Terahertz Time-Domain Spectroscopy of ZnO Thin Films and Nanostructures

M.Sc. Thesis

By Udit Kumar



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Terahertz Time-Domain Spectroscopy of ZnO Thin Films and Nanostructures

A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of

Master of Science

by **UDIT KUMAR**



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE June 2022



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Terahertz Time-Domain Spectroscopy of ZnO Thin Films and Nanostructures** in the partial fulfilment 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 August 2020 to June 2022 under the supervision of Prof. Krushna R. Mavani, IIT Indore.

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

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

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DEDICATED TO MY PARENTS & TEACHERS

Abstract

The need of modern technology is to investigate new materials with rich fundamental physics and diverse technological applications.

ZnO is a typical transparent conductive material (TCO) extensively studied for its UV photosensing and gas sensing applications. The conductivity of the films and nanostructures under UV illumination is an important property that governs the feasibility for practical applications. THz radiation can be used to examine material systems without affecting them to change their current states because of its low energy. As a result, it is a non-perturbative technique for material study.

In this work, we have used PLD and GLAD techniques to deposit highly crystallographically aligned ZnO thin films and nanostructures on Quartz substrate. Further, we have studied the effect of the environment and UV illumination on the conductivities of the two samples using Terahertz Time-Domain Spectroscopy (THz-TDS).

It was found that, in comparison to thin film, the porosity of the nanostructures was significantly high. Further, when compared to thin films, the conductivity of nanostructures decreases by an order due to increased adsorption of nitrogen and oxygen gases which results in band bending. Furthermore, the conductivities in vacuum environment are higher than nitrogen atmosphere both in the presence and absence of UV light. The conductivities of both samples increase monotonously with increasing UV light intensity.

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ACRONYMS

Zinc Oxide	ZnO
Pulsed Laser Deposition	PLD
Glancing Angle Deposition	GLAD
X-Ray Diffraction	XRD
Scanning Electron Microscopy	SEM
Ultraviolet	UV
Full Width at Half Maximum	FWHM
Terahertz	THz
Terahertz Time-Domain Spectroscopy	THz-TDS

Chapter 1

Introduction

1.1 Overview

Wide band gap semiconductors such as ZnO, GaN, SnO₂ etc. have attracted much attention because of their increased emphasis on an ultraviolet (UV) response [1]. Amongst these, Zinc Oxide (ZnO) based materials are one of the most studied materials. For decades, it has been extensively explored, owing to the unique combination of electrical, structural and physical properties.

The first study on ZnO was started in the 1900s, and the first electronic application came in radio sets in the 1920s [2]. With the discovery of piezoelectric properties in the 1950s and the electronic application in thin film surface wave acoustic devices, new applications were introduced. It is an II-VI group n-type semiconductor with a wide bandgap of 3.4 eV [3][4] which corresponds to emission in the ultraviolet range in the electromagnetic spectrum. Along with UV emission, it also shows emissions in the visible region of the electromagnetic spectrum due to the intrinsic defects present in ZnO [5]. It was earmarked as a potential candidate for use in LED fabrication due to its high exciton binding energy of 60 meV which led to an increase in research into p-type doping. However, this idea is challenging due to self-compensation caused by native defects and irreproducible results. There has been a revival of research in ZnO due to the synthesis of nanostructures. Further, in the absence of Ultraviolet (UV) light, the ZnO thin films are nearly transparent to THz waves. However, with UV light-induced amplification, zinc oxide has been shown to achieve a 35 % modulation in amplitude [6]. ZnO is still being studied by researchers due to its attractive properties.

Because of its low photon energy, great transparency, and broadband features, Terahertz (THz) wave technology holds potential for biological imaging, security inspection, and communication. Recent advances in THz generation and detection have played a significant role in the promotion of THz technology. THz Time-Domain spectroscopy is an excellent non-destructive method for probing the optical and electrical properties of materials. Progress in the THz realm has huge implications for both cutting-edge technologies and fundamental physics. Because of the materials' picosecond time response, high-speed

computers with terabit per second rates and electronic devices with picosecond time scales are possible. THz radiation has a wide range of applications due to its high penetration depth, non-ionizing nature, high opacity to metals while being transparent to insulators, and great sensitivity to water. THz radiation can be used in the detection of explosives, epithelial cancer, quality control, security checks, etc [7]. Because THz radiation has such low energy, it can be utilised to study material systems without causing them to change their current states. As a result, it is a non-perturbative material investigation technique.

This research is mainly inspired by the fascinating electrical and optical properties of ZnO thin film and nanostructures and their behaviour under UV illumination in different environments. We analyse the variation in conductivities of two samples, viz thin film and nanostructures, with and without UV illumination, in vacuum and nitrogen environments. Terahertz Time-Domain Spectroscopy (THz-TDS) is used to probe the conductivities of the samples. Diverse properties of ZnO thin film and nanostructures come into play, including porosity, reaction to different gases, and band bending, which broadens the horizon for Terahertz studies on various properties of ZnO thin film and nanostructures.

1.2 ZnO crystal structure

ZnO belongs to the category of binary compounds and crystallizes into three different structures: Wurtzite, Zinc blend and Rocksalt as shown in Fig.1.1



Fig.1.1 Crystal structures of ZnO (a) Cubic Rocksalt, (b) Cubic Zinc blende, (c) Hexagonal wurtzite

Under normal atmospheric conditions, the hexagonal wurtzite structure is thermodynamically stable. The Zinc blende structure is stabilized by growing it on a cubic substrate like GaAs (001) and the Rocksalt structure is obtained under relatively high pressure.

The most stable *i.e.*, wurtzite structure, has lattice constants a=3.25 Å and c=5.21 Å with a c/a ratio of nearly 1.6 at a temperature of 297 K [8]. As depicted in Fig.1.2, the wurtzite structure of ZnO comprises of two interpenetrating hexagonal closed-packing (hcp) sublattices of Zn²⁺ and O²⁻ ions arranged such that each Zn ion is surrounded by a tetrahedron of oxygen ions and vice versa. The Zn 3d e⁻ hybridizes with the O 2p e⁻ [9], which has important implications on the electrical and optical properties of ZnO.



