Nucleation and Growth of ZnO Thin Films via Combined SILAR and Modified CBD Methods and Its Opto-Electrical, Morphological Characterization

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Submitted By

SOURAV GHOSAL

Examination Roll No: M4ENR24006

Registration No: 163828 of 2022-2023

Under the Guidance of

Prof. (Dr.) RATAN MANDAL
Supervisor
&
Dr. SUGATA BHATTACHARYYA
Co-Supervisor

School Of Energy Studies
Jadavpur University
Kolkata–700032
India

2024

Master of Technology in Energy Science & Technology
Course affiliated to
Faculty of Engineering & Technology
Under
Faculty Council of Interdisciplinary Studies
Law & Management, Jadavpur University
Kolkata, India

CERTIFICATE OF RECOMMENDATION

This is to certify that the thesis entitled "**Nucleation and Growth of ZnO Thin Films via Combined SILAR and Modified CBD Methods and Its Opto-Electrical, Morphological Characterization**" is a bonafide work carried out by **Mr. Sourav Ghosal** under our supervision and guidance for partial fulfillment of the requirements for the Post Graduate Degree of Master of Technology in Energy Science and Technology, during the academic session 2022-2024.

THESIS CO-SUPERVISOR
Dr. SUGATA BHATTACHARYYA

THESIS SUPERVISOR
Dr. RATAN MONDAL
Director and Professor
School of Energy Studies
Jadavpur University
Kolkata–700032

DEAN
Faculty Council of Interdisciplinary Studies,
Law and Management
Jadavpur University
Kolkata–700032

Master of Technology in Energy Science & Technology
Course affiliated to
Faculty of Engineering & Technology
Under
Faculty Council of Interdisciplinary Studies
Law & Management, Jadavpur University
Kolkata, India

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Name	**:**	**Sourav Ghosal**
Examination Roll No.	**:**	**M4ENR24006**
Thesis Title	**:**	**Nucleation and Growth of ZnO Thin Films via Combined SILAR and Modified CBD Methods and Its Opto-Electrical, Morphological Characterization.**
Signature	**:**	
Date	**:**	

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SOURAV GHOSAL

Examination Roll No: M4ENR24006

Registration No: 163828 of 2022-2023

School of Energy Studies

Jadavpur University

Kolkata–700032

Dedicated

to

My Parents

and

Teachers

Nomenclature

ARPES	Angle-resolved photoemission spectroscopy
CBD	Chemical Bath Deposition
EDX	Energy dispersive X-ray
E_g /E_{bg}	Band gap
HRXRD	High-resolution X-ray diffraction
IPA	Isopropanol
ITO	Indium Tin Oxide
I-V	Current-Voltage
KOH	Potassium hydroxide
NaOH	Sodium hydroxide
NH_3	Ammonia
$NH_4(OH)$	Ammonium hydroxide
pH	Potential of Hydrogen
PV	Photovoltaic
S_1-S_7	Sample 1 to Sample 7
SEM	Scanning Electron Microscopy
SILAR	Successive Ionic Layer Adsorption and Reaction
TCO	Transparent Conducting Oxide
TFT	Thin Film Transistor
UV-Vis	Ultraviolet-visible
W.r.t	With Respect to
XPS	X-ray photoelectron spectroscopy
$Zn(OH)_2$	Zinc hydroxide
ZNAs	ZnO Nanorod Arrays
$ZnCl_2$	Zinc Chloride
ZnO	Zinc Oxide

