Li$_{0.05}$Ni$_{0.95}$O films are shown in (Fig.7.7 inset). The band gap increases from 3.4 eV to 3.7 eV with increasing $T_s$ from RT to 450°C.

![Graph showing band gap variation with substrate temperature](image)

Figure 7.7. Direct band gap estimation of Li$_{0.05}$Ni$_{0.95}$O thin films at different substrate temperatures. The inset shows the $(\alpha h \nu)^2$ vs $h \nu$ plots for the Li$_{0.05}$Ni$_{0.95}$O films.

Higher band gap values at elevated substrate temperatures can be attributed to improved crystallinity and fewer stoichiometric defects that cause band tailing. The same trend of band gap variation with $T_s$ was also found for undoped NiO$_{1+x}$ in our work.
It is known that stochiometric NiO film is an insulator with a room temperature resistivity value of about $10^{13} \ \Omega\cdot\text{cm}^2$. But if the sufficient concentration of Ni$^{2+}$ vacancies is present, nickel oxide (non-stoichiometric) can exhibit p-type extrinsic semiconducting behavior\(^2\). The resistivity of NiO\(_{1+x}\) thin films has been reported to be in the range of $10^1 - 10^6 \ \Omega\cdot\text{cm}^{17}$. The lowest room temperature resistivity of undoped NiO in our case is $3 \ \Omega\cdot\text{cm}$. Table 7.1 shows the electrical resistivity values of Li\(_x\)Ni\(_{1-x}\)O films with different Li\(^+\) dopant concentration. As it can be seen, electrical resistivity decreases gradually with increasing dopant concentration up to x=0.07 where minimum resistivity of 0.15 $\ \Omega\cdot\text{cm}$ is achieved. The type of majority carrier in Li\(_{0.05}\)Ni\(_{0.95}\)O films was confirmed to be p-type by Hall effect measurement and the carrier concentrations were in the order of $\sim 10^{18} \ \text{cm}^{-3}$. Our data is indicative of our films having better crystallinity, and more efficient substitution of Li$^+$ into Ni$^{2+}$ sites. This behavior is in contrast with Joesph et al\(^{18}\) where room temperature resistivity of Li\(_x\)Ni\(_{1-x}\)O films decreased up to 2 at % Li$^+$ doping and increased with further increase in doping concentration. Our resistivity values are slightly lower than those reported by Jang et al\(^{19}\) and Pushpharajah et al\(^{13}\) for the same doping concentration. It should be noted that electrical conductivity of NiO\(_{1+x}\) films depends on microstructural defects. The different deposition methods and growth conditions strongly affect the microstructure, composition and consequently the electrical conductivity. Our resistivity data is in accordance with our XRD data. X-ray ($\theta$-2$\theta$) analysis clearly manifests that Li$^+$ is going into Ni$^{2+}$ substitutional sites which in turn, create new holes, thereby enhancing the p-type conductivity.

The optimized conductivity of Li\(_{0.05}\)Ni\(_{0.95}\)O film was achieved by varying the substrate
temperature ($T_s$) and in-growth $O_2$ partial pressure ($P_{O_2}$). Figure 7.8 shows the room
temperature electrical resistivity variation of the $Li_{0.05}Ni_{0.95}O$ films deposited at different
substrate temperatures, $T_s$. The lowest resistivity of 0.3 $\Omega$-cm was obtained for the films
deposited at $T_s$ ~ 200°C. For substrate temperatures greater than 200°C, resistivity data
showed a gradual increase with increasing substrate temperature, $T_s$. Figure 7.8. also shows
the room temperature electrical resistivity variation of the $Li_{0.05}Ni_{0.95}O$ film with respect to
the oxygen pressure. On increasing the in-growth $O_2$ partial pressure, a decreasing trend of
electrical resistivity was observed, although the rate of decrease was much less above $10^{-2}$
Torr.

Figure 7.8. Resistivity variation of $Li_{0.05}Ni_{0.95}O$ thin films w.r.t substrate temperature and
oxygen pressure.
The room temperature resistivity of Li$_{0.05}$Ni$_{0.95}$O (thermal resistivity neglected due to measurement under constant temperature) can be controlled by Li$^+$ doping concentration as well as the point defects, such as Ni$^{2+}$ vacancies in NiO crystallites. The variant resistivity behavior of Li$_{0.05}$Ni$_{0.95}$O with different $T_s$ (shown in fig. 7.8) was observed at moderate O$_2$ partial pressure ($PO_2 = 10^{-3}$ Torr) indicating the contribution of defects in addition to Li ion doping towards the carrier concentration. Increasing the substrate temperature results in improved crystallinity and thus reduces the concentration number of carriers that arises due to related defects. The resistivity of the undoped and Li doped NiO thin films were found to decrease with increasing temperature ($T$), indicating semiconducting behavior. Figure 7.9 shows the temperature dependence of resistivity for Li$_x$Ni$_{1-x}$O and NiO$_{1-x}$ thin films (shown in inset) in the temperature range 250-350 K. The curves plotting ln ($\sigma$) vs. 1000/T for different films were found to be linear (Arrhenius relation Eq.2) and the thermal activation energy was estimated from the slope of the best fit line as shown in fig. 7.10 (a) and (b).

$$\sigma = \sigma_0 e^{\frac{-E_a}{kT}} \quad (7.2)$$

where $E_a$ is the activation energy, $k$ is Boltzman constant and $T$ is absolute temperature.

The activation energy estimated for undoped NiO$_{1-x}$ and Li$_x$Ni$_{1-x}$O films are given in Table 7.1. The activation energies are in the range of 0.11eV to 0.14 eV. These values are lower than the values reported by Mahmoud et al.\textsuperscript{20} (0.78 eV) but are in good agreement with the values reported by Nandy et al\textsuperscript{21}. 
The electronic transport mechanism in nickel oxide is still controversial and there is lot of variation in the reported activation energy values. We observed that the activation energy for the undoped NiO$_{1+x}$ and Li doped NiO is nearly the same. This suggests that the carriers are activated from the same energy level in both NiO$_{1+x}$ and Li$_x$Ni$_{1-x}$O films and the dopants in NiO$_{1+x}$ are already activated for all Li$^+$ doping concentration.