Fig.1.2 ZnO wurtzite cell, representation of tetrahedral coordination for both types of atoms (Zn: yellow and O: grey).

The tetrahedral coordination is an indicator of sp³ covalent bonding and due to the high difference in electronegativity (1.65 for Zn and 3.44 for O), it shows ionic character which increases the bandgap value above the value expected for a covalent bond. Polarity is induced due to this tetrahedral coordination.

The [000/] signifies directions parallel to the c-axis. ZnO has a natural predisposition to develop in [000/] orientations because it has the highest surface energy as compared to

other low-index planes of the wurtzite structure. The surface energy of ZnO nanostructures is critical for their nucleation and development.

1.3 Electronic properties of ZnO

Intrinsically, it is an n-type II-VI semiconductor with a wide band gap of $E_g = 3.4 \text{ eV}$ at room temperature which corresponds to the UV spectral region and is transparent in the visible region. It has a high electron mobility of 205 cm² V⁻¹ s⁻¹, and low excitons' binding energy of 60 meV [10] which keeps excitons stable at ambient temperature, and it can also be doped with various group elements to improve its properties.

On doping with group III elements, n-type conductivity increases as they occupy Zn sites due to similarity in ionic radii and act as electron donors. Similarly, it can be doped with group I and V elements to obtain p-type conductivity but the stability and reproducibility are very poor due to self-compensation caused by native defects as certain native defects which act as donor may spontaneously form and compensates the deliberately introduced acceptors [11].

The fascinating electrical properties of doped and undoped ZnO make it a good contender for a wide range of technological applications.

1.4 Photoresponse in ZnO:

The existence of oxygen vacancies in ZnO semiconductors is primarily responsible for their conductivity. And these vacancies are deep level donors [12], [13]. Moreover, they are more likely to be present at the surface of ZnO [14], [15] and serve as surface trap centres which trap electrons and create a depletion layer, which decreases the conductivity of the material.

The trapping of electrons with oxygen adsorption can be described as:

$$O_2(g) + e^- \rightarrow O_2^-(ad)$$

where $O_2(g)$ and $O_2^-(ad)$ indicate oxygen in its free and adsorbed states, respectively.

Now, when the material is illuminated with UV light with energy greater or equal than the band gap of the material, electron-hole pairs are generated by the photon absorption. These generated electrons and holes take part in the photo-desorption process. The desorption of oxygen requires a photo-generated hole:

$$h^+ + O_2^-(ad) \rightarrow O_2(g)$$

The depletion region is eliminated and the photo-generated electron remains and contributes to the increase in photocurrent. When the UV light is turned off, again re-adsorption of oxygen takes place and conductivity of material decreases.

So, the rate of adsorption, desorption, and re-adsorption of oxygen on the surface of ZnO determines its conductivity and photoresponse [16].

1.4.1 Photoresponse and conductivity of ZnO thin films and nanostructures in vacuum and nitrogen:

As we know, the main mechanism behind the photoresponse and conductivity of ZnO is the rate of adsorption, desorption and re-desorption of oxygen on the surface. It is observed that the conductivity of film and nanostructures in vacuum is more than the conductivity of film and nanostructures in nitrogen. The binding energy of stable nitrogen is -1.42 eV and for oxygen is -2.47 eV, according to density functional theory investigations by M Breedon *et al* [17]. This demonstrates that nitrogen molecules have a much lower adsorption rate and interaction with the surface than oxygen molecules.

Theoretical studies confirmed that nitrogen is adsorbed on the surface of ZnO via ionictype bonding, whereas oxygen atoms are adsorbed via covalent-type bonding, implying that the interaction (bonding) in the case of nitrogen adsorbate associated with physisorption is very weak, whereas oxygen adsorbate is adsorbed via chemisorption process. Thinning of depletion width can be observed as compared to oxygen backgrounds. So, the conductivity of film and nanostructures in nitrogen will be more than in oxygen/air environments [18].

The easy desorption of oxygen molecules from the surface is related to the vacuum-assisted increase in conductivity. Additionally, the photo-generation process generates more carriers as trapped electrons are released, increasing the photocurrent and hence the conductivity. UV irradiation is thought to remove loosely bound oxygen from the surface, which is then followed by the removal of lattice oxygen via surface hydrocarbons in vacuum.

1.5 Thin films:

Thin film is a layer of material having dimensions in the nanoscale range. Fabrication of thin films opens a pathway for exploring a plethora of novel phenomena for various applications. Further, it allows the fabrication of miniaturized devices with tunable desirable properties. Thin films differ from bulk materials in terms of transmission, reflection, absorption, hardness, abrasion resistance, corrosion, penetration, and electrical behaviour. The fundamental benefit of having high-quality big single crystals of ZnO is that thin films or layers of ZnO can be epitaxially formed with lower concentrations of extended defects, without contamination from the substrate, and without a thermal mismatch.

The substrate on which thin films are grown is critical in defining the film's orientation and characteristics. The majority of ZnO epitaxial layers have been produced on sapphire, GaAs, CaF₂, ScAlMgO₄ and Si substrates. Scandium-Aluminium-Magnesium Spinel (ScAlMgO₄) offers the lowest lattice mismatch for ZnO ($\Delta a/a=0.09\%$), therefore highest quality films, with mobilities comparable to or even higher than mobilities of a single ZnO crystal (>=205 cm² V⁻¹ s⁻¹) [19]. Large, high-quality Sapphire substrates are popular as they are cheap and easily available. However, for practical applications, the high cost of such substrates acts as one of the limiting factors.

The growth of thin film consists of the nucleation process followed by the development stage. Both the processes depend upon different factors like substrate temperature, chemistry and structure of substrate and material, growth rate and angle of deposition.

1.6 Nanostructures:

In recent years, low-dimensional semiconductor nanostructures and their integration into functioning devices have transformed semiconductor technology. As a result, nanostructures such as wires, tubes, rods, and belts with tiny dimensions (e.g., 1D) have sparked major basic research in scientific communities. Some features of Nanostructures are as follows:

• <u>Low dimension</u>: The electrical energy levels in bulk materials are continuous, however, the case for nanostructured materials is different due to the quantum size effect [20]. The development of quantization effects owing to the confinement of

electron movement is one of the most immediate results of shrinking materials to the nanoscale range. As a result, separate energy levels emerge.