Contents

List of Figures

List of Tables

Chapter-1
Introduction

1.1 Introduction and Backgound

Transparent conducting oxide (TCO) thin films are of great interest to the scientific community today because of their widespread application in optoelectronic technologies, including light-emitting diodes, solar cells, touch screens, and liquid crystal displays or LCDs. In ideal circumstances, TCOs should put up significant electrical conductivity and optically outstanding transparency in the visible light spectrum. ITO (indium tin oxide) has been the most accessible TCO because of its attractive electric conductivity properties and excellent transparency to the visible light spectrum. Since indium, the main ingredient in ITO is highly expensive, rare, and hazardous, it is more important than ever to identify suitable substitutes. Furthermore, in a hydrogen plasma atmosphere, certain electrical and optical characteristics of ITO vanished. In this sense, transparent conducting zinc oxide (ZnO), a cheap, non-toxic, and abundant source of zinc, is a very attractive replacement material for ITO. It also has remarkably good optical and electrical properties. This has led to a recent rise in interest in wide bandgap (~3.1-3.37 eV) semiconductor ZnO (II-VI). The fact is that ZnO is easily produced using wet chemical etching and others using low-cost, low-temperature techniques and in a range of nanostructured morphologies. Spray pyrolysis, spin coating, dip coating, and radio frequency (RF) based magnetron sputtering are the deposition techniques that have been studied the most. As a wide band gap semiconductor material for use in transparent thin-film transistors (TFTs), ZnO has also attracted a lot of interest. Oxide TFTs have played a significant role in driving the active matrix of organic light-emitting diodes, which offer a broad range of colours and superior viewability for next-generation flexible displays. But here our primary focus for producing such ZnO TFT films is by SILAR and CBD which is based on a chemical deposition technique. The favourable band edges of ZnO semiconductor oxide photocatalysts help in straddling the redox potential of water photoelectrolysis and it is low-cost, non-toxic and environment-friendly. Instead of growing on substrates, which prevents photocatalysts from aggregating and thus helps to increase active surface area and photocatalytic performance, the fabrication of doped ZnO photocatalysts for hydrogen production has concentrated more on powder or precipitate form synthesis via hydrothermal or wet chemical routes. Like photocatalytic hydrogen evolution from water or other sources, the photo-generated holes in ZnO also have a greater oxidizing ability for the destruction of environmental pollutants. The majority of device-grade ZnO thin-film nanostructure fabrication has been carried out mainly at high temperatures. This includes physical vapour deposition Sputtering, Pulsed Laser Deposition, Electron-Beam Gun based Deposition or Atomic Layer Deposition which can be carried out with or without substrate heating. Although aqueous and hydrothermal chemical growth approaches are also utilized, they

necessitate a significant amount of heat input throughout the growth phase. On the other hand, low-temperature, substrate-based synthesis can also result in uniform nanocrystalline thin-films. ZnO thin film is used in transparent conductive thin films and solar cell devices as in the visible range, it has high optical transmittance.

Currently, very small size (nano, micro) materials have great consideration due to their lesser size and huge scope of utilization in certain fields such as industry, environment and health. ZnO has also been employed extensively as a potential medium in the development and assembly of transistors due to its n-type electric properties. Various chemical processes, such as chemical bath deposition (CBD), sol-gel spin coating, chemical vapour deposition (CVD), electrochemical deposition (ED) and printing deposition can be used to produce ZnO thin films. These chemical reactions are inexpensive, straightforward, and simple to modify or dope with other components. ZnO has significant absorption in the UV spectrum and appears to have an anisotropic crystal structure. As a result, it has some potential uses in windows for heterojunction and photovoltaic solar cells, as well as in infrared reflective coatings, piezoelectric and phosphors, diodes that emit blue and ultraviolet light, transducers and solid-state gas sensors. However, relatively less attempts have been made in this direction of fabrication of ZnO thin film by the combination of successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) Process, without any application of heat during the growth process. The current project work hopes to dwell in this direction of combined modified CBD and SILAR-based fabrication of ZnO nano-crystalline thin films, without heat-application during the growth process.

1.2 Methods for Thin Film Deposition

Very thin material layers can be created on a substrate surface using a method called thin film deposition. These layers, typically ranging from a few nano-meters to several micro-meters in thickness, can be composed of various materials, including metals, semiconductors, oxides, and polymers. Thin films are crucial components in a wide range of electronic, optical, and functional devices, as they can impart specific properties to the substrate or modify its surface characteristics. Overall, the history of thin film deposition techniques reflects a continuous evolution driven by the quest for precise control over material properties and the development of new applications across various industries. As technology continues to advance, thin film deposition techniques will likely play an increasingly vital role in shaping the future of materials science, energy science and engineering.