Figure 7.9. Dependence of resistivity with temperature (T) for different Li$_x$Ni$_{1-x}$O thin films. The inset shows the resistivity behavior of undoped NiO.
Figure 7.10. Determination of activation energy ($E_a$) of undoped NiO (a) and Li$_{0.05}$Ni$_{0.95}$O (b) thin films from Arrhenius plots.
<table>
<thead>
<tr>
<th>NiO(% doping)</th>
<th>Resistivity(Ohm-cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>3</td>
<td>0.14</td>
</tr>
<tr>
<td>Li$<em>x$Ni$</em>{1-x}$O (x = 0.02)</td>
<td>0.47</td>
<td>0.13</td>
</tr>
<tr>
<td>Li$<em>3$Ni$</em>{1-3}$O (x = 0.035)</td>
<td>0.41</td>
<td>0.13</td>
</tr>
<tr>
<td>Li$<em>x$Ni$</em>{1-x}$O (x = 0.05)</td>
<td>0.30</td>
<td>0.12</td>
</tr>
<tr>
<td>Li$<em>x$Ni$</em>{1-x}$O (x = 0.07)</td>
<td>0.15</td>
<td>0.11</td>
</tr>
</tbody>
</table>

In our case, undoped NiO shows semiconducting behavior due to non-stoichiometry present in the film owing to the non-equilibrium nature of the growth process. The films contain many Ni$^{2+}$ vacancies, which in order to maintain the charge neutrality near the Ni$^{2+}$ vacancies result in the formation of O$^{1-}$ ligand holes. These holes due to non-local screening effects reside primarily on Oxygen orbitals near Ni sites (known as Oxygen “ligand holes”) and lead to hopping p-type conductivity\textsuperscript{22}. Moreover, its p-type conductivity can be enhanced by Li$^+$ doping. When Li$^+$ ions are introduced in the NiO$_{1+x}$ film as dopants, Li$^+$ goes into the substitutional sites of Ni$^{2+}$, traps electrons and generates an excess of uncompensated holes. We interpret that the carriers in both the doped and the undoped NiO$_{1+x}$ are the same localized holes present at the Ni$^{3+}$ centers. Therefore the activation energy in conductivity measurements must be associated with the thermally activated mobility. Austin et al\textsuperscript{23} concluded that conduction in Li-doped NiO takes place via hopping process of polarons with an activation energy of 0.1-0.14 eV.
Observation of similar activation energy values in our undoped and Li doped NiO films suggests similar conduction mechanism.

7.4. Conclusions

Li doped NiO (LiₓNi₁₋ₓO) thin films were epitaxially grown with a [111] orientation on c-sapphire by pulsed laser deposition (PLD). Detailed structural, optical and electrical characterization were performed to examine the conduction mechanism in these p-type LiₓNi₁₋ₓO epitaxial thin films which showed lowering of resistivity with increasing Li⁺ doping concentration. Resistivity values as low as ~ 0.15 Ω-cm were achieved for LiₓNi₁₋ₓO thin films (for x = 0.07). The decrease in resistivity with increasing Li⁺ dopant concentration is attributed to the efficient substitution of Li⁺ into Ni²⁺ sites, owing to the high quality of thin film. Above a critical doping concentration (x=0.05), a secondary phase starts to form; however, the films still maintained their high crystalline quality. Conductivity and transmittance of LiₓNi₁₋ₓO was found to be strongly dependent on deposition parameters and dopant concentration. Optimum properties in terms of conductivity and transmittance were found for composition, x = 0.05. The electronic transport measurements show that the activation energies for undoped NiO₁₊ₓ and Li doped NiO are nearly same, suggesting that the conduction in Li-doped NiO thin films takes place via a polaron hopping process.
References:


Chapter 8

Epitaxial Li doped NiO/ ZnO Heterostructures Integrated on Sapphire (0001) Substrates for p-n junction

The objective of this chapter is to demonstrate epitaxial p-n heterojunction fabrication for the optimized p-Li doped NiO with n-ZnO. Results on structural and electrical characterization of p-Li_{x}Ni_{1-x}O/i-Mg_{x}Zn_{1-x}O/n-ZnO/sapphire (0001) heterostructures are presented. The insertion of i-MgZnO between the p and n layer led to improved I-V characteristics due to reduced leakage current. In the diode architecture, a heteroepitaxial relationship of [111]_{NiO} || [0001]_{MgZnO} || [0001]_{ZnO} || [0001]_{GZO} || [0001]_{Al_{2}O_{3}} among the layers was obtained. The p-i-n heterojunction showed good rectification behavior with turn on voltage of 2.8 V and breakdown voltage of 8.0 V.

8.1 Introduction

For most semiconductor devices, a p-n junction is the key structure. ZnO is considered a promising material for advanced optoelectronic applications, such as ZnO-based ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes operated at room temperature (RT) as it is a wide band gap semiconductor ($E_{g}$=3.37 eV) with a large exciton binding energy (60 meV) and a strong cohesive energy (1.89 eV) [1-3]. Although highly conductive n-type ZnO can be obtained by proper doping with group III donor impurities [4], p-type ZnO has not been successful due to its irreproducibility and low quality [5]. So the possibility of homojunction ZnO structures appears unlikely [6].
As heterojunction structures provide a lot of advantages for electronic and optical confinement, $n$-type ZnO has been used for p-n heterojunctions with various $p$-type semiconductors including ZnRh$_2$O$_4$, NiO, and SrCu$_2$O$_2$ [7]. Among these, NiO is preferable because of its simple structure and composition. Several research groups reported on fabrication and photoresponse of p-NiO/n-ZnO heterojunctions for UV detector applications [6, 7]. Polycrystalline NiO$_{1+x}$ thin films have been used as the p-type layer in most of the oxide p/n junction devices. It should be noted that electrical properties of these devices strongly depends on microstructure and crystalline quality of their constituent thin film layers. Wide distribution of interface states and grain boundaries in polycrystalline films can provide traps and recombination centers, thereby reducing the performance of solid state devices. Hence, high quality epitaxial films are extremely desirable for p-n junctions. In addition, band gap engineering technique permits the design of devices with MgZnO based semiconductor materials and devices [8]. It is believed that Mg$_x$Zn$_{1-x}$O (MZO) can be an excellent material for photonic applications such as UV detector, blue and UV light-emitting diode, and laser diode [9].

We have investigated the suitability of using Li$_x$Ni$_{1-x}$O as a p-type layer by fabricating a p-n junction diode structure. In this work, we have fabricated heteroepitaxial p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO junction on c-sapphire with n$^+$-Ga$_x$Zn$_{1-x}$O as bottom conducting electrode. And for this purpose, we have chosen Li$_{0.05}$Ni$_{0.95}$O (LNO) film which is devoid of any secondary phases (previous chapter). Li$_{0.05}$Ni$_{0.95}$O (LNO) films with optimum conductivity were employed in the fabrication of heteroepitaxial p-n junctions using the configuration of
p-LixNi1-xO/i-MgxZn1-xO/n-ZnO/n+-GaxZn1-xO/c-sapphire. The p-n junctions exhibit rectification behavior in I-V measurements. It has been shown that the electrical properties of the p-n junctions can be improved with i-MgxZn1-xO.