- <u>Large surface to Volume ratio</u>: The reduction in the size of material has a direct relation to the surface-to-volume ratio. As the size reduces, the ratio increases due to the increase in surface area per unit volume. Consequently, the increased surface area induces porosity in the material. And this porosity increases adsorption rate and is essential for applications like photo-sensing [21].
- <u>Boundary effects:</u> Grain boundaries play a crucial role in the properties of material because a significant portion of atoms resides in the grain boundaries. Therefore, with the reduction in grain size, the interfacial region must be considered for the nano grain size of materials. And the surface activity of adsorption and desorption increases with the reduction of grain size [22].

1.7 Terahertz Spectroscopy:

Terahertz (THz) radiation lies between infrared and microwave radiation in the electromagnetic spectrum. It is also known as submillimeter radiation as its wavelength range is 0.03 mm to 3 mm. Its frequency ranges from 0.1 THz to 10 THz with energy between 0.4 meV to 40 meV [23]. With photon energy in the meV range, it interacts strongly with materials or systems having a characteristic lifetime in picosecond ($\sim 10^{-12}$ s) [24]. The THz band attracted attention at first because it was more difficult to generate and detect THz frequencies than other well-established technologies in electronics and optics. A terahertz gap arises from the nature of the sources and detectors used in spectroscopy both at the optical (high-frequency) side and electronic (low-frequency) side of the gap. The upper cutoff of an electronic device's frequency response, which is governed by the physical size and carrier mobility of the device material, limits its scaling into the THz range. The lower cutoff of optical devices to bring into the THz band has the same constraint because THz photons cannot stimulate electrons into the conduction band in photodiodes [25]. Recent advances in the fabrication of new semiconducting materials, as well as the capacity to confine electrons at the quantum level, are driving high-speed devices towards the THz gap.



Fig.1.3 Terahertz radiation in Electromagnetic Spectrum

In THz Time-Domain Spectroscopy, a THz pulse is measured without any sample and this pulse is used as a reference. Another pulse after passing through the sample is recorded and with the two pulses, optical constants like refractive index, conductivity, transmission coefficients, and dielectric constants can be calculated. The transmitted THz waveform is in time domain, Fourier transform of which gives THz waveform in frequency domain *i.e.*, amplitude and phase of THz wave as a function of THz frequency. THz spectroscopy measures the intensity of electromagnetic radiation rather than its electric/magnetic field component which is an advantage over optical spectroscopic techniques.

1.8 Drude-Smith Model:

The Drude model assumes a free electron gas with complete momentum randomization following elastic scattering events, and it states that the real component of conductivity maximizes at direct current (DC), whereas the imaginary component is positive and maximizes at the carrier scattering rate frequency. The Drude model cannot produce negative imaginary conductivity or real conductivity with a non-DC maximum.

The preferential backward scattering of electrons following collisions is responsible for the negative imaginary conductivity. The electron reflects from surfaces, grain boundaries, and imperfections, accounting for a portion of backward scattering. A Coulombic restoring force from positively charged holes or defects could also cause it. This restoring force, also known as backward scattering, can be modelled by adding a persistence of velocity parameter to Drude model by Smith to describe the scattering event [26].

The Drude-Smith model has been extremely successful in recreating the localization signatures observed in a wide range of materials. It has been used as the microscopic conductivity of metallic nanoparticles in EMTs to simulate THz spectroscopy data because it can reproduce the conductivity signature of weak confinement.

According to the Drude-Smith model for conductivity:

$$\sigma = \frac{\varepsilon_o \omega_p^2 \tau}{1 - i\omega\tau} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{1 - i\omega\tau} \right] - i\varepsilon_o \omega(\varepsilon_{\infty} - 1)$$

where ω_p , τ and c are plasma frequency, characteristic scattering time and persistence of velocity parameter respectively [26]. Further, the plasma frequency and carrier concentration are related by the equation

$$N_e = \frac{\varepsilon_o \omega_p^2 m^*}{e^2}$$

where N_e is the electron density and m^* is the effective mass of electron.

Chapter 2

Experimental and Characterization techniques

This chapter describes the techniques used for the synthesis and characterisation of samples in this project. Synthesis techniques include solid state reaction method followed by thin film synthesis using Pulsed Laser Deposition (PLD) technique and nanostructure synthesis using Glancing Angle Deposition (GLAD) technique. We used X-Ray Diffraction technique and Raman Spectroscopy for structural analysis of samples followed by Terahertz Time-Domain Spectroscopy to compare the complex conductivity, refractive index and permittivity of the samples.

Experimental techniques used in this project:

- 1. For samples preparation:
 - 1. Bulk synthesis by solid state reaction method
 - 2. Thin film synthesis using Pulsed Laser Deposition (PLD) technique
 - Nanostructure synthesis using Glancing Angle Deposition (GLAD) Technique
- 2. For characterization:
 - 1. X-Ray Diffraction
 - 2. Raman Spectroscopy
 - 3. Scanning Electron Microscopy
 - 4. Terahertz Time-Domain Spectroscopy

2.1.1) Bulk synthesis by solid state reaction:

The bulk materials (i.e., pellets) have been synthesized using solid-state reaction route. This method is solvent-free and a widely used conventional method for making the bulk material of oxides. For the present work, ZnO (99.99% pure, Aldrich) powder have been used to make the pellets. The powder grinding was done for 1 hr using pestle mortar. After proper mixing of powder, the pellets were made using the die-set of the 20 mm diameter. To make the pellet, the powder was pressed with 5 tons of pressure using the hydraulic press (PCI

Analytics, India). This pellet was then sintered at 1000 °C for 10h in the Box furnace with the same cooling and heating rate in a controlled manner.



Fig.2.1 Different stages of the Solid State Reaction method

For this project, 1 pellet of ZnO has been synthesised in order to prepare thin films and nanostructures of ZnO.

2.1.2) Thin film synthesis using Pulsed Laser Deposition (PLD) technique

The thin films have been synthesised using Pulsed Laser Deposition (PLD) technique. PLD technique is a Physical Vapour Deposition technique. It is generally known for the fabrication of thin films. The main underlying mechanism for the synthesis of thin film is the formation of the deposited material's vapour (target) and subsequently its development or condensation on surface to be coated (substrate). PLD provides a great range of flexibility for parameters that significantly affect the properties of deposited thin films. Fig. 2.2 and Fig. 2.3, show a schematic and real experimental setup of the PLD system used for this work.



