INVESTIGATIONS ON PULSED LASER DEPOSITED Li-DOPED ZnO THIN FILMS

M.Sc. Thesis

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INVESTIGATIONS ON PULSED LASER DEPOSITED LI-DOPED ZnO THIN FILMS

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Science

> by REENA YADAV



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2018



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Investigations on Pulsed Laser Deposited Li-doped ZnO Thin Films" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2016 to June 2018 under the supervision of Prof. Krushna R Mavani, Discipline of Physics, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date (REENA YADAV)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor of M.Sc. thesis (with date) (Prof. KRUSHNA R. MAVANI)

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Date:	Date:		

DEDICATION

Dedicated to my Parents and Teachers

LIST OF PUBLICATIONS

Reena Yadav, Ankit Soni, Komal Mulchandani, K. R. Mavani*. "Photoinduced electronic transition and thickness dependent changes in temperature dependent resistivity of Li-doped ZnO thin films" (Submitted in Materials Research Express).

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Abstract

Li-doped ZnO ($Zn_{1-x}Li_xO_2$, with x = 0.000, 0.005, 0.010 and 0.015) thin films were deposited by pulsed laser deposition (PLD) method and the effect of variation of various parameters like Li-doping percentage, substrate, thickness variation and effect of UV radiation on the resistivity and other properties of thin films was observed. The $Zn_{1-x}Li_xO_2$ films with different Li content were grown epitaxially on c-axis oriented sapphire -Al₂O₃ (001) substrate with dominant (002) peak of ZnO hexagonal wurtzite structure. We observed that the resistivity increased on increasing Li content due to decrease in carrier concentration. The next series was made on Quartz substrate and the optical band was observed to be decreasing which is a contradiction to the results observed in case of Sapphire Substrate. Further, for the study of thickness variation, $Zn_{1-x}Li_xO_2$ (x=0.015) thin films with thickness 50nm, 75nm and 100nm were deposited. We observed that there is only slight change in the FWHM (Full Width Half Maximum) showing the highly oriented nature despite of different thicknesses. The resistivity gradually increased on increasing the thickness of films due to the increased scatterinf centres for carriers. Since the band gap of ZnO lies in the near UV spectral region, an unusual feature of metal-to-semiconductor transition (MST) was observed in the temperature range of 200-250 K on illuminating UV radiation (λ = 365nm) on undoped and Li-doped ZnO thin films while the same films in dark condition manifested purely semiconductor characteristics throughout the entire range of temperature (300-10K). This unexpected behavior can be explained on the phenomenon of trapping and de-trapping of carriers in the defect band of ZnO.

KEYWORDS: Optoelectronic devices, Exciton, Epitexial, Strain, Piezoelectric, Luminescence, Pulsed Laser Deposition, Calcination, Plume, ablation, nucleation, laser fluence, annealing, refinement, diffraction, single phase, amorphous, substrate, UV illumination, trapping and de-trapping.

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Abbrevations

Direct Current Sputtering	DC Sputtering
Radio Frequency Sputtering	RF Sputtering
Chemical Vapor Deposition	CVD
Low Pressure Chemical Vapor Deposition	LPCVD
Plasma Enhanced Chemical Vapor Deposition	PECVD
Atomic Layer Deposition	ALD
Physical Vapor Deposition	PVD
Pulsed Laser Deposition	PLD
X-Ray Diffraction	XRD
Full Width Half Maximum	FWHM
Metal-Semiconductor Transition	MST
Valance Band	VB
Defect Band	DB
Conduction Band	CB

Chapter 1

Introduction

In this chapter we will discuss the structure, properties of ZnO and its wide applications in electronic devices.

ZnO attracted the interest of researchers by its incomparable uses in optoelectronics devices due to its direct and wide band gap (3.3 eV) at 300 K. The large exciton binding energy (60 meV) plays the role for intense near band-edge excitonic emission at room and higher temperatures. High-quality ZnO films can be grown at relatively low temperatures (less than 700 °C). The naturally occurring ZnO is an *n*-type semiconductor. The structural, electrical and optical properties of ZnO can be improved or manipulated by doping it with suitable dopant.

1.1. Crystal structure

ZnO can exist in wurtzite, zinc blend, and rocksalt structure depending on the conditions provided. These structures are shown schematically in Fig. 1.1.



Fig.1.1 (a) Wurtzite structure of ZnO



Fig.1.1 (b) Zinc Blend structure of ZnO



Fig.1.1 (c) Rock Salt structure of ZnO

These structures are interconvertible from wurtzite to Zinc-blend or rocksalt depending on the applied pressure and the type of substrate used in case of thin film. Under normal conditions, the thermodynamically stable structure is wurtzite. The zinc-blend structure of ZnO thin films can be obtained by growing it on substrates having cubic lattice. ZnO can change its structure to rocksalt at relatively high pressures (about 10 GPa). Using the LDA (local-density approximation) calculation technique, the equilibrium cohesive energy of ZnO was reported as –9.769, –9.754, and –9.611 eV for wurtzite, zinc-blende, and rocksalt structures, respectively [1].