8.2 Experimental Details

KrF excimer pulsed laser deposition (λ = 248 nm) was used to grow p-LixNi1-xO/n-ZnO/n+-Ga_xZn1-xO/c-sapphire and p-LixNi1-xO/i-MgxZn1-xO/n-ZnO/n+-Ga_xZn1-xO/c-sapphire heterostructures. Prior to deposition, the sapphire substrates were ultrasonically cleaned with acetone and methanol. High-purity solid state targets were used for all the materials. The laser fluence used in this study was ~ 2-3 J/cm². A target-substrate distance of 4.0 cm was utilized. First, a Ga_{0.05}Zn_{0.95}O (GZO) film was deposited on the c-sapphire to act as a transparent conducting bottom electrode layer for the p-n junction. The growth was performed at a temperature of 200°C and an oxygen partial pressure of 1 mTorr. Growth of ZnO was performed at temperatures in the range 400°C and with oxygen pressures in the range 0.1 mTorr. For Mg_{x}Zn_{1-x}O (MgZnO) layer, the growth temperature was maintained at 500°C and an oxygen partial pressure of 1 mTorr. Finally, the optimized Li_{x}Ni_{1-x}O layer was deposited on top of Mg_{x}Zn_{1-x}O layer. The growth temperature was maintained at 200°C for deposition with an oxygen partial pressure of 50 mTorr. In this case, we have used Mg_{x}Zn_{1-x}O (x = 0.3). X-ray diffraction studies were done using a Philips X’Pert PRO x-ray diffractometer with Cu Kα radiation. Cross-sectional samples of the Li_{x}Ni_{1-x}O/Mg_{x}Zn_{1-x}O/ZnO/Ga_xZn1-xO/c-sapphire heterostructures were characterized using a JEOL 2000FX and 2010F high resolution transmission electron microscopes. Electrical characterization was performed using an HP8545 semiconductor parameter analyzer. Resistivity was measured as
a function of temperature by a four-probe method configuration with Au contact pads as the
top electrodes. A schematic layout of the diode configuration is shown in fig.1.

Figure 8.1. Schematic diagram of p-Li_{x}Ni_{1-x}O/i-Mg_{x}Zn_{1-x}O/n-ZnO/n^{+}-Ga_{x}Zn_{1-x}O/c-
sapphire p-n heterojunction diode.

8.3 Results and Discussion

8.3.1 Structural characterization

Figure 8.2. shows the X-ray diffraction pattern (θ-2θ scan) of the heterostructure. Diffraction
peaks from ZnO (0002), ZnO (0004), LNO (111) and LNO (222) were observed. The sharp
and strong (0002) peak shows the growth of singly oriented ZnO along (0001) sapphire. The
(0002) type reflections from the Ga_{x}Zn_{1-x}O, ZnO and Mg_{x}Zn_{1-x}O layers were all merged into
a single peak position. This is suggestive of negligible lattice mismatch between ZnO and
Ga/Mg doped ZnO. The XRD pattern also indicates that cubic Li_{0.05}Ni_{0.95}O layer is singly
oriented on the Mg_{x}Zn_{1-x}O (0001) layer. Therefore, we can say that the heterojunction grows
epitaxially with the following out of plane orientation relationship: [111]_{LNO} || [0001]_{MgZnO} ||
[0001]_{ZnO} || [0001]_{GZO} || [0001]_{Al_{2}O_{3}}.
Heteroepitaxial growth of the p-n junction is technologically important as it minimizes the electron scattering at the interface.

![X-ray diffraction](image)

**Figure 8.2** X-ray diffraction (θ-2θ scan) of Li$_x$Ni$_{1-x}$O/Mg$_x$Zn$_{1-x}$O/ZnO/Ga$_x$Zn$_{1-x}$O/c-sapphire hetrojunction structure.

X-ray diffraction involving Φ-scan was performed to get the information about the in-plane orientation and establish the epitaxial growth of the bilayer film on sapphire substrate. The Φ scan for (101) ZnGa$_{0.05}$O planes, which are inclined at 61.07° from (0001) planes was performed with 2θ = 36.25° (fig. 8.3). The Φ scan result shows the six fold symmetry of ZnGa$_{0.05}$O reflection.
It can be concluded from the Φ scan that ZnGa$_{0.05}$O grows epitaxially on [0001] α-Al$_2$O$_3$ at 200°C with the following orientation relationship: (a) [0001]$_{ZGO}$ || [0001]$_{α\text{-}Al_2O_3}$ (out of plane) (b) [2110]$_{ZGO}$ || [1010]$_{Al_2O_3}$ and [1010]$_{ZGO}$ || [2110]$_{Al_2O_3}$ (in plane). This epitaxial relationship is known as 30° or 90° rotation, where ZnGa$_{0.05}$O rotates by 30° with respect to the basal c-plane of α-Al$_2$O$_3$.

Figure 8.3. Azimuthal (Φ scan) of LNO/ GZO / Al$_2$O$_3$ (0001) heterostructure. (1102) reflections of sapphire, at 2θ = 25.58°, and Ψ = 57.61°; (101) reflections of GZO, at 2θ = 36.25°, and Ψ = 61.07°; (200) reflection of LNO, at 2θ = 43.28°, and Ψ = 54.73°.

This epitaxy occurs by matching of integral multiple of lattice planes (where 5 or 6 (2110) planes of ZnO matches with 6 or 7 (3030) planes of sapphire) and accommodates 15.4%
misfit between the film and the substrate [10]. To determine the in-plane orientations in the
Li$_x$Ni$_{1-x}$O/Mg$_x$Zn$_{1-x}$O/ZnO/Ga$_x$Zn$_{1-x}$O/c-sapphire heterostructure, Φ scan was performed for
(200) LNO planes, which are inclined at 54.73° from (111) planes and was done with 2θ =
43.28° (fig. 8.3). The 6 fold symmetry observed in Φ scan confirmed that LNO grows
epitaxially on ZnO. Hence, the epitaxial relationship can be written as: [111]$_{\text{LNO}}$ || [0001]$_{\text{ZnO}}$(out of plane) (b) [110]$_{\text{LNO}}$ || [210]$_{\text{ZnO}}$ and [112]$_{\text{LNO}}$ || [1010]$_{\text{ZnO}}$ (in plane). This misfit is
again accommodated by domain matching epitaxy.