Fig.2.2 Schematic Diagram of Pulsed Laser Deposition Chamber

Following are the components of a typical PLD setup:

- A laser source (KrF excimer lasers, ArF excimer lasers, Nd:YAG lasers, femtosecond lasers)
- ✤ A stainless-steel vacuum chamber
- Lens for focusing the laser onto the target
- ✤ Gas flow assembly
- Vacuum pump (Rotary pump, turbomolecular pump)
- Rotating target holder assembly
- Substrate holder connected with a programmable heater

For this project work, a pulsed excimer laser KrF (Compex Pro 102 F, Coherent, Germany) of wavelength λ =248 nm, pulse width=20 ns, has been used as an ablation source. A vacuum chamber (Excel Instruments, India) has been used as a deposition chamber. The vacuum chamber contains a target holder, substrate holder, heater, gate valves and assembly for gas inlets. A high vacuum of the order of ~10⁻⁴ Pa is achieved using the efficient rotary and the turbomolecular pumps (Pfeiffer Vacuum GmbH). The laser beam is focused onto the target pellet using a focusing lens (focal length, f=30 cm). The laser beam impinges onto the surface of the target (ZnO pellet) for ablation and an elliptical plasma plume is formed. Fig.2.4 shows a photograph of a plasma plume generated from

ZnO target material during deposition. This plasma plume comprises of ejected species from the target material.



Fig.2.3 Experimental setup of Pulsed Laser Deposition System at Thin Film laboratory (IIT Indore)



Fig.2.4 Photograph of plasma plume generated from ZnO target

The mechanism of PLD is divided into two parts:

- 1. Laser interaction with the target
- 2. Plume interaction with the substrate

1. Laser interaction with target:

The laser pulse at controlled frequency and energy strikes the surface of the target for a fixed number of shots depending upon the thickness of the film required. The energetic UV(ultraviolet) photons strike the target surface and break the bonds, which results in the ejection of particles from the surface layer of material. This is known as photo ablation, and it results in a forward-directed vapour of particles. The ablation process, on the other

hand, is highly dynamic. The beam's energy is far greater than the threshold energy, allowing the material to evaporate. The penetration depth of the pulse depends on the wavelength (λ) of the laser beam and the refractive index (n) of the target material. The amount of material ejected from the surface is determined by the laser fluence (intensity), which is set according to the requirements.

2. Plume interaction with substrate:

The material vaporized from the target comprises energetic electrons, ions, neutral atoms and molecules. It is highly forward directed plasma perpendicular to the target surface.

The plume interaction can be divided into three parts:

- Particles in plasma plume are energetic enough to be scattered by background gases.
- The coulombic interaction between the particles causes the plume to spread forward and react with the background gases.
- Finally, the plume further diverges and condenses on the substrate's surface which is kept at a particular temperature.

Thin film synthesis:

The mechanism of PLD has already been discussed in the previous section. Certain parameters play an important role in optimizing and stabilization of the epitaxial nature of ZnO thin film.

These parameters are:

- <u>Laser fluence</u>: It plays an important role in the kinetics of ZnO film development. The species' kinetic energy is minimal at lower levels of laser fluence, and their limited surface mobility leads to an island growth mode. The film quality degrades at higher levels of laser fluence due to the bombardment of the film by energetic species.
- <u>Partial pressure of background gases</u>: It impacts both deposition rate and kinetic energy of the species. When oxygen partial pressure is high, there is high number of collisions with background gas molecules due to which the kinetic energy of ablated species decreases, and the plume size decreases. So, the substrate to target

distance is kept low in such cases. When oxygen partial pressure is low, it can lead to Oxygen vacancy defect in ZnO film.

- <u>Substrate temperature</u>: The surface mobility of the ejected species deposited on the substrate surface is activated by the substrate temperature. The nucleation process is driven by the substrate temperature and is dependent on the interfacial energies between the substrate surface and the condensing species. A high substrate temperature promotes rapid Zn atom oxidation and optimal diffusion of the species, whereas a low substrate temperature promotes the formation of a poorly crystallized film.
- <u>Substrate to target distance</u>: If the substrate is very far from the target, then the possibility of the plume reaching the substrate is very low.
- <u>Target features:</u> The film's quality is directly proportional to the target material's quality. The surface of the target heats up due to laser-matter interaction, and it is observed that if the density of the target material is low, its thermal conductivity is low. As a result, the surrounding areas around the point where the laser pulse strikes the target, heat up faster before dissipating the heat to the surrounding regions, resulting in a loss of the thin film's quality.

Synthesis of ZnO thin films:

The film deposition was carried out on Quartz substrates having dimensions of (5*10*0.5) mm respectively. First, the substrate was sonicated in acetone and then in propanol for 10 minutes each.

The following parameters were maintained during the deposition:

Laser Ablation Energy	170 mJ
Laser Wavelength	248 nm
Target	ZnO
Substrate	Quartz
Target to Substrate distance	4 cm
Base Pressure	~ 10 ⁻⁴ Pa
Oxygen Partial Pressure	8 Pa
Deposition Temperature	650 °C
Repetition rate	5 Hz
No. of shots	14400

Table 2.1 Synthesis parameters used for thin film

2.1.3) Nanostructure synthesis using Glancing Angle Deposition (GLAD) Technique:

For the synthesis of nanostructures, GLAD assisted Pulsed Laser Deposition technique has been used. The GLAD technique was first developed using a sputtering setup by M. J. Brett 's group in the 1990s [27], and since then it has been extensively used in the synthesis of nanostructures by combining it with PLD and other Physical Vapour Deposition (PVD) systems. In this, the substrate is kept at an angle with the incident plume as shown in Fig.2.5 and the shadowing effect gives rise to tilted columnar structures called nanostructures.



Fig.2.5 Schematic of a basic GLAD apparatus, where ' α ' defines the angle between the axis of vapour flux and substrate normal.