Typically, the wurtzite structure has a hexagonal unit cell with two lattice parameters, a and c, in the ratio of $\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$. It has four atoms per unit cell and every atom of one kind is surrounded by four atoms of the other kind or vice versa, which are coordinated at the edges of a tetrahedron. In a real ZnO crystal, the wurtzite structure deviates from the ideal arrangement, by changing the c/a ratio to 1.602. It can be said that ZnO exists in distorted wurtzite structure. Wurtzite ZnO can be transformed to the rock salt structure at relatively high external pressures. The reason for this is that the reduction of the lattice dimensions causes the interionic Coulomb interaction to dominate the ionicity over the covalent nature [1]. In ZnO, the pressure-induced phase transition from the wurtzite to the rock salt phase occurs at approximately 10 GPa and a large

volume of about 17% gets decreased, as reported by Bates et al.(1962)[2]. The two phases coexist over a pressure range of 9.1–9.6 GPa.

The zinc-blende ZnO structure is metastable and can be stabilized only by heteroepitaxial growth on substrates having cubic lattice, such as ZnS, GaAs [3] and Pt/Ti/SiO₂/Si [4] having reflecting topological compatibility to overcome the tendency of forming a wurtzite phase. In case of highly mismatched substrates, there is usually a certain amount of the zinc-blende phase of ZnO separated by crystallographic defects from the wurtzite phase. There are four atoms per unit cell and every atom of one type is tetrahedrally coordinated with four atoms of the other type and vice versa. Because of the tetrahedral coordination of wurtzite and zinc-blende structures, the four nearest neighbours and 12 next-nearest neighbours have the same bond distance in both structures. The main difference between these two structures lies in the stacking sequence of closedpacked planes. The wurtzite structure consists of triangularly arranged alternating diatomic close-packed (0001) planes. The stacking sequence of the (0001) plane is AaBbAaBb... in the (0001) direction. In contrast, the zinc blende structure consists of triangularly arranged atoms in the closedpacked (111) planes along the <111> direction that causes a stacking order of AaBbCcAaBbCc.... The small and large letters indicate two different kinds of constituents.

1.2.Lattice Parameters

The lattice parameters of a semiconductor usually depend on the following factors:

- (i) The concentration of impurities or defects and their ionic radii
- (ii) Strain in case of thin film due to substrate
- (iii) Temperature

The lattice constants mostly range from 3.2475 to 3.2501 Å for the *a* parameter and from 5.2042 to 5.2075 Å for the *c* parameter. The c/a ratio varies in a slightly wider range, from 1.593 to 1.6035. The deviation from

that of the ideal wurtzite crystal is probably due to lattice stability and ionicity [5].

1.3. Properties and device applications

1. **Direct and wide band gap:** The band gap of ZnO is 3.44 eV at low temperatures and 3.37 eV at room temperature [6]. As mentioned above, this enables applications in optoelectronics in the UV region, including light-emitting diodes, laser diodes and photodetectors. Lasing by optically pumping has been reported in ZnO platelets, thin films, clusters consisting of ZnO nanocrystals and ZnO nanowires [7].



Fig.1.2 : Light Emitting diode http://antekel.blogspot.in/2015/04



Fig.1.3: Laser diode http://visiblediodelaser

- Exciton binding energy: The free-exciton binding energy in ZnO is 60 meV. This much large exciton binding energy makes ZnO a good material for optical devices that are based on excitonic effects.
- 3. **Piezoelectric constants:** In piezoelectric materials, an applied voltage generates a deformation in the crystal and vice versa. Such

materials are generally used as sensors, transducers and actuators. ZnO is one of the piezoelectric materials having large piezoelectric constant.

4. **Strong luminescence:** Due to a strong luminescence in the greenwhite region of the spectrum, ZnO is a suitable material for phosphor applications like vacuum fluorescent displays and field emission displays. The emission spectrum has a peak at 495 nm and a very broad half-width of 0.4 eV [8].





Fig.1.4 : Vacuum fluorescent display https://hackaday.com/2014/05/24

Fig.1.5 : Field emission displays
Image ref. : Bizled.co.in

- 5. **Radiation hardness:** Radiation hardness is an important factor which makes ZnO a promising material for its use at high altitude or in space. It has been observed that ZnO exhibits exceptionally high radiation hardness [9], the cause of which is still unknown.
- 6. **Thermal conductivity:** ZnO can be used as an additive in rubber industry because the thermal conductivity of ZnO is high (Thermal conductivity of tires can be increased). The high thermal conductivity of ZnO also enables its use in devices operating at high temperature.

7. Availability of large bulk single crystals: Large area single crystals are available for ZnO which makes it the most promising and attractive among other semiconductors.