Figure 8.4 Cross-sectional High resolution TEM micrograph showing Ga$_x$Zn$_{1-x}$O/c-
sapphire interface.
Figure 8.5  

a) Cross-sectional High resolution TEM micrograph showing Li$_x$Ni$_{1-x}$O/Mg$_x$Zn$_{1-x}$O interface, b) Inverse fast Fourier transform image obtained by selecting the (21$\overline{1}$0)$_{\text{MgZnO}}$ and the (220)$_{\text{LNO}}$ diffraction spots from the fast Fourier transform in part (a), which indicates that nine MgZnO planes match ten LiNiO planes across the Li$_x$Ni$_{1-x}$O/Mg$_x$Zn$_{1-x}$O interface.
Further structural characterization of Li$_x$Ni$_{1-x}$O/Mg$_x$Zn$_{1-x}$O/ZnO/Ga$_x$Zn$_{1-x}$O/c-sapphire heterostructures was done by transmission electron microscopy studies. From the images the estimated thickness of GZO, MgZnO and LNO layers are 450 nm, 100 nm and 400 nm, respectively. The high resolution TEM image of ZGO/Sapphire interface (fig.8.4) shows that this interface is clean and sharp. Figure 8.5 (a) shows the interface of MgZnO/LNO. The interface clearly shows some misfit dislocation strain contrast. The cross sectional selected area diffraction (SAD) pattern of this heterostructure along a [112] zone axis of LNO is shown in (fig. 8.5 (a)) inset. In all the directions marked in this SAD pattern the diffraction spots of MgZnO and LNO are aligned. This confirms that LNO grows epitaxial on MgZnO template. The planar matching is shown in IFFT (Inverse fast Fourier transform) image, which shows the planes perpendicular to the MgZnO/LNO interface (fig. 8.5 (b)). This IFFT was obtained from the HRTEM image shown in fig. 8.5 (a) by masking all but the planes perpendicular to the interface. It is clear from fig. 8.5 (b) that 10 planes of LNO matches with 9 planes of MgZnO to accommodate the 9 % misfit in the MgZnO/LNO system. The domains themselves are separated by dislocations or half planes (marked in fig. 8.5 (b)).

8.3.2 Electrical characterization

The room temperature I-V characteristics of the p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO heterojunction fabricated under this research are shown in fig.8.6. Good rectification behavior of the p-n junction is evident from the highly asymmetric I-V curve. At first, the p-n junctions with p-Li$_x$Ni$_{1-x}$O/n-ZnO configuration were fabricated without employing i-Mg$_x$Zn$_{1-x}$O interlayer. The I-V curve obtained from such a p-n junction is shown in (fig.8.6 inset).
The p-Li$_{x}$Ni$_{1-x}$O/n-ZnO junction has a small forward threshold voltage ($V_{on}$) of ~ 0.4 V and the breakdown also occurred at a small reverse voltage of ~ 0.6 V. Next, an i-Mg$_x$Zn$_{1-x}$O inter-layer was introduced in the heterojunction. The p-Li$_{x}$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO diode showed improved forward threshold voltage ($V_{on}$) of ~ 2.8 V and increased breakdown voltage ($V_{BR}$) of ~8 V as shown in fig.8.6. The small leakage current of $6 \times 10^{-6}$ A was detected at -4 V. So, the leakage current was reduced by the Mg$_x$Zn$_{1-x}$O layer.

![Figure 8.6. I-V characteristics of diode with i-MgZnO layer. The inset shows I-V characteristics of diode without i-MgZnO layer.](image)
Fig. 8.7 shows I-V characteristics of LNO/Au junction. It shows linear behavior verifying the formation of ohmic contact between LNO/Au. The effect of i-Mg$_{x}$Zn$_{1-x}$O layer can be explained by the energy band structure (Fig. 8.8). Fig. 8.8 shows the energy band alignment of the diode p-Li$_{x}$Ni$_{1-x}$O/n-ZnO with i-MgZnO layer at equilibrium ($V_a=0$ V), in forward bias ($V_a=\Delta E_f$) and in forward bias ($V_a>\Delta E_f$). For structures containing the i-Mg$_{x}$Zn$_{1-x}$O interlayer, the quasi Fermi level needs to be raised to a higher level to achieve the threshold current (Fig. 8.8(c)). As the electrons need to cross an additional energy barrier across the junction, the forward threshold voltage increases. For reverse biased condition, the effective reverse depletion width increases with the insertion of the i-Mg$_{x}$Zn$_{1-x}$O. Moreover, due to the higher bandgap of Mg$_{x}$Zn$_{1-x}$O, the critical reverse breakdown increases as more energy is required to produce an ionizing collision. Thus, a higher reverse voltage will be required to achieve the same critical electric field that results in reverse breakdown to occur. A higher breakdown voltage and lower leakage current in the p-n junctions are favorable for electronic devices.

Figure 8.7. I-V characteristics of Au/LNO showing ohmic behavior.
Figure 8.8. Energy band alignment of diode p-Li$_x$Ni$_{1-x}$O/n-ZnO with i-MgZnO layer a) Equilibrium ($V_a = 0$ V), b) forward bias ($V_a = \Delta E_f$), c) forward bias ($V_a > \Delta E_f$).
It should be mentioned that in a simplistic case of a p-n junction at the equilibrium zero bias, the difference between the intrinsic fermi level of the p and n side is equal to the built-in voltage which is also equal to the threshold voltage for the diode operation. When the diode is forward biased, until the applied bias is equal to this built-in voltage the diode is essentially off as the current is less than the threshold current and in this regime the p conduction edge is above the n edge. When the bias becomes equal to the built-in voltage, the p and n conduction band edges match up and the diode current starts increasing exponentially. At this point any small increase in forward bias voltage $\Delta V_a$ leads to large increase in current, I, and the band edges essentially get pinned, which is why in most of the representations the p side is not shown below the n side. In our case, the situation is different because the intrinsic region is of different material and band gap. When this structure is forward biased and the p conduction edge becomes level with the n conduction edge, there is still the energy barrier for the electrons and holes across the junction and the current flow is still just the leakage current. For the carriers to conduct across this barrier, the fermi level on the n side has to be higher than the p- side so that a substantial number of carriers can tunnel through this intrinsic barrier for the diode to be in ON condition.