This GLAD technique is divided into two stages:

- Stage 1: Substrate seeding
- Stage 2: Nanostructures growth

Stage 1: Substrate seeding: The synthesis of nanostructures begins with the growth of seeds of the target material on the surface of the substrate which acts as nucleation sites and supports the growth of nanostructures. In this stage, the surface of the substrate is kept parallel to the target's surface to produce highly ordered nanostructures. Basically, this stage is like a normal PLD geometry. The seed layer's quality is considered to be the most influential component in nanostructure development [28]. Brett et al. [29] investigated the influence of a seed layer on nanorod growth extensively, finding that the individual nanocolumns are more uniform in seeded substrates due to less competitive growth. Furthermore, the seed layer allows for smooth electron conduction without the usage of a conducting substrate. The target material ZnO pellet is employed as seeding material in this study.



Fig.2.6 Schematic diagram of stages of GLAD technique

Stage 2: Nanostructures growth: The formation of seeds during the initial stage is crucial to the final growth of nanostructures. For the formation of nanostructures in stage II, the

seeded substrate is kept at an 85° angle to the incident plume as shown in Fig 2.6. The shadowing effect', which limits particle deposition in regions behind initially formed nuclei (shadowed regions), is the mechanistic component at this stage that governs nanostructure development [30]. The tilted columnar and highly porous nanostructures of the target material are formed by ballistic deposition during this process.

Synthesis of ZnO Nanostructures:

The deposition was carried out on Quartz substrates having dimensions of (5*10*0.5) mm respectively. First, the substrate was sonicated in acetone and then in propanol for 10 minutes each.

The following parameters were maintained during the deposition:

Laser Ablation Energy	170 mJ
Laser Wavelength	248 nm
Target	ZnO
Substrate	Quartz
Target to Substrate distance	4 cm
Base Pressure	~ 10 ⁻⁴ Pa
Oxygen Partial Pressure	8 Pa
Deposition Temperature	650 °C
Stage I: Seeding	2400 shots with 5 Hz rate
Stage II: Nanostructures Growth ($\alpha = 85^{\circ}$)	12000 shots with 10 Hz rate

Table 2.2 Synthesis parameters used for nanostructures growth

2.2 Characterization Techniques:

A range of characterization methods have been used to examine the synthesized thin films and nanostructures. XRD measurements have been used to determine the phase purity or crystalline nature. Raman spectroscopy has been used to investigate the vibrational modes. SEM has been used to determine the surface topography and growth. THz-TDS was also employed to investigate the materials' optical properties. The following sub-sections provide a comprehensive description of various techniques.

2.2.1 X-Ray Diffraction:

The X-rays are scattered by subsequent atoms in the crystals, causing diffraction effects. The basic principle of XRD is as follows: when X-rays enter a crystal, each atom acts as a diffraction point, and the entire crystal acts as a three-dimensional diffraction grating. The diffraction pattern obtained contains information about the internal arrangement of atoms in crystals, which aids in crystal structural analysis.

In 1912, W. L. Bragg anticipated the interaction between numerous parameters and developed a diffraction law known as Bragg's law [31]. When a monochromatic X-ray of wavelength falls on a material, it is diffracted by the various atomic planes present in the crystal structure, according to this law.

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

Where d is the inter-planar distance, θ is the incident angle, n is a positive integer and λ is the X-ray wavelength. Constructive interference occurs between diffracted waves when this relation is satisfied and a peak in the diffraction pattern appears at a particular angle.



Fig.2.7 Schematic diagram of XRD measurement for θ -2 θ scan

In the schematic diagram shown in Fig.2.7, θ is the angle formed by the incident X-ray beam and the sample's surface, ϕ is the angle formed by rotation around a plane

perpendicular to the surface, ψ is the angle formed by rotation around a line parallel to the surface, and 2 θ is the angle formed by the incident beam and diffracted beam. The electron density over the diffracting miller plane determines the strength of these X-ray diffracted peaks. As a result, the intensity distribution changes as the angle between the incident and diffracted beams changes. We can calculate the structure of the sample, the composition of the crystal, the gap between two planes, the lattice constant, and other parameters by knowing those planes.

The structural phase purity and crystalline nature of prepared thin films and nanostructures have been studied by X-ray diffraction (XRD) with Cu K α radiation (λ =1.54 Å) using a Rigaku SmartLab X-ray diffractometer.

2.2.2 Raman Spectroscopy:

Sir Chandrasekhara Venkata Raman, an Indian physicist, discovered the Raman effect in 1928. The sample is treated with a laser beam and the scattered light is observed in this technique and due to the nature of incident light's interaction with the sample, scattered light can have the same, higher, or lower frequency than the incident light. The sample's vibrational, rotational, and other low-frequency excitations are revealed by the observed frequency shift.

The fundamentals of Raman scattering are as follows: An electric dipole moment $P(=\alpha E)$ is induced when an electromagnetic wave of electrical vector E interacts with a molecule, where ' α ' is a proportionality constant termed polarizability [32]. The polarizability of the lattice is modulated by phonon deformations at the phonon characteristic frequency v_m . The frequency of the incident photon is v_0 . Photons scatter inelastically in Raman scattering. When the scattered photon has same the frequency as the original incident photon, it is known as Rayleigh scattering. When the frequency of the incident photon (v_0+v_m) it is called anti-Stokes Raman scattering and when the frequency of the scattered photon is less than the frequency of the incident photon(v_0-v_m), it is called Stokes Raman scattering.



Fig. 2.8 Schematic diagram of Raman Spectroscopy setup

Fig.2.8 shows a schematic of Raman Spectroscopy setup. A He-Ne laser source (633.3 nm), spatial filters, microscope, sample stage, monochromator, and charge-coupled device (CCD) detector are typical components of a Raman spectroscopy system. The incident laser beam is focused using a suitable microscope objective, which usually operates in the backscattering geometry. The Raman modes were studied using a commercially available JOBIN-YVON HORIBA LabRAM HR Evolution micro-Raman spectrometer in this research work.

2.2.3 Scanning Electron Microscopy:

For the morphological analysis of thin films and nanostructures, resolving power more than that of an optical microscope is required. SEM is one of the most important and widely used tools to analyse the surface morphology of thin films and nanostructures.