Fig.1.6: large bulk ZnO single crystals grown by hydrothermal method Rep. Prog. Phys. **72** (2009) 126501

1.4. Native point defects in ZnO

Native point defects are basically the imperfections in the crystal lattice. They include vacancies (missing atoms from lattice positions), interstitials (extra atoms or impurities occupying the extra space between the lattice points) and antisites (Zn atom occupying the lattice site of O or vice versa). Native defects can strongly influence the electrical and optical properties of a semiconductor. Understanding the incorporation and behaviour of point defects in ZnO is therefore essential to its successful applications in semiconductor devices.

ZnO shows high levels of unintentional *n*-type conductivity. Oxygen vacancies and zinc interstitials have often been invoked as sources of *n*-type conductivity in ZnO [10] but the exact cause of the commonly observed unintentional *n*-type conductivity in ZnO is still in dilemma. It is still a challenge to control the unintentional electrical conductivity of ZnO.

1.4.1. Doping

Intentionally adding an external agent into the fixed lattice of a material is called doping. It can change the structural, electrical and optical properties of the material from the undoped one. p-type and n-type conductivity can be achieved in a pure semiconductor by doping it with a suitable dopant. Majority charge carriers in n-type and p-type semiconductors are electrons and holes respectively. In case of ZnO, n-type conductivity can be achieved by doping it with the donor dopants and p-type conductivity can be gained by the doping of acceptors.

1.4.1.1 Donor impurities

Donor impurities are responsible for the *n*-type behaviour of a semiconductor. For ZnO, the dopants which act as donors are: Boron, Aluminum, Gallium, Indium, Fluorine and Hydrogen [11].

1.4.1.2 Acceptor impurities

An acceptor impurity causes the *p*-type behaviour of ZnO. Some of the acceptor impurities for ZnO are:

Lithium, Sodium, Potassium, Copper, Nitrogen, Phosphorus, Arsenic and antimony [11].

1.4.1.3 Co-doping

It is very difficult to achieve p-type behaviour of ZnO because its naturally occurring n-type behaviour compensates it. To overcome this effect and get p-type ZnO, a new phenomenon is developed called Co-doping. It is an effective method to achieve p-type behaviour in ZnO. Co-doping means, acceptors are doped along with the donors during growth. When the film gets fully grown, donor impurities are then removed afterwards by annealing at modest temperature range. Experimentally, Joseph *et al*

(1999) [12] is the first to report *p*-type ZnO through co-doping using N, with Ga as a co-dopant.

1.5 Motivation

The controlled synthesis of materials as thin films is a fundamental step in many applications. In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. In case of thin films, material can be studied in more pure form than the bulk.

At ambient conditions, undoped ZnO exhibits *n*-type charge conductance which is not sufficient because *p*-type conductance is required to bring ZnO-based optoelectronic devices into applications. Since Li has the ionic radius (0.76 Å) very close to that of Zn (0.74 Å), hence it can substitute for Zn site and act as an important factor in obtaining *p*-type ZnO. Many studies have already been done on the *p*-type characteristics of Li-doped ZnO thin films. In view of that, the effects of Li-doping on physical properties of thin films have been studied in this project work. Also, the electrical properties are studied under UV light illumination in order to see the Li-doping effects on photo-response of these materials. Undoped ZnO thin films usually show semiconducting behavior. However, Nistor et al. observed the presence of a MST (Metal to Semiconductor transition) at low temperature in undoped ZnO thin film epitaxially grown by pulsed electron beam deposition (PED) method on sapphire substrate [13]. These results have been interpreted through the quantum corrections to conductivity in a disordered oxide conductor. Since the band gap of ZnO lies in the near UV spectral region, it is worth studying its properties in the presence of UV radiation. Previous studies on the UV irradiation evoked excellent properties of doped ZnO samples [14]. It is expected that new properties will arise on UV illumination.

1.6. Synthesis methods

Synthesis techniques of thin films are broadly divided in two categories

i.e.

- Physical deposition
- Chemical deposition

1.6.1. Physical deposition

Techniques used for synthesis under this category are:

1.6.1.1. Evaporation techniques

- Vacuum thermal evaporation
- Electron beam evaporation
- Laser beam evaporation
- Arc evaporation
- Molecular beam epitaxy
- Ion plating evaporation

1.6.1.2. Sputtering techniques

- Direct current sputtering (DC sputtering)
- Radio frequency sputtering (RF sputtering)

1.6.2. Chemical deposition

- 1.6.2.1. Sol-gel technique
- 1.6.2.2. Chemical bath deposition
- 1.6.2.3. Spray pyrolysis technique
- 1.6.2.4. Plating
 - Electroplating technique
 - Electroless deposition

1.6.2.5. Chemical vapor deposition (CVD)

- Low pressure (LPCVD)
- Plasma enhanced (PECVD)
- Atomic layer deposition (ALD)

As grown thin films can have significantly different properties, depending on the chosen technique. Each method offers some advantages over other techniques while suffering limitation from the others.

Chapter 2

Experimental

This chapter describes the details of various synthesis and characterization techniques used during the project work. Here, synthesis of samples is described which is divided in two parts:

- (i) Synthesis of bulk
- (ii) Thin film deposition

2.1 Synthesis of bulk

We adopted the solid state reaction method for the preparation of bulk material. Powder mixtures are pressed in the form of disc shaped pellets of diameter 20mm and weight 3.5gm. These pellets are then used as targets for the deposition of thin films.