8.4 Conclusions

Growth of heteroepitaxial p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO junctions on c-sapphire by PLD was investigated. Structural characterization of films by x-ray diffraction and transmission electron microscopy established that all the layers in the film were epitaxial. I-V characteristics of heteroepitaxial p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO junctions on c-sapphire
with $n^+\text{Ga}_x\text{Zn}_{1-x}\text{O}$ as the bottom conducting electrode have also been reported and discussed. This multilayered structure exhibited the orientation relationship: $[111]_{\text{LNO}} \parallel [0001]_{\text{MgZnO}} \parallel [0001]_{\text{ZnO}} \parallel [0001]_{\text{GZO}} \parallel [0001]_{\text{Al}_2\text{O}_3}$. Introduction of $i\text{-Mg}_x\text{Zn}_{1-x}\text{O}$ interlayer facilitated the reduction of leakage current and improved the junction characteristics.
References


Chapter 9

Ultrafast p-type to n-type Conductivity transformation in NiO thin films
by UV- laser irradiation

Abstract

This paper reports the systematic changes in structural, electrical and optical properties of NiO thin films introduced by nanosecond duration pulses of an Ultraviolet Excimer laser. At laser energy density of 0.275 J/cm², NiO films showed conversion from p-type semiconducting to n-type conductive behavior with three order of magnitude decrease in resistivity, while maintaining its cubic crystal structure and good epitaxial relationship. The laser-induced n-type carrier transport and conductivity enhancement can be reversed through subsequent thermal annealing in oxygen.

Keyword: Semiconductor, thin films, laser irradiation, Ni⁰ centers.

9.1. Introduction

Nickel oxide, a p-type semiconductor with band gap energy from 3.6 to 4.0 eV, is a candidate for potential applications in spin-valve giant magneto resistance (GMR) sensor [1], gas sensors [2], electrochemical display devices [3] and p-type transparent conducting electrodes [4]. NiO₁+ₓ has also been used as an interfacial contact layer with anode in organic solar cells and organic light emitting diodes (OLEDs) owing to its high work function [5],[6],[7]. Moreover, NiO has been applied as the p-type layer in the fabrication of oxide p-n heterojunction devices [8]. However, these devices showed unsatisfactory rectifying
characteristics i.e. large reverse-bias leakage current due to interface states and grain boundaries present in polycrystalline film heterojunctions.

There have been several reports of high quality nickel oxide growth by electron-beam evaporation [9], molecular-beam evaporation [10], r-f sputtering [11], spray pyrolysis [12] and pulsed laser deposition [13]. Stoichiometric NiO is now understood as a charge transfer insulator with a resistivity of $\sim 10^{13}$ $\Omega$-cm at room temperature. However, nickel defects which manifest as core-hole states at nickel sites result in extra valence hole states which reside primarily on oxygen orbitals near Ni sites. These hole states also known as Oxygen “ligand holes” result in p-type doping in pure NiO [14]. Hereafter in this report, the hole-doped NiO is referred to as p-type which behaves like a semiconductor and the electron-doped NiO is referred as n-type which is not necessarily a conventional semiconductor (as observed in our resistivity measurements) but has electrons as the majority carriers. This p-type conductivity can be further enhanced by Li$^+$ doping, where the Li$^+$ ions substitute for Ni$^{2+}$ and then maintain charge neutrality through the formation of O$^{1-}$ ligand holes. The resistivity as low as 0.15 $\Omega$-cm has been obtained by Li$^+$ doping [13].

Point defects can be introduced in excess of the thermodynamic limit using non-equilibrium electronic, photonic and ion irradiation processes. Controlling these defects will be interesting and may lead to the new opportunities to improve future optoelectronic devices. Recently, there have been several reports on the modification of many materials using excimer lasers, including polymers, carbon cages and inorganic materials like ZnO [15],[16].
Laser irradiation induces a rapid local increase in temperature which results in restructuring of the chemical bonds with preferential ejection or evaporation of certain atomic or ionic species. The laser treatment leads to creation of oxygen vacancies in the near surface regions, which can diffuse into deeper regions during the transient heating cycle via an interstitial-substitutional diffusion mechanism. Here, we report the growth of epitaxial single-crystal NiO films grown on c-sapphire, and alteration of its electrical and optical properties as a function of pulsed laser irradiation and subsequent thermal annealing. Our results show transformation of p-type (hole doped) to n-type (electron doped) conductivity in NiO thin film via laser irradiation. This transformation was found to be reversible by thermal annealing in O$_2$ ambient.

9.2. Experimental Detail

In this study NiO thin films have been deposited on single crystal c-plane sapphire substrates in a PLD system using KrF Excimer laser ($\lambda=248$ nm, $\tau=25$ ns). The energy density and repetition rate were kept at 2-3 J/cm$^2$ and 5 Hz, respectively, and the target-substrate distance was maintained at 4.0 cm during deposition. Thin film growth was carried out at 200°C and in an oxygen partial pressure of 10$^{-2}$ Torr. The thickness of the film was about 250 ± 20 nm. Subsequently, laser irradiation of films was performed at room temperature in air ambient with a laser energy density of 0.275 J/cm$^2$ and a frequency of 1 Hz for different number of pulses. The laser energy was kept below the melting threshold, which was easily identified as by visible damage to the film (at higher energies) by optical microscopy.
The structure of these films was characterized by X-ray diffraction using a Rigaku X-ray diffractometer with Cu K\textsubscript{α} radiation (\(\lambda=0.154\) nm) and a Ni filter. Detailed microstructural characterization was performed using a JEOL-2010 field-emission high resolution transmission electron microscope (HR-TEM) equipped with a Gatan image filter (GIF) tuning attachment. Quantitative chemical analysis was carried out using Electron Energy Loss Spectroscopy (EELS) and X-ray photoelectron Spectroscopy (XPS). Optical measurements were performed using a Hitachi spectrophotometer. Room-temperature electrical resistivity measurements were conducted using a four-point-probe method and Hall measurements were carried out using Ecopia Hall Effect Measurement system.

9.3. Results and discussions

Figure 9.1(a) shows X-ray diffraction characterization (2\(\theta\)-Intensity scan) of as-grown, laser irradiated NiO thin films with 10 laser pulses and post-irradiation annealed NiO thin film at 700 °C. The laser irradiated films were annealed at 300 °C and 700 °C in oxygen ambient for various durations. The XRD pattern shows that the films are highly textured or epitaxial with [111] as preferred orientation. The peak intensity decreased significantly after laser irradiation, which was accompanied by broadening of its full width at half maximum (FWHM) from 0.29° to 0.58°. This clearly suggests the degradation of crystalline quality upon laser irradiation. The peak intensity recovered partially in the oxygen ambient annealed sample as the stoichiometry improved but did not recover completely as the mosaicity induced in the film by laser pulses could not be eliminated by annealing.
Figure 9.1. (a) Room temperature X-ray diffraction pattern of as deposited, laser irradiated and oxygen annealed NiO thin films (b) X-ray φ-scan of (200) and (1-102) reflection of NiO and Al₂O₃ respectively.
Interestingly, the peak shifted toward a higher angle for the laser irradiated sample indicating a decrease in the lattice parameter in the c-direction. This suggests that the NiO crystal lattice, which originally had in-plane compressive strain, went through a lattice relaxation process due to thermal treatment upon laser irradiation. Within the detection limit of the x-ray diffraction apparatus there was no evidence of precipitation or impurity clustering in the films following the laser irradiation.