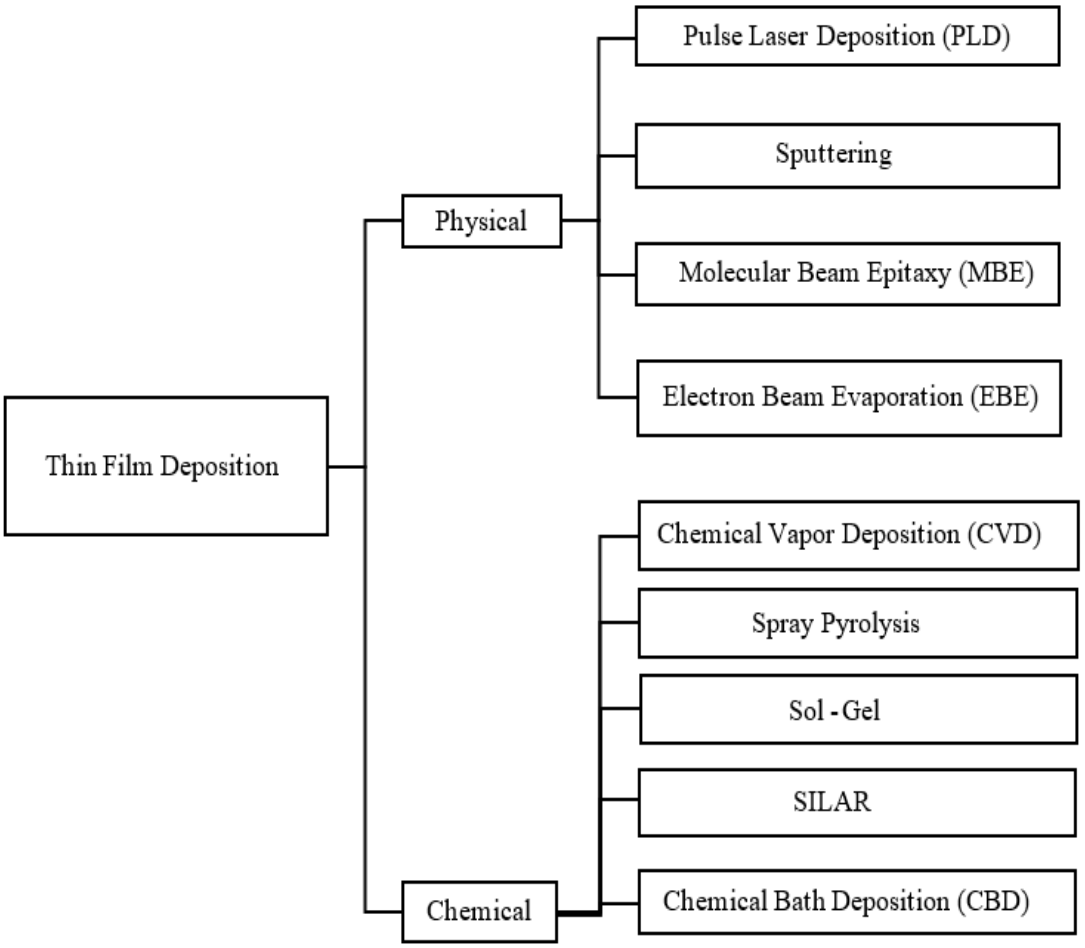

Fig. 1.1 Different types of thin film deposition methods

Thin film deposition techniques are selected based on factors such as the desired film properties, substrate material, deposition rate, and scalability. These techniques play a crucial role in the fabrication of various devices, including integrated circuits, solar cells, displays, sensors, and coatings, enabling advancements in electronics, energy, optics, and other fields.

1.2.1 Physical Process for Thin-Film Deposition

Pulsed Laser Deposition (PLD):

Under the physical vapour deposition (PVD) technique, pulsed laser deposition (PLD) is used to deposit thin films of materials onto substrates. It involves vaporizing a target material with the help of a high-power pulsed laser beam, which is then deposited onto a substrate in a vacuum chamber. Pulsed laser deposition (PLD), is a versatile approach for a variety of purposes. Ultrahigh vacuum (UHV) and ambient gas can both be used in this method because the energy source is situated outside the chamber. Polymers, metals, oxides, and nitrides may all be

deposited using pulsed laser deposition (PLD), which is also scalable for use in large-scale manufacturing. It finds applications in various fields such as microelectronics, optics, photonics, sensors, and biomedical devices, where precise control over thin film properties is crucial. The pictorial representation of a typical pulsed laser deposition (PLD) is shown in the below Fig. 1.2.

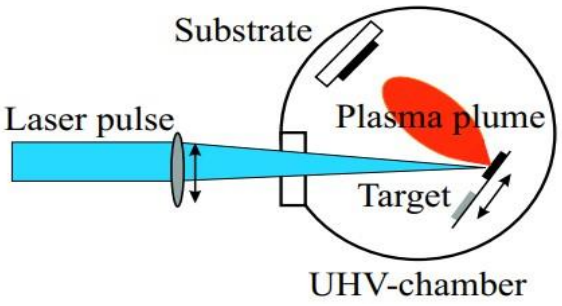

Fig. 1.2 Pictorial representation of a typical laser deposition set-up

Sputtering:

Under the physical vapour deposition (PVD) method Sputtering deposition is used for thin film deposition onto substrates in a wide range of industries, from semiconductor manufacturing to optical coatings. Metals, insulators, semiconductors, and other materials can all be synthesized using the general sputtering process. Additionally, this method's large coating area, easy controllability, robust adherence, and simple apparatus are its advantages. Since low-temperature substrates allow for the production of high-quality films, sputtering techniques are usually utilized in commercial processes. Nevertheless, there are several drawbacks to reactive sputtering, such as target toxicity, low deposition rates, and arcing that results in thin film flaws. Also, Sputtering is widely used in the manufacturing of integrated circuits, solar cells, magnetic storage devices, and architectural glass coatings, among other applications.