2.1.1 Solid state reaction method

Solid state reaction method is one of the most commonly used processes of making bulk samples of oxides because it is simpler and cheaper than other processes.

The Solid state reaction method involves weighing and mixing of two or more highly pure powders in appropriate stoichiometric ratio. To ensure homogenous mixing, it is required that the mixture is thoroughly grinded. This decreases the particle size and increases the surface area hence ensures better reactivity between the cations and anions present in the mixture. The grinding is done by using mortar and a pestle. Acetone can be added to the mixture once or twice during the grinding process to facilitate the proper grinding. As it is volatile organic liquid, it evaporates gradually during grinding process. The grinding process is usually done for 3-4 hours for 3.4gm mixture. After the first grinding, the mixture has to be calcinated to remove volatile components like CO_2 , NO_2 *etc.* Calcination is done by heating the grinded mixture at high temperatures. The calcinated mixture is then again re-grinded for 15-10 minutes.

The final mixture is then pressed in the form of disc shaped pellets of required diameter using hydraulic press. The pellets are then sintered in air or in presence of a gas (*e.g.* O_2 , Ar, *etc.*) depending on the requirement.

2.1.2 Synthesis of Zn_{1-x}Li_xO₂ targets

Zn_{1-x}Li_xO₂ targets (*x*=0, 0.005, 0.01, 0.015 and 0.02) were prepared by using solid state reaction method. A 99.9995% pure chemical reagent of ZnO (Alfa Aesar) and Li₂O (Aldrich) of purity 97% powders were taken as source materials and mixed together in appropriate stoichiometric ratio. The powder mixture was then grinded for 3 hours using pestle-mortar so as to decreases the particle size (or increases the surface area) and hence increase the reaction rate. It was then heated in the tube furnace at 650 0 C for 3 hours followed by re-grinding for 30 minutes to ensure uniformity in mixture. After the second grinding, the batches of powder were made in the form of pellets (20mm diameter) using hydraulic press under 4 ton pressure. Finally, the pellets were sintered at 850 0 C for 10 hours in tube furnace.

2.2 Synthesis of Thin films

A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties.

Thin Film Deposition is usually divided into two broad categories -

Chemical Deposition and Physical Vapor Deposition

Chemical Deposition is when a volatile fluid precursor produces a chemical change on a surface leaving a chemically deposited coating. One example is Chemical Vapor Deposition or **CVD** used to produce the highest-purity, highest-performance solid materials in the semiconductor industry today.

Physical Vapor Deposition refers to a wide range of technologies where a material is released from a source and deposited on a substrate using mechanical, electromechanical or thermodynamic processes. The two most common techniques of Physical Vapor Deposition or **PVD** are Thermal Evaporation and Sputtering.

For the deposition of thin films in our lab, we are using Pulsed Laser Deposition (PLD), which is a type of Physical Vapor Deposition technique. Pulsed Laser Deposition (PLD) has many advantages over other deposition techniques:

- (i) Flexible, easy to implement
- (ii) Exact transfer of complicated materials
- (iii)Variable growth rate
- (iv)Epitaxy at low temperature
- (v) Greater control of growth (*e.g.* by varying deposition parameters such as laser energy, substrate temperature, target to substrate distance *etc.*)
- (vi)Atoms arrive in bunches, allowing for much more controlled deposition.

2.2.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a physical vapor deposition (PVD) technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target (in a plasma plume) which

deposits it as a thin film on a substrate. This process can occur in ultrahigh vacuum or in the presence of a background gas, such as oxygen which is commonly used when depositing oxides to fully oxygenate the deposited films.

While the basic setup is simple relative to many other deposition techniques, the physical phenomena of laser-target interaction and film growth are quite complex. When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then into plasma formation. The ejected species expand into the surrounding vacuum in the form of a plume containing many energetic species including atoms, molecules, electrons, ions, clusters, particulates and molten globules, before depositing on the typically hot substrate.

Process

The process of PLD can generally be divided into five stages:

- Laser absorption on the target surface
- Laser ablation of the target material and creation of a plasma
- Dynamic of the plasma
- Deposition of the ablation material on the substrate
- Nucleation and growth of the film on the substrate surface

Each of these steps is crucial for the crystallinity, uniformity and stoichiometry of the resulting film.

Laser absorption on the target surface

For our PLD setup, we are using KrF Excimer laser (λ =248 nm) with maximum energy upto 400mJ, pulse width 20ns and a maximum repetition rate of 20Hz.

Laser ablation of the target material and creation of plasma

The ablation of the target material upon laser irradiation and the creation of plasma are very complex processes. The removal of atoms from the bulk material is done by vaporization of the bulk at the surface region in a state of non-equilibrium. In this the incident laser pulse penetrates into the surface of the material within the penetration depth. This dimension is dependent on the laser wavelength and the index of refraction of the target material at the applied laser wavelength and is typically in the region of 10 nm for most materials. The strong electrical field generated by the laser light is sufficiently strong to remove the electrons from the bulk material of the penetrated volume. The free electrons oscillate within the electromagnetic field of the laser light and can collide with the atoms of the bulk material thus transferring some of their energy to the lattice of the target material within the surface region. The surface of the target is then heated up and the material is vaporized.