To investigate the in-plane orientation and establish the epitaxial growth of the film, high resolution X-ray $\phi$ scan studies were carried out. $\phi$ scans were performed for the (200) reflection of NiO film and the (1102) reflection of Al$_2$O$_3$ substrate which are inclined at $\psi = 54.73^\circ$ and $57.61^\circ$, respectively, from the growth plane. The substrate reflection exhibits threefold symmetry about the film normal $<111>$ rotation axis. From Fig. 9.1(b), it can be observed that 6 diffraction peaks from NiO (200) reflection are present at discrete values of $\Phi$, separated by $60^\circ$. Since (111) planes of cubic NiO have threefold symmetry, six fold symmetry of NiO (200) reflections about the film normal $<111>$ suggests that NiO film growth takes place with twin formation on sapphire where two types of domains have $60^\circ$ in-plane rotation with respect to each other about the [111] growth direction.
Figure 9.2. High resolution TEM image of laser irradiated NiO showing highly epitaxial film on sapphire with (a) an atomically sharp interface and (b) the upper surface region of the thin film cross-section. No Nickel metal clusters are observed. (c) indexed SAD pattern of NiO/Al₂O₃ interface.
A detailed TEM study was performed in order to investigate the microstructure and verify the epitaxial relationship of the laser-irradiated films. The selected area electron diffraction (SAED) pattern from a large area cross-section of the film/substrate interface is shown in Fig. 9.2(a). It should be noted here that there are two sets of spots that are indicated by different color line pattern in Fig. 9.2(a). These two sets of pattern belong to the same [110] zone axis of NiO, but they are mirror to each other in (111) plane. The presence of two domains was confirmed with dark field imaging in NiO/[0001] α-Al2O3 by selecting the individual sets of f.c.c electron diffraction spots (Figure shown in Chapter 6). The epitaxial growth of (111) NiO on (0001) α-Al2O3 can be explained in the framework of DME, where matching of planes are taken into account instead of lattice matching [17]. The misfit between NiO and α-Al2O3 is 7.5% in both the in-plane directions. Along the [21\bar{1}0] direction, twelve NiO (110) planes match with thirteen α-Al2O3 (30\bar{3}0) planes. Similarly, along the [01\bar{1}0] direction, twelve NiO 3-(224) planes match with thirteen α-Al2O3 1/2(21\bar{1}0) planes.

The HR-TEM micrograph (Fig. 9.2(b)), of the laser irradiated film, reveals the epitaxial nature of the film and the atomically sharp interface with no evidence of any interfacial reaction or precipitation as a result of laser irradiation. Figure 9.2(c) shows the cross-section at the surface of laser irradiated NiO thin film which is devoid of any Ni precipitation or clustering.

The effect of laser irradiation on the optical properties of NiO thin films was investigated. The optical transmission spectra (Fig. 9.3.) in the wavelength range of 200-900 nm shows the comparison of as-deposited, laser irradiated (10 pulses) and annealed NiO thin film at 700°C.
The films appeared much darker after laser irradiation than the as-deposited one and recovered the original color after annealing. The transmittance decreased from 75% to 58% after laser irradiation and improved to 83% after annealing. Moreover, the annealed film shows a blue shift in the absorption edge which corresponds to the widening of the band gap. The higher band gap due to annealing at high temperature can be attributed to improved crystallinity and stoichiometry that reduces band tailing.

Figure 9.3. UV-Vis transmission spectra of as deposited, laser irradiated and oxygen annealed NiO thin films.

In order to determine any change in the electrical properties of laser irradiated NiO, room temperature (RT) four probe resistivity and Hall measurements were performed.
As-grown films deposited at T_s (substrate temperature) \equiv 200 \, ^{\circ}\text{C} show p-type nature with the RT resistivity of 3.0 \, \Omega\text{-cm} and carrier concentration of $1 \times 10^{17} \, \text{cm}^{-3}$. The NiO films were irradiated with different energy density of UV laser pulses. The threshold laser energy density was estimated to be 0.275 \, J/cm^2. No significant variations in appearance and conductivity were seen below 0.275 \, J/cm^2. Above an energy density of 0.350 \, J/cm^2, film surface damage due to melting of the entire film was observed. No change was observed with 1 or 2 laser pulses of 0.275 \, J/cm^2 energy density. Interestingly, with more than 5 laser pulses of the same energy density, there was three orders of magnitude decrease in resistivity (~$1.5 \times 10^{-3} \, \Omega\text{-cm}$) observed in NiO. Moreover, a conversion from p-type semiconducting to n-type conducting nature was observed in these films. The n-type NiO showed a carrier concentration of $5 \times 10^{19} \, \text{cm}^{-3}$. These results were reproducible and the conductivity type and magnitude remained unaffected even after 30 days. The effect of annealing after the laser treatment on the electrical properties of NiO is summarized in table 9.1. The film annealed at 300\,^{\circ}\text{C} in O_2 ambient for 5 minutes remained n-type with marginal increase in resistivity. On increasing the annealing time duration to 30 min, the resistivity increased beyond the measurement limit of our instrument and became essentially insulating. The film annealed at 700\,^{\circ}\text{C} in O_2 ambient for 5 minutes also showed similar behavior. It should be noted that electrical conductivity of NiO_{1+x} films depends on microstructural defects and is correlated to the valence state of nickel extracted from electronic spectra. To understand the correlation between the electronic configuration and the conductivity behavior in NiO, XPS analysis was performed.
For XPS measurements, the surfaces of NiO films were sputter cleaned with Ar$^+$ ions for 2 min in UHV. Figure 9.4 shows the XPS spectra of the Ni 2p$_{3/2}$ states in the NiO films from the as-deposited, laser irradiated and annealed films at 300°C and 700°C in O$_2$ ambient. The spectrum for the unirradiated film consists of two peaks in the region 853.7 eV-855.4 eV in addition to the electron loss peak in the region with binding energy above 860 eV. Conventionally the signal peaks at 853.7 eV and 855.4 eV correspond to Ni$^{2+}$ (2p$_{3/2}$) and Ni$^{3+}$ (2p$_{3/2}$) electronic states where Ni is assumed to take multiple +2 and +3 oxidation states. Theoretically suggested by Veenendaal et al [18] and further supported in Ref.[19][20], it is interpreted that the Ni$^{3+}$ ionic sites are not energetically favorable charge compensating states in the case of NiO and the observed Ni$^{3+}$-like signal intensity in XPS is intrinsic to NiO because of non-local site, charge transfer screening effects. The resulting states are referred to as cd$_{L-1}$ for the Ni$^{2+}$-like main line and cd$_{8}$ state for the Ni$^{3+}$-like shoulder. The fact that the intensity at ~855.4 eV binding energy doesn’t relate to Ni$^{3+}$ ion states is corroborated by data from XAS experiment [19] performed by others in which only Ni$^{2+}$ valency is formally resolved. With this much mentioned, we should stress this point that the above interpretation is limited to pure Nickel oxide and hole doped (Li$^+$) nickel oxide with some discrepancies that still need to be resolved.