A high-energy electron beam hits the sample in the SEM imaging method and either interacts with the entire volume of the sample or passes the sample unscathed. The energy exchange between the primary electron beam and the sample causes inelastic scattering, resulting in the emission of secondary electrons. Specialized detectors can detect these secondary electrons.



Fig.2.9 Schematic representation of Scanning Electron Microscope

Fig.2.9 shows the working of SEM. The electron beam is emitted via thermionic emission from an electron gun with a tungsten filament cathode. Condenser lenses focus this electron beam, which has an energy range of 0.2 keV to 40 keV. The beam is then deflected in x and y directions by a pair of scanning coils, which cause it to scan in a raster motion over the sample surface area. The secondary electrons created are mostly used as a signal to create the sample's topography. A collector grid, which is kept at higher voltages to attract the low-energy electrons, collects these secondary electrons. The electrons are converted into photons using a scintillator. The photomultiplier tube directs the photons, which are then transformed into electrons and amplified to generate an electrical current. The signal is converted to a grey value and shown on a computer screen as brightness variations.

In this research work, Supra T M 55; Carl Zeiss FESEM was used to record the images of samples.

2.2.4 Terahertz Time-Domain Spectroscopy (THz-TDS):

The term "spectroscopy" refers to the analysis of the energy, wavelength (λ), or frequency (v) of photons that pass through a sample. THz-TDS is a spectroscopic technique that uses short pulses of terahertz radiation to investigate the characteristics of materials. The effect of the sample on the amplitude and phase of the terahertz radiation is sensitive to the generation and detection schemes. In THz-TDS, the time-domain signal directly measures

the transient electric field rather than its intensity. It requires the generation of an ultrafast terahertz pulse from an even faster femtosecond optical pulse. Fig.2.10 shows a schematic of THz-TDS.



Fig.2.10 Schematic diagram of THz-TDS

This technique can be divided into two parts:

- 1. Generation of THz waves
- 2. Detection of THz waves

Photoconductive Antennas (PCAs) can be used as both THz emitters and detectors. It is made up of two electric contact pads and a highly resistive direct semiconductor thin film (Lt-GaAs). as shown in Fig. 2.11. A short width laser pulse is focused on the electrodes of the PCA. Photons having energy more than the band gap of the semiconductor are absorbed and create a free electron in the conduction band and a hole in the valence band making the semiconductor conduct until the carriers are combined.



Fig.2.11 Schematic diagram of Photoconductive Antenna

For the generation of THz, DC bias is applied at the electrodes of PCA which accelerates the excited charge carriers resulting in a short broadband EM(electromagnetic) pulse with a time-dependent electrical field E(t) and frequencies in the THz region.

For the detection of THz, the electrical contacts are connected to an amplifier. The excited carriers are accelerated by the electric field component of the incident terahertz pulse with the time-dependent electrical field E(t) during the optical pulse. As a result, a voltage signal is generated across the antenna gap.

A typical THz-TDS setup consists of a femtosecond laser (Ti: sapphire laser), beam splitter, delay stage, emitter and detector. A beam splitter splits the optical pulse coming from the femtosecond laser into two arms of equal power (~10 mW each). One of the arms falls on PCA and generates a THz pulse which transmits through the sample before being detected and the other passes through a translational stage with a reflector to provide a relative time delay. The THz induced transients are measured by the probe pulses. In THz-TDS, the THz pulses are measured with and without a sample.

The time delay and phase difference between the two waves allows us to study various properties of the material such as conductivity, refractive index, dielectric constant etc.

The THz-TDS of a thin film is done in three steps: First, the THz pulse is transmitted through free space through a 7 mm aperture within a cryostat, and the temporal waveform is recorded (Fig. 2.12 (a)). In the second step, the temporal waveform of the passing THz pulse through the blank substrate is recorded by placing a blank substrate of thickness L_1

on the aperture of the cryostat (Fig. 2.12 (b)). Then a thin film of thickness L_2 is formed on the same substrate and placed on the aperture for capturing the temporal waveform of the passing THz pulse through both substrate and film in the final third step (Fig. 2.12 (c)).



Fig. 2.12 Schematic representation of THz pulse transmission through (a) air, (b) substrate and (c) film on substrate. Transmission and reflection of THz pulse from inner layers of substrate and film is shown by the black arrows.

The transfer function for the electric field signal via the blank substrate for the second step was derived using Fresnel's equations [33] as shown below:

$$E_{sub}(\omega) = E_{initial}(\omega)t_{01}t_{03}P_s(\omega, L_1)P_{air}(\omega, L_2)$$

The transmission of the THz wave through the blank substrate is represented by $P_s(\omega, L_1)$. 't' represents transmission coefficients. After this, the substrate is replaced by the film+substrate for final step. New transfer function is:

$$E_{sub}(\omega) = \frac{E_{initial}(\omega)t_{01}t_{12}t_{23}P_s(\omega, L_1)P_f(\omega, L_2)}{FP}$$

The transmission of the THz wave through the film is represented by $P_f(\omega, L_2)$. FP stands for Fabry-Perot effect due to multiple reflections that may occur inside the sample.

$$FP = 1 + r_{12}r_{23}[P_f(\omega, L_2)]^2$$

As a result, the final complex model transfer function will be the THz beam ratio via film

and substrate, which is given as follows:

$$H = \frac{E_{film}(\omega)}{E_{sub}(\omega)} = \psi(\omega)\phi(\omega)$$

Where $\psi(\omega)$ and $\phi(\omega)$ represents the amplitude and phase shift components of the complex function ratio, respectively. We get the most simplified form for the condition $L_2 \ll \lambda$ (wavelength) :

$$A = \frac{\frac{(1+n_1)c}{\omega L_2} \left[\psi \sin \phi + \frac{\omega L_2}{c} \psi \cos \phi\right]}{\psi^2}$$

$$B = \frac{\frac{(1+n_2)c}{\omega L_2} \left[\psi^2 - \psi \cos \phi \frac{\omega L_2}{c} \psi \sin \phi\right]}{\psi^2}$$

Where, n_1 and n_2 represents the complex refractive indices of substrate and film respectively. These parameters can also be used to extract the optical constants of the film.

$$\varepsilon_2 = n_2^2 = A - n_1 + jB$$

 $n_2 = Re\sqrt{\varepsilon_2} \text{ and } k_2 = Im\sqrt{\varepsilon_2}$

The optical conductivity and dielectric constant of the thin-film on the substrate can be determined using the aforementioned equations and knowing the thickness of the substrate and film.