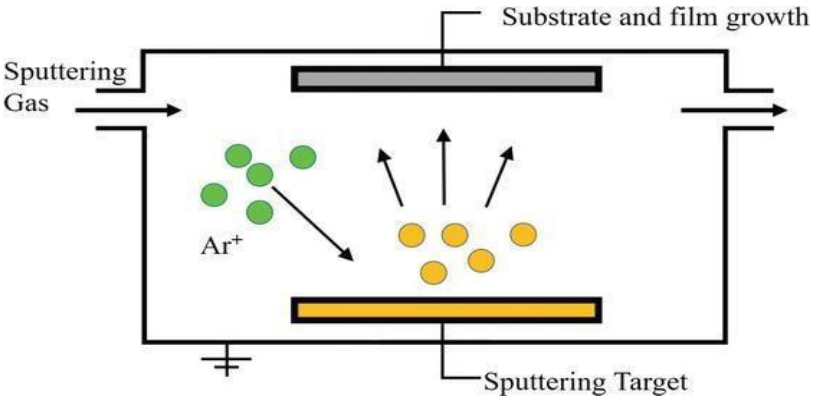

Fig. 1.3 Pictorial representation of DC sputtering

Molecular Beam Epitaxy (MBE):

Molecular Beam Epitaxy (MBE) is a highly precise thin-film deposition technique used to create crystalline layers of materials with atomic-scale precision. The two uniqueness of molecular beam epitaxy is first, it is carried out in ultrahigh vacuum (UHV); secondly, it relies on the response of crystalline-surface atomic and molecular beams, which depends on desorption, adsorption, dissociation, migration, reaction, and incorporation, those are kinetic processes. To provide ideal conditions for stoichiometry and epitaxy, during the film growth and substrate formation, the control and monitoring of real-time in situ is enabled by these highlights. Advanced semiconductor devices such as semiconductor quantum dots, quantum cascade lasers, and high-electron mobility transistors (HEMTs) are developed using MBE extensively. It is also used in the research of basic surface science phenomena and to manufacture optoelectronic devices like light-emitting diodes and PV cells.

Electron Beam Evaporation (EBE):

Electron Beam Evaporation (EBE) is a widely used physical vapour deposition (PVD) method for depositing the materials of thin films onto substrates. Electron Beam Evaporation is a versatile and powerful technique for thin film deposition with high precision and uniformity, making it indispensable in numerous industrial and research applications. Using the Electron beam deposition method in a vacuum, the electron beams are produced from an electron source, irradiating, vaporizing and heating the target material. Then the vaporized material forms as a thin film on a substance, for example, a lens or a substrate. In addition, the large and potent direct-type electron sources are capable of vaporizing quickly and also these electron sources are used for long film deposition and deposition onto substrates with large areas. EBE finds applications in diverse fields, including semiconductor device fabrication, optical coatings, thin-film solar cells, and decorative coatings. Since EBE can deposit films of high-quality with proper control over thickness and composition it is a valuable technique in materials science and engineering.

1.2.2 Chemical Process for Thin-Film Deposition

Chemical Vapour Deposition (CVD):

Using the chemical vapour deposition process, one or more vaporised volatile precursors are transferred into the reaction chamber to degrade on a heated substrate. Because of a chemical

reaction, the process of depositing solid materials at a high temperature is complex. This deposition forms a unique kind of material that is typically referred to as ordered crystal produced from vapour. With CVD and similar techniques, a wide range of materials can be deposited. CVD is a responsive type of procedure, which is different from other PVD processes, such as sputtering, physical evaporation process and sublimation processes. CVD has several benefits, including the capacity to coat intricate structures and substrates, exact control over film composition and thickness, and scalability for industrial manufacturing. It is used in many different industries, including the creation of graphene and carbon nanotubes, thin-film solar cells, protective coatings, and semiconductors. However, the CVD technique has been utilized for the deposition of various types of materials.