In the case of the laser irradiated film, another peak at 852.7 eV appeared which corresponds to the nickel (Ni$^0$) state [21]. This was accompanied by a decrease in the O1s peak intensity positioned at 535 eV. The XPS spectra showed that intensity of Ni$^0$ bonding state decreased for the film annealed at 300°C (5 min). And for the film annealed at 700°C (5 min), the Ni$^0$
bonding state completely disappeared. Also, a shift of 0.32 eV towards lower binding energy for the film annealed at 700°C was observed in the Ni 2p\textsubscript{3/2} spectra. The presence of a Ni\textsuperscript{0} bonding state in the irradiated sample indicates that laser irradiation creates Ni\textsuperscript{0} like defect states in NiO.

Table 9.1 Summary of electrical properties of as deposited, laser irradiated and annealed films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistivity (Ω-cm)</th>
<th>Carrier Conc (cm\textsuperscript{-3})</th>
<th>Carrier Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>3</td>
<td>1x 10\textsuperscript{17}</td>
<td>p-type</td>
</tr>
<tr>
<td>Laser Irr (1 pulse)</td>
<td>3</td>
<td>1x 10\textsuperscript{17}</td>
<td>p-type</td>
</tr>
<tr>
<td>Laser Irr (10 pulse)</td>
<td>1.5 x 10\textsuperscript{-3}</td>
<td>5x 10\textsuperscript{19}</td>
<td>n-type</td>
</tr>
<tr>
<td>Annealed (300°C) 5 min</td>
<td>7 x 10\textsuperscript{-3}</td>
<td>-</td>
<td>n-type</td>
</tr>
<tr>
<td>30 min</td>
<td>-</td>
<td>-</td>
<td>p-type</td>
</tr>
<tr>
<td>Annealed (700°C) 5 min</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 9.4. Ni 2p XPS spectra of NiO for as deposited, laser irradiated and annealed samples at 300°C and 700°C.
It was necessary to investigate whether these Ni$^0$ states created by laser irradiation are present only at the surface of NiO film which may also give rise to such low resistivity values. For that, XPS depth profiling measurements were performed on NiO films. For sputter depth profiling, Ar$^+$ ions of 3.5 KeV energy were used with a scan size of 2mm x 2mm and 2 min sputter intervals. Fig. 9.5 shows the profile of concentration ratio of Ni$^0$/ (Ni$^0$ + Ni$^{2+}$ + Ni$^{3+}$) from Ni 2p$_{3/2}$ spectra at different sputter time intervals. The Ni$^0$ defects concentration was nearly invariable with sample depth. These results establish that the defects created through laser irradiation are throughout the NiO film and not confined to the surface.
However, the possibility of Ni$^0$ states forming amorphous Nickel metal clusters could not be ruled out. To resolve this, detailed EELS measurement was carried out in the laser irradiated sample. Figure 9.6 shows the EELS spectra of laser irradiated NiO sample in the range of 400 – 1000 eV. In the higher energy loss region, the observable ionization edges are the oxygen K edge at ~532 eV and the Nickel L$_{2,3}$ edges at ~850.4 and 868 eV, respectively. It should be noted that no signal corresponding to Ni metal plasmon resonance was found within the detection limit of EEL spectrometer, which rules out the presence of amorphous metallic Nickel clusters in NiO [22].
Therefore, we conclude that laser irradiation generated Ni$^{0}$ defects in NiO thin films and they are related to the n–type conductivity.

It can be demonstrated that in the pulsed laser irradiation process, the defect states like Ni$^{0}$ cannot cluster to form metal precipitates via interstitial diffusion. The ultrafast heating and cooling cycle time duration for such a laser irradiation is in the order of $\sim 10^{-7}$ sec. The temperature change upon laser irradiation can be estimated by eq [23].

$$\Delta T = \frac{2(1-R)\alpha}{k} \left( \frac{\alpha}{\pi \tau} \right)^{1/2}$$  (1)

Where $R$ is reflectivity of NiO, $\alpha$ is thermal diffusivity, $k$ is thermal conductivity and $\tau$ is nominal pulse width. Assuming the extreme case scenario, the highest temperature achieved is $\sim 1500^0C$ (which is below its melting point); at these temperatures the diffusion coefficient of Ni$^{+}$ in the oxides is $D_{t} \sim 10^{-12}$ cm$^2$s$^{-1}$. The average diffusion distance is $X = \sqrt{2D_{t}\tau} \sim 0.1$ Å. Therefore no agglomeration and precipitation of the nickel is possible by this laser pulse processing.

Upon irradiation, the phonon energy of the KrF excimer laser with a wavelength of 248 nm (5 eV) is sufficiently high to break Ni–O bonds (4.24 eV) [24]. Therefore, the evaporation of oxygen into the air resulted in oxygen vacancies. It is surmised that for every removed oxygen O$^{2-}$ ion, Ni$^{2+}$ ion takes 2 electrons and converts to Ni$^{0}$ like states.
Figure 9.7. Temperature dependent resistivity measurement of laser irradiated NiO thin film.

The temperature dependent resistivity measurement for the laser irradiated sample is shown in Fig. 9.7. Contrary to expectation the dependence was linear unlike a conventional semiconductor behavior. From the photo-emission and inverse photo-emission spectroscopy these Ni$^{0}$-like defects have been reported to generate two deep level states, one occupied and the other unoccupied at 0.6 eV below and above the Fermi level respectively in the middle of the charge transfer gap [14].
How these midgap states play a role in determining the resistivity temperature dependence needs further theoretical study. We stipulate that the major scattering of the carriers is due to phonons, typical of metal-like behavior. By this method, 16-17% of Ni\(^0\) defects (Fig. 9.5) could be produced without changing the crystal structure of NiO. It is suggested that laser irradiation may offer an ultrafast approach of creating n-type NiO. The shape and lateral dimensions of the zone affected by laser irradiation can be easily chosen by apertures. This approach opens up new possibility of lateral NiO homoepitaxial p-n junctions.