Dynamic of the plasma

In the next stage, the material expands in the form of plasma parallel to the normal vector of the target surface towards the substrate due to Coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure inside the PLD chamber. The dependency of the plume shape on the pressure can be described in three stages:

- The vacuum stage where the plume is very narrow and forward directed, almost no scattering occurs with the background gases.
- The intermediate region where a splitting of the high energetic ions from the less energetic species can be observed.

• High pressure region where we find a more diffusion-like expansion of the ablated material. Naturally this scattering is also dependent on the mass of the background gas and can influence the stoichiometry of the deposited film.

The most important consequence of increasing the background pressure is the slowing down of the high energetic species in the expanding plasma plume. This results in a lower deposition rate and can furthermore result in a change in the stoichiometry of the film.



Figure 2.1 : Schematic of ablation by laser during thin film deposition

Deposition of the ablation material on the substrate

The third stage is important to determine the quality of the deposited films. The high energetic species ablated from the target are bombarding the substrate surface and may cause damage to the surface by sputtering off atoms from the surface but also by causing defect formation in the deposited film. The sputtered species from the substrate and the particles emitted from the target form a collision region, which serves as a source for condensation of particles. When the condensation rate is high enough, a thermal equilibrium can be reached and the film grows on the substrate surface at the expense of the direct flow of ablation particles and the thermal equilibrium is obtained.

Nucleation and growth of the film on the substrate surface

The nucleation process and growth kinetics of the film depend on several growth parameters including:

- Laser parameters several factors such as the laser fluence [Joule/cm²], laser energy, and ionization degree of the ablated material will affect the film quality, the stoichiometry and the deposition flux. Generally, the nucleation density increases when the deposition flux is increased.
- **Surface temperature** The surface temperature has a large effect on the nucleation density. Generally, the nucleation density decreases as the temperature is increased.
- Substrate surface The nucleation and growth can be affected by the surface preparation (such as chemical etching), as well as the roughness of the substrate.
- **Background pressure** Common in oxide deposition, an oxygen background is needed to ensure stoichiometric transfer from the target to the film. If, for example, the oxygen background is too low, the film will grow off stoichiometry which will affect the nucleation density and film quality.



Figure 2.2:Schematic of the PLD experimental setup

2.2.2 Synthesis of Zn_{1-x}Li_xO₂ Thin films

The thin films are grown on single crystal sapphire (001) substrates of dimensions (2.5 X 5 X 0.5) mm and heated to 600 $^{\circ}$ C during the thin film deposition. Initially, Substrates were sonicated in acetone for 10 minutes and then in propanol for another 10 minutes.

Parameters during deposition are as follows:

Parameter	Value of parameter
Target to substrate distance	5 cm
Substrate temp.	600 °C
Repetition Rate	4 Hz
Deposition time	2 minutes
Laser Pulse Energy	160 mJ
Total Laser shots	480
O ₂ partial pressure	26 Pa

Table 2.1 : Value of various parameters kept constant during deposition

2.3 Annealing

Annealing is a heat treatment that alters the physical and sometimes chemical properties of a material. It involves heating a material above its recrystallization temperature, maintaining a suitable temperature, and then cooling. Annealing can be done in vacuum or in presence of gases $(e.g. O_2)$.

In our case, we have annealed a series of $Zn_{1-x}Li_xO_2$ thin films by varying the value of *x* (0, 0.005, 0.01, 0.015 and 0.02) in flowing oxygen using tube furnace.

Tube furnace consists of a quartz tube, with flanges at both ends, placed in a refractory chamber provided with heating elements and a thermocouple to monitor the temperature. For the annealing of samples in the presence of a particular gas, the desired gas cylinder is connected to one of the flanges using a gas pipe. At the other end, a small piece of gas pipe is connected which is immersed in oil. The gas flow is generally controlled by maintaining the number of bubbles per minute. The sample to be annealed is placed at the center of tube.

In our case, annealing was done at 500°C for 12 hours in flowing oxygen in the tube furnace.



Figure 2.3 : Tube furnace used for annealing

2.4 Characterization Techniques

Depending on the nature of the material being investigated, a suite of techniques may be utilized to assess its structure and properties. This part of chapter will focus on the most effective and widely used techniques available to characterize solid-state compounds.