Fig. 2.13(a) shows the time-domain THz electric field signal after passing through air, substrate and thin film on substrate respectively. Figure 2.13 (b) shows their respective Fourier transform spectra (amplitudes of the THz pulse in frequency domain).



Fig. 2.13 A typical example of (a) THz waveform in time-domain and (b) its spectrum calculated in frequency domain

Chapter 3

Results and discussion:

Using the Pulsed Laser Deposition (PLD) technique and Glancing Angle Deposition (GLAD) techniques, two samples were prepared: ZnO thin film and nanostructures with 14400 shots. In this section, the structural properties of both the samples were investigated using XRD and Raman spectroscopy, the morphological investigation with SEM, and complex conductivity using Terahertz-TDS.

3.1 X-Ray Diffraction:

Fig. 3.1 shows the XRD patterns of ZnO thin film and nanostructures. A sharp and prominent peak (002) in XRD patterns of both thin film and nanostructures shows that the samples are pure and highly crystallographically oriented along the c-axis.



Fig. 3.1: XRD patterns of ZnO thin film and nanostructures on Quartz substrate

The narrow full width at half maximum (FWHM) and intense peaks demonstrate the good crystallinity of the samples. The crystallinity of thin films is better than that of nanostructures.

The Scherrer equation [34] was used to calculate the crystallite size of the samples, as shown below:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where D is the crystalline domains' mean size, K is a dimensionless form factor with a value close to unity, λ is the X-ray wavelength, β is the line broadening at half maximum intensity, and Θ is the Bragg angle.

The XRD patterns' abstracted information is shown in Table 3.1, which illustrates the variation in crystallite size and FWHM of thin film and nanostructures.

	FWHM (°)	Crystallite size (nm)
ZnO Thin Film	0.188	46.02
ZnO Nanostructures	0.222	39.04

Table 3.1 FWHM and crystallite size of thin film and nanostructures.

3.2 Raman Spectroscopy:

The samples were further analysed using the Raman spectroscopy in order to better understand the vibrational modes and related structure of produced thin films and nanostructures. Fig.3.2 shows the room temperature Raman spectra of ZnO thin films and nanostructures on a quartz substrate.

As we know, under normal atmospheric conditions, the wurtzite structure of ZnO is most stable. It consists of two interpenetrating sublattices of Zn^{+2} and O^{-2} ions.

Each Zn^{+2} ion is surrounded by a tetrahedron of O^{-2} ions and vice versa which forms a polar symmetry along the c-axis of the hexagonal wurtzite structure.

The optical modes of the wurtzite structure of ZnO are represented by the group theory:

$$\Gamma_{opt} = A_1 + E_1 + 2E_2 + 2B_2$$

where A_1 and E_1 are oxygen dominated polar modes and are both Raman and IR active [35].

 B_1 and E_2 modes are non-polar modes due to mutual compensation of displacement vectors within each sublattice and E_2 modes are Raman active only while B_1 branches are silent modes.

The E_2 mode splits into two branches $E_2(low)$ and $E_2(high)$.



Fig. 3.2: Room temperature Raman spectra of ZnO thin films and nanostructures on a quartz substrate

In Fig. 3.2, the Raman spectra of ZnO thin film and nanostructures show two intense peaks $E_2(low)$ and $E_2(high)$ at 99 cm⁻¹ and 436 cm⁻¹ respectively which are the fingerprints of the wurtzite structure of ZnO. The $E_2(low)$ mode is associated with the vibration of heavy Zinc sublattices and the $E_2(high)$ mode is associated with the motion of oxygen atoms in sublattices. The sharp E_2 peaks show that film and nanostructures are highly crystalline.

3.3 Scanning Electron Microscopy

Fig. 3.3 shows the SEM images of ZnO thin film and nanostructures grown on Quartz substrate.

The micrographs confirm the porosity and growth of nanostructures.



Fig. 3.3: SEM images of ZnO thin films and nanostructures grown on a quartz substrate (a), (b), (c) – thin films; (d), (e), (f) – nanostructures

The porosity of the nanostructures is approximately 17.2 (% area) which was calculated using ImageJ software. Now, by comparing XRD and Raman data, we can see the decrease in crystallinity as we go from film to nanostructures. This is due to the formation of porous nanostructures as confirmed by SEM images.

3.4 Terahertz Time-Domain Spectroscopy:

THz-TDS has been used to calculate the complex conductivity of ZnO thin film and nanostructures in vacuum and nitrogen environments. The native n-type conductivity in ZnO is mainly due to the donor defects *viz* Oxygen vacancies (V_O) and Zinc interstitials (Zn_i) present in the lattice. The conductivity is governed by the rate of oxygen adsorption and desorption on the surface. The desorption of oxygen takes place due to the presence of V_O and trap centres near the surface, which results in the trapping of electrons, thereby forming a depletion layer on the surface which decreases the conductivity of the material. Upon UV illumination, photo-desorption of oxygen takes place by creating more electronhole pairs and the hole oxidises the adsorbed oxygen and it gets desorbed from the surface resulting in the thinning of the depletion layer, and hence conductivity increases.

As the surface area to volume ratio increases in nanostructures due to the formation of pores, more V_0 are found on the surface of nanostructure which increases the rate of adsorption of Oxygen. This mechanism causes a depletion layer to form at the surface, bending the conduction and valence bands, as well as the trap centre-related band in an upward direction. The band bending is further exacerbated by the formation of a significant amount of ionised oxygen on the surface of the nanostructures, which results in a very low conductivity of nanostructures as compared to thin films [36].

The THz-TDS of ZnO film and nanostructures were performed both with and without UV illumination in vacuum as well as nitrogen gas environments.

3.4.1 THz-TDS of ZnO thin film and nanostructures in vacuum and nitrogen without UV illumination:

Fig. 3.4 shows the complex conductivity vs frequency plot of ZnO thin film and nanostructures in vacuum environment without UV illumination. The real part of conductivity is positive and increases with frequency, whereas the imaginary part is negative and also increases with frequency before becoming positive beyond a certain frequency value in both the cases of thin film and nanostructures.