9.4. Conclusions

Our results show that laser irradiation at energy densities below the threshold for melting can induce the formation of defects in NiO films that lead to significant changes in structural, optical and electrical properties. NiO thin films were found to be more relaxed upon laser irradiation, while maintaining the crystal structure and good epitaxial relationship. It has been demonstrated that a p-type to n-type conductivity transformation with simultaneous enhancement in conductivity up to 3 orders of magnitude can be achieved in NiO thin films by laser irradiation and this phenomena is reversible via oxygen annealing. From XPS analysis, a strong correlation has been established between n-type conductivity and non-equilibrium concentrations of laser induced Ni\(^0\)-like defect states.
References

Chapter 10

Summary

1. We have demonstrated the growth of bilayered structures consisting of very thin MoO$_x$ ($2.0 < x < 2.75$), and/or p-Li$_x$Ni$_{1-x}$O ($0 \leq x \leq 0.07$) overlayers on Zn$_{0.95}$Ga$_{0.05}$O (GZO) film on glass substrates by pulsed laser ablation. The primary aim of this study was to study the effect of thin MoO$_x$ and NiO$_{1+x}$ overlayers on TCO properties of GZO with an eye towards OPV applications. All the films deposited on glass were highly oriented. This preferred [0001] orientation was due to the lowest surface energy of the basal plane and high energy of the ablated species. Excellent crystalline quality was found in the growth temperature range of 200°C to 400°C. For the case of (NiO$_{1+x}$ / GZO) bilayer films, the NiO$_{1+x}$ layer shows preferred orientation along [111] direction on GZO (0001) and this crystallographic orientation possesses relatively higher work function with respect to the other orientations. The effect of varying the NiO$_{1+x}$ thickness and doping (Li$_{0.05}$Ni$_{0.95}$O) on the electrical and optical properties of (NiO$_{1+x}$ / GZO) bilayer films has also been investigated and optimum results were found for the thickness range of (4 -8 nm). The multiple oxidation states present in the overlayers (Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$ in MoO$_x$ and Ni$^{2+}$ and Ni$^{3+}$ in NiO$_{1+x}$), that result in optimized TCO characteristics were determined and controlled by growth parameters and optimal target composition. These optimized bilayer films exhibited good optical transmittance ($\geq 80\%$) and low resistivity of $\sim 10^{-4}$ Ω-cm. The MoO$_x$ layer was found to affect the electrical transport behavior of the ZnGa$_{0.05}$O films. Hall mobility values in NiO$_{1+x}$ / ZGO films were higher than MoO$_x$ / ZGO films by $\sim 50\%$. The optimized NiO$_{1+x}$ /
GZO and MoOx / GZO bilayers showed significant increase in work function with maximum value of 5.3 eV. The work function of the bilayer films was tuned by varying the processing conditions and doping of the overlayers. The oxygen pressure during the growth of NiO_{1+x} layer seems to affect the Ni^{3+}/Ni^{2+} ratio. On the basis of these results, it is suggested that the work function of this composite TCO can be tuned by changing the deposition parameters and/or thickness of the overlayers. Preliminary test device results of the OPVs based on these surface modified GZO layers have shown an increase in the open circuit voltage (Voc) and the power conversion efficiency of these devices. Further, it has also been shown that by optimizing film and active layer processing conditions, power conversion efficiencies comparable to ITO based OPVs (bulk heterojunction) can be achieved in GZO based OPVs. Moreover, NiO_{1+x}/GZO based OPV exhibited an improvement of FF by 17% compared to ITO based OPV. These results suggest that the surface modified GZO films have a potential to substitute for ITO in transparent electrode applications.

2. In this study, we have investigated the microstructural, electrical and optical characteristics of NiO thin films grown by PLD on c-plane α-Al₂O₃. It was established from φ scan and TEM results that the growth of NiO occurs epitaxially in [111] direction with two types of crystalline grains rotated by 60° with respect to each other. In this study the properties of the NiO films have been studied as a function of Li dopant concentration. Lowering of resistivity with increasing Li⁺ doping concentration was achieved and a minimum resistivity of ~ 0.15 Ω-cm was achieved in LiₓNi_{1-x}O thin films (for x = 0.07). The decrease in resistivity with increasing Li⁺ dopant concentration is attributed to the efficient substitution of Li⁺ into Ni^{2+} sites that avoided any degradation of film. Above a critical doping concentration (x=0.05), a
secondary phase starts to form, however, the films still retained their high crystalline quality. Conductivity and transmittance of Li$_x$Ni$_{1-x}$O was found to be strongly dependent on deposition parameters and dopant concentration. Optimum properties in terms of conductivity and transmittance were found for the composition, $x = 0.05$. It is concluded from electronic transport measurements that the conduction in Li-doped NiO thin films takes place via polaron hopping process. NiO has significant technological merit as p-TCO and may provide an important means of realizing transparent electronic devices with enhanced functionality. In view of this, p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO heterojunctions were integrated with c-sapphire by PLD. Structural characterization of films by x-ray diffraction and transmission electron microscopy established that all of the layers in the film were epitaxial. The epitaxial growth can be understood in the framework of DME. I-V characteristics of heteroepitaxial p-Li$_x$Ni$_{1-x}$O/i-Mg$_x$Zn$_{1-x}$O/n-ZnO junctions on c-sapphire with n$^+$-Ga$_x$Zn$_{1-x}$O as the bottom conducting electrode have also been reported and discussed. Introduction of i-Mg$_x$Zn$_{1-x}$O interlayer facilitated the reduction of leakage current and showed improvement in junction characteristics with turn on and breakdown voltage of 2.8 V and 8.0 V, respectively.

It has been shown that laser irradiation at energy densities below the threshold for melting can induce defects into NiO films that lead to significant changes in structural, optical and electrical properties. NiO thin films were found to be more relaxed upon laser irradiation, while maintaining the crystal structure and good epitaxial relationship. It has been demonstrated that a p-type to n-type conductivity transformation with simultaneous enhancement in conductivity up to 3 orders of magnitude can be achieved in NiO thin films.
by laser irradiation and this phenomena is reversible via oxygen annealing. From XPS analysis, a strong correlation has been established between n-type conductivity and non-equilibrium concentrations of laser induced Ni$^0$-like defect states.