2.4.1 X-Ray Diffraction

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials. With specialized techniques, XRD can be used to:

- determine crystal structures using Rietveld refinement
- determine of modal amounts of minerals (quantitative analysis)
- characterize thin films samples by:
- determining lattice mismatch between film and substrate and inferring stress and strain
- determining dislocation density and quality of the film by rocking curve measurements
- determining the thickness, roughness and density of the film using glancing incidence X-ray reflectivity measurements
- make textural measurements, such as the orientation of grains in a polycrystalline sample

Working

The atomic planes in the crystals have separation of about a few to several angstroms, which is of the order of the wavelength of X-Rays. Thus, when X-Rays are incident on crystalline materials they get diffracted by the crystallographic planes. The diffracted X-rays undergo constructive interference when they satisfy the Bragg's condition:

$$2d \sin\theta = n\lambda$$

Where, d is the separation between the planes, θ is the angle of diffraction, n is the order of diffraction and λ is the wavelength of the incident X-Rays (λ of Cu- $k_{\alpha} = 1.5406$ Å).

These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice are attained. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.



Figure 2.4 : Illustration of X-Ray diffraction

2.4.2 Resistivity measurement

Resistivity measurement is the most important parameter for studying electrical properties of samples. For the measurement of resistivity of thin films, we used four probe method.

The experimental set up consists of probe arrangement, heater, constant current generator, compressor and digital panel meter (measuring voltage and current). This method is employed when the sample is in the form of thin film. The sample is millimeter in size and having a thickness t. It consists of four probe arranged linearly in a straight line at equal distance S from each other. A constant current is passed through the two probes and the potential drop V across the middle two probes is measured. An oven is provided with a heater to heat the sample so that behavior of the sample is studied with increase in temperature.



Figure 2.5: Arrangement of four probe method

At a constant temperature, the resistance, R of a conductor is proportional to its length L and inversely proportional to its area of cross section A.

$$R = \rho \frac{L}{A}$$
$$A = at$$
$$\rho = A \frac{R}{L} = at \frac{R}{S}$$

Where, ' ρ ' is the resistivity of the conductor and its unit is ohmmeter.

't' is the thickness of thin film under measurement

- 'a' is the width of thin film
- 'S' is the distance between the two middle probes

The four point probe is preferable over a two-point probe because the contact and spreading resistances associated with the two point probe are large and the true resistivity can't be actually separated from the measured resistivity. In a four point probe, very little contact and spreading resistance is associated with the voltage probes and hence one can obtain a fairly accurate calculation of the resistivity. Using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and semiconductor material.

Temperature dependence of resistivity of semiconductors:

Total electrical conductivity of a semiconductor is the sum of the conductivities of the valence band and conduction band carriers. Resistivity is the reciprocal of conductivity and its temperature dependence is given by

$$\rho = A \exp \frac{E_g}{2KT}$$

Where, E_g – band gap of the material

T – Temperature in kelvin

K – Boltzmann constant (8.6x10-5 eV/K)

The resistivity of a semiconductor rises exponentially on decreasing the temperature.

A semiconductor has electrical conductivity intermediate in magnitude between that of a conductor and insulator. Semiconductor differs from metals in their characteristic property of decreasing electrical resistivity with increasing temperature.

According to band theory, the energy levels of semiconductors can be grouped into two bands, valence band and the conduction band. There is a band gap between conduction band and valance band. At 0K, all the electrons are in valance band and the conduction band remains unoccupied. Therefore, conduction is not possible at 0K, and resistance is infinite. As temperature increases, some electrons are thermally excited into the conduction band and the occupancy of conduction band goes up, thereby resulting in increase of conductivity and decrease of electrical resistivity of semiconductor.

Chapter 3

Results and discussion

ZnO targets with nominal 0%, 0.5%, 1.0%, 1.5% and 2% Li-doping were prepared according to the chemical formula $Zn_{1-x}Li_xO_2$ where *x*=0, 0.005, 0.01, 0.015 and 0.02 mole fraction for the seven samples.

XRD Analysis of targets:



Figure 3.1: XRD analysis of Zn_{1-x}Li_xO₂

There is no seperate peak of Li or any other impurity peak in the XRD pattern of $Zn_{1-x}Li_xO_2$ targets which shows that Li^+ is well doped in interstitial sites of ZnO and all the targets are of high purity.

We examined the four set of thin films from the prepared targets which are as follows:

- Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire (Al₂O₃) substrate.
- A series of varied thickness of Li-doped ZnO thin films with 1.5% Li content.
- 3. $Zn_{1-x}Li_xO$ thin films on quartz substrate
- Photo-induced study for Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire

The analysis of various measurements for each set of thin films was done and described as follows:

1. Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire (Al₂O₃) substrate.



1.1 XRD analysis

Figure 3.2: XRD analysis of Zn_{1-x}Li_xO₂ thin films on Sapphire substrate

XRD pattern shows that the films are epitaxially grown on the c-axis oriented sapphire substrate (Al₂O₃). The peaks of ZnO coincide for each doping percentage. It implies that there is no notable effect of doping on structural properties of ZnO thin films. Moreover, no additional diffraction peaks are observed in result which confirms the single-phase structure and high purity of $Zn_{1-x}Li_xO_2$ thin films.