The conductivity of the nanostructures is an order lower than that of the thin film, as expected.



Fig. 3.4 Conductivity of ZnO thin film and nanostructures in vacuum environment with fits of Drude-Smith model

According to Drude-Smith model for conductivity:

$$\sigma = \frac{\varepsilon_o \omega_p^2 \tau}{1 - i\omega\tau} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{1 - i\omega\tau} \right] - i\varepsilon_o \omega(\varepsilon_{\infty} - 1)$$

where ω_p , τ and c are plasma frequency, characteristic scattering time and persistence of velocity parameter respectively [26]. Further, the plasma frequency and carrier concentration are related by the equation

$$N_e = \frac{\varepsilon_o \omega_p^2 m^*}{e^2}$$

where N_e is the electron density and m^* is the effective mass of electron. As shown in Fig. 3.4, the conductivities of both film and nanostructures are very well estimated by the Drude-Smith model. The adjustable parameters ω_p , τ and c are shown in Table 3.

	Vacuum Environment		
	Plasma Frequency (THz)	Scattering time (ps)	Persistence of Velocity C
Thin Film	89.31092 ± 4.213	0.58659 ± 0.050	-0.70807 ± 0.028
Nanostructures	31.9451 ± 1.878	0.45541 ± 0.058	-0.55543 ± 0.032

Table 3.2 Parameters for Drude-Smith Fits of Conductivity in vacuum

From Table 3, we can see that the value of plasma frequency of film is more than the plasma frequency of nanostructures. These results indicate that the carrier concentration in nanostructures decreases, presumably due to band bending and increased rate of adsorption in nanostructure as compared to thin films. Also, c becomes less negative as we go from film to nanostructures, indicating that the nanostructures are taking on the characteristics of a Drude conductor.

Fig. 3.5 shows the complex conductivity vs frequency plot of ZnO thin film and nanostructures in nitrogen environment without UV illumination. Same as the previous case, the real part of conductivity is positive and increases with frequency, whereas the imaginary part is negative and increases with frequency before becoming positive beyond a certain frequency value both thin film and nanostructures.

The conductivity of the nanostructures is an order lower than that of the thin film, as expected.



Fig. 3.5 Conductivity of ZnO thin film and nanostructures in nitrogen environment with fits of Drude-Smith model

As shown in Fig. 3.5, the conductivities of both film and nanostructures are very well estimated by the Drude-Smith model. The adjustable parameters ω_p , τ and c are shown in Table 4.

	Nitrogen Environment		
	Plasma Frequency (THz)	Scattering time (ps)	Persistence of Velocity C
Thin Film	85.29381 ± 4.030	0.62738 ± 0.054	-0.72929 ± 0.031
Nanostructures	30.4854 ± 2.633	0.40959 ± 0.065	-0.63009 ± 0.032

Table 3.3 Parameters for Drude-Smith Fits of Conductivity in nitrogen

From Table 4, we can see that the value of plasma frequency of film is more than the plasma frequency of nanostructures following the same trend as in Table 3. These results indicate that the carrier concentration in nanostructures decreases, presumably due to band bending and increased rate of adsorption in nanostructure as compared to thin films. Also, c becomes less negative as we go from film to nanostructures, indicating that the nanostructures are taking on the characteristics of a Drude conductor.

3.4.2 THz-TDS of ZnO thin film and nanostructures in vacuum and nitrogen in UV:

As explained earlier, the depletion layer is formed due to the adsorption of oxygen and trapping of electrons. Upon UV illumination, electron-hole pairs are generated and the desorption of oxygen causes a rise in photocurrent. The holes oxidise the ionised oxygen adsorbates and the depletion layer starts depleting. Also, there is contribution of free electrons generated due to UV light in increasing the photocurrent.

Fig. 3.6 shows the conductivity versus frequency plots of ZnO thin film and nanostructures in vacuum in UV light. It can be seen that the conductivity increases with increase in intensity of UV light for both the samples. Also, a dip can be seen at 0.93 THz frequency which might be due to the presence of moisture.



Fig. 3.6 (a) Real part of complex conductivity of thin film in vacuum and (b) Real part of complex conductivity of nanostructures in vacuum, under UV illumination

Fig. 3.7 shows the conductivity versus frequency plots of ZnO Thin film and nanostructures in nitrogen in UV light. It can be seen that the conductivity increases with increase in intensity of UV light for both the samples. Also, a dip can be observed at 0.93 THz frequency which again might be due to the presence of moisture.



Fig. 3.7 (a) Real part of complex conductivity of thin film in nitrogen and (b) Real part of complex conductivity of nanostructures in nitrogen, under UV illumination

Fig. 3.8 shows the comparison of conductivity of ZnO Thin films and nanostructures in vacuum and nitrogen respectively at two different fixed frequencies i.e., 0.26 THz and 0.8 THz. It can be clearly observed that the conductivity of samples in vacuum is more than the conductivity of samples in nitrogen.





Fig. 3.8 Variation of conductivity of ZnO Thin films at fixed frequency with UV illumination in different environments

From Fig. 3.9, we can say that the conductivity of both samples in vacuum is more than the conductivity of both samples in nitrogen. Also, the conductivity increases with the increase in intensity of UV light in all the cases.





Fig. 3.9 Variation of conductivity of ZnO Nanostructures at fixed frequency with UV illumination in different environments

3.5 Conclusion:

Highly crystallographically oriented ZnO thin film and nanostructures were deposited on Quartz substrate using PLD and GLAD techniques. The nanostructures were highly porous as compared to thin film with porosity 17.2 (% area). The conductivities of the samples were successfully probed using THz-TDS in vacuum and nitrogen environments, as well as with and without UV illumination. The conductivity of nanostructures decreased by an order in all the cases as compared to that in nitrogen environment for both samples, with and without UV illumination. The conductivities for both samples increase monotonously with increasing intensity of UV light. Specifically, the influence of the environment and UV illumination causes an increase in conductivity, as expected, whereas nitrogen gas causes a decrease in conductivity due to its adsorption on the surface.

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