1.2 Resistivity measurements



Figure 3.3: Temperature dependent resistivity measurements for $Zn_{1-x}Li_xO_2$ thin films

From the analysis of resistivity versus temperature plot, it can be clearly said that Li-doping gives rise to the semi-insulating characteristics of ZnO thin films. On increasing the Li content and keeping the thickness constant, resistivity increases. This can be due to the decrease in carrier

concentration. Since Li^+ is monovalent and Zn^{2+} is divalent, there is decrease in carrier concentration when Zn^{2+} is substituted by Li^+ ion.

2. A series of varied thickness of Li-doped ZnO thin films with 1.5% Li content

2.1 XRD analysis



Figure 3.4: XRD pattern of $Zn_{1-x}Li_xO_2$ (x= 0.015) thin films with different thickness.



Figure 3.5: Change in FWHM of thickness dependent series



Figure 3.6: Plot of calculated FWHM versus Film thickness

The crystalline structure of obtained Li-doped ZnO films was analyzed by X-Ray Diffraction (XRD) using Rigaku X-ray diffractometer of $Cu_{k_{\alpha}}1.54$ Å wavelength. Fig.3.4 shows the XRD patterns of 1.5% Lidoped ZnO thin films on sapphire substrate which unveil that all the films are highly oriented along the c-axis with hexagonal wurtzite structure. As shown in the fig.3.6, FWHM (Full Width Half Maximum) corresponding to ZnO (0 0 2) peak for 50nm, 75nm and 100nm thick film is calculated to be 0.29344, 0.36779 and 0.37261 respectively by Gaussian fitting. There is slight increase in the FWHM, consequences of which can affect the resistivity of the films and are discussed in the resistivity measurement section. It is clear from the XRD pattern that there is no shift in the peaks and no impurity peaks are found, therefore the grown films are highly crystalline.

2.2 Resistivity measurements



Figure 3.7: Temperature dependent resistivity measurement of the thickness dependent study of ZnO thin film with 1.5% Li content



Figure 3.8: $ln(\rho)$ Versus T⁻¹ plots for the thickness dependent study of ZnO thin film with 1.5% Li content

To understand the conduction mechanism, the temperature dependent electrical resistivity measurements were carried out using the four-probe point method. The ohmic contacts were made on the film by conductive silver paste. The electrical resistivity behavior of doped ZnO thin films with varied thickness was examined in the temperature range of 300K to 10K. Fig.3.8 shows the variation of log electrical resistivity with reciprocal of the absolute temperature for the three prepared thin films. It can be interpreted from the plot that the electrical resistivity increases as temperature decreases and obeys the well-familiar Arrhenius equation:

$$\rho = \rho_{\circ} e^{\Delta E/kT}$$

Or,

$$\ln \rho = \ln \rho_{\circ} + \frac{\Delta E}{kT}$$

Where,

 ΔE is the activation energy

k is the Boltzmann constant $(8.614 \times 10^{-5} \text{ eVK}^{-1})$

T is the absolute temperature (in kelvin)

 ρ_0 is the pre-exponential factor

Deposition time	Film thickness	ρ at 300 K	ΔΕ
(min.)	(nm)	(Ω-cm)	(meV)
2	50	0.303	13.62
3	75	0.645	17.58
4	100	1.835	22.73

Table 3.1: calculated value of activation energy for thickness dependent series

It can also be clearly observed that at a particular temperature, as the thickness of films increases, resistivity also increases. This signifies that the films tend to show bulk properties with thickness. The plots fit in Arrhenius equation at higher temperature range and the value of activation energy for each film is given in table 3.1.

The plot corresponding to the 100nm thick film is fit with and the estimated activation energy is 22.73 meV. The change in the slope of plots specifies the change in activation energy of the films. The activation energy calculation provides the information of the trapping levels. It can be clearly interpreted from the fittings that activation energy increases as the film thickness increases. This can be due to the increase in the trap sites on increasing thickness.

In the literature, the resistivity increased on increasing thickness of film due to the decrease in carrier concentration [15-16]. However, it was also reported that resistivity decreased on increasing film thickness upto a certain thickness and thereafter increases [17-18]. These differences in results can be arising due to the difference in deposition methods and deposition parameters. Here in our case, we can relate the resistivity with the change in FWHM. As the thickness of film increases, FWHM corresponding to ZnO (0 0 2) peak also increases, which means the crystallinity is degrading or the grain size decreases. As a result of which the charge scattering centers increases. The Li⁺ ion scatters from the grain boundaries. Above described reason can be possible for the increase in resistivity on increasing thickness.

3. Zn_{1-x}Li_xO₂ thin films on quartz substrate



3.1 XRD analysis

Figure 3.9: XRD analysis of Zn_{1-x}Li_xO₂ thin films on quartz substrate

The crystalline structure of obtained Li-doped ZnO films was analyzed by X-Ray Diffraction (XRD) using Rigaku X-ray diffractometer of $Cu_{k_{\alpha}}1.54$ Å wavelength. Since quartz is amorphous in nature, the two peaks in the XRD data corresponds to (002) and (004) planes of ZnO. There is no extra peak of impurity which indicates that the films are of high quality.

3.2 UV-Visible analysis



Figure 3.10: UV-Visible data analysis for oxygen deficient $Zn_{1-x}Li_xO_2$ thin films on quartz substrate



Figure 3.11: Variation in optical band gap of $Zn_{1-x}Li_xO_2$ thin films on quartz substrate

For pure ZnO thin film on quartz substrate, the optical band gap comes out is 3.20 eV. It can be clearly interpreted from the plot that optical band gap of the Li-doped ZnO gradually increases on increasing the doping percentage. The similar result was obtained on sapphire substrate where resistivity increased on increasing doping percentage and the reason for same is describe in that section.

4.Photo-induced study for Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire

To observe the effect of UV radiation on the electrical properties of Lidoped ZnO thin films, temperature dependent resistivity measurements were performed in the presence of UV radiation of wavelength 365 nm.



Figure 3.12: Temperature dependent resistivity measurement of undoped ZnO in dark and under UV illumination



Figure 3.13: Metal to semiconductor transition in $Zn_{1-x}Li_xO_2$ thin films

The electrical resistivity versus temperature curve shows Meta-Semiconductor transition (MST) in the temperature range of 200 K-250 K for undoped ZnO thin film and it shifts towards higher temperature range in case of doped ZnO thin films as shown in fig.3.12 and fig.3.13 respectively. However, complete semiconducting behavior was manifested in the entire range of temperature in dark condition. This behavior of shift in MST temperature range on doping can be utilized for photo-switching in the presence of UV radiation at room temperature.

With reference to previous literature [14], the reason behind such behavior of undoped ZnO on UV radiation illumination can be interpreted from the trapping and detrapping processes in the impurity band arising from the native defects in ZnO. At lower temperature, the photo-excited carriers from the valence band (V.B) get trapped in the vacant defect band (D.B), causing decrease in carrier concentration. As the temperature increases, both thermal and photo-excitation takes place. The carriers gets detrapped from defect band and thermally excited to conduction band (C.B), as a result of which carrier concentration increases. At transition temperature, due to increased carrier concentration, coulombic interactions start to act between the carriers and resistivity increases as temperature further increases.



Figure 3.14: Trapping and detrapping of carriers in Defect band of $Zn_{1-x}Li_xO_2$

This process of trapping and detrapping of carrier concentration allows MST in undoped and Li-doped ZnO thin film. Also there is all over increase of resistivity in the presence of UV radiation due to the columbic interactions and surface scattering. The shift in MST temperature range for Li-doped ZnO thin films can be explained by the fact that Li-doping shifts the defect band of ZnO as shown in Fig. 3.14.

Chapter 4

Conclusions

This chapter elaborates important conclusions drawn from the present investigations.

4.1. Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire (Al₂O₃) substrate

4.1.1. Pure Li-doped ZnO thin films on Sapphire substrate have successfully been deposited by Pulsed Laser Deposition method.

4.1.2. X-ray diffraction study indicates the high c-axis orientation of the Li-doped ZnO thin films on sapphire substrate. The patterns consist of sharp peaks, which are matched with the common ZnO hexagonal phase, *i.e.*, wurtzite structure.

4.1.3. Temperature dependent resistivity measurements of deposited films unveils that the samples are semi-insulating in nature. The resistivity at a particular temperature increases as Li content increases due to decrease in carrier concentration.

4.2. A series of varied thickness of Li-doped ZnO thin films with 1.5% Li content

4.2.1. Li-doped ZnO (1.5% Li content) thin films with different thickness (50nm, 75nm and 100nm) were deposited successfully on Sapphire substrate by PLD method.

4.2.2. X-ray diffraction pattern shows the change in FWHM corresponding to (002) peak of ZnO with increasing thickness. This means that the crystallinity is degrading.

4.2.3. Resistivity at a constant temperature increases as the thickness of film increases. The curve of log of electrical resistivity versus reciprocal of the absolute temperature obeys well familiar Arrhenius equation for each film. This can be explained as a result of charge scattering from the grain boundaries. The activation energy calculated from the fitting of Arrhenius equation at higher range of temperature increases on increasing film thickness.

4.3. Zn_{1-x}Li_xO₂ thin films on quartz substrate

4.3.1. $Zn_{1-x}Li_xO_2$ (*x*=0, 0.005, 0.010, 0.015 and 0.020) thin films are successfully deposited on quartz substrate using PLD method.

4.3.2. X-ray Diffraction shows the peaks corresponding to (002) and (004) planes of ZnO.

4.3.3. UV-Visible data shows the gradual increase in optical band gap with increase in Li content.

4.4. Photo-induced study for Zn_{1-x}Li_xO₂ thin films on c-axis oriented single crystal Sapphire

4.4.1. Temperature dependent resistivity measurements were performed in the presence of UV radiation of wavelength 365 nm. The electrical resistivity versus temperature curve shows MST in the temperature range of 200 K-250 K for undoped ZnO thin film and it shifts towards higher temperature range in case of Li-doped ZnO thin films. However, complete semiconducting behavior was manifested in the entire range of temperature in dark condition.

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