Spray Pyrolysis:

A chemical procedure called spray pyrolysis is used to apply thin layers of compounds to a substrate's surface. It starts with the creation of a precursor solution or suspension, which is sprayed onto a heated substrate after being atomized. The solvent evaporates when the droplets come into contact with the substrate, leaving behind a thin film of the desired substance. Spray pyrolysis has several numbers of preferences, such as the temperature for processing is very low, its homogeneity is high and the purity of its output products, etc. spray pyrolysis is a reasonable and very basic technique for getting excellent smooth thin and thick films, coatings of ceramic and powder of metal oxide in broad scale. Spray pyrolysis is an extremely fundamental technique, which is financially savvy to handling. It is not necessary to use premium chemicals or substrates for spray pyrolysis. The technique has been chosen for the manufacturing of powder as well as the deposition of thick and permeable films. This versatile method makes it simple to manufacture even stacked films.

An overview of the spray pyrolysis deposition process is presented in Fig. 1.4. Spray pyrolysis offers several advantages, including simplicity, scalability, and the ability to deposit thin films over large areas and on complex substrates. It is widely used in various applications, including the production of thin-film solar cells, transparent conductive coatings, solid oxide fuel cells, sensors, oxide thin films for electronics, and protective coatings.

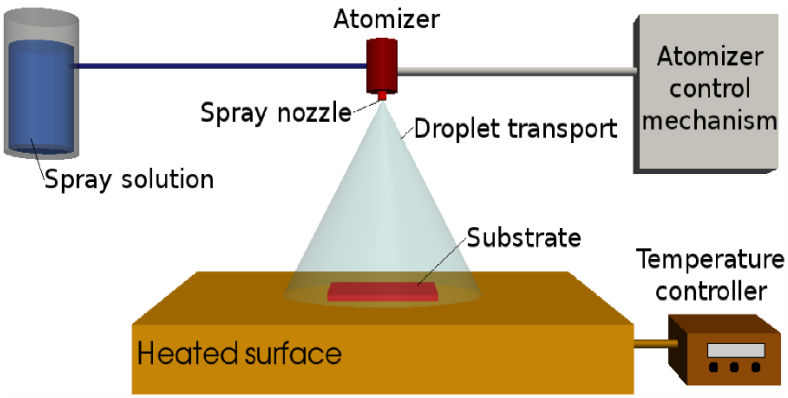

Fig. 1.4 Pictorial representation of a spray pyrolysis deposition process

Sol-Gel:

Sol-gel is a chemical method that turns small molecules into solid materials. The process entails converting a sol, or precursor solution, into a gel-like substance and then solidifying it to create a solid network (gel). With the use of the adaptable sol-gel technique, a variety of materials with specific properties, such as composites, glasses, and ceramics, can be created. Inter-particle forces govern the stability of emulsions and suspensions in the face of coagulation. It is assumed that dispersion will be constant if the particles are free indefinitely. When tiny particles are distributed in a fluid, Brownian motion is the cause of the frequent attacks between the particles. These attacks have the potential to create an enduring link or to keep the particles free by relying on the forces that tied them.

The sol-gel process offers several advantages, including the ability to produce homogeneous materials with tailored compositions, structures, and properties. It also allows for the incorporation of dopants, nanoparticles, or organic molecules into the final product, enabling the synthesis of functional materials for various applications like monoliths, composites, porous membranes, powders, fibres and applications from coatings to the preparation of thin films. Also, it does not require special or expensive equipment. Sol-gel-derived materials find widespread use in areas such as optics, electronics, catalysis, biomaterials, and coatings. Sol-gel process consumes very less energy as in this process there is no requirement to reach the melting temperature and at the low temperature, we can get the network structure.

Successive Ionic Layer Adsorption and Reaction (SILAR):

Under the chemical Deposition technique, the SILAR deposition process also known as successive ionic layer adsorption and reaction (SILAR), is a method used for depositing thin

films of materials onto substrates. It involves the sequential immersion of a substrate into solutions containing precursor ions, followed by rinsing and drying steps. Thin films are produced in SILAR by dipping the substrate alternately into cationic and anionic precursors that are set apart and allowed to react at specific temperatures. Also, SILAR involves complex ion layer adsorption on the substrate after which the adsorbed ion layer's reaction occurs.
Here's a general outline of the process:

1) **Preparation of precursor solutions:** Solutions containing ions of the desired material are prepared. These solutions can include metal salts or other compounds that can dissociate to yield the desired ions.
2) **Substrate preparation:** The substrate onto which the thin film will be deposited is cleaned thoroughly to ensure proper adhesion of the film.
3) **Sequential immersion:** The substrate is dipped into the first precursor solution, allowing the precursor ions to adsorb onto its surface. After a certain time, the substrate is removed, rinsed to remove excess solution, and dried.
4) **Repeat deposition steps:** The immersion and rinsing steps are repeated for each precursor solution in a predetermined sequence. Each cycle adds a new layer of material to the growing thin film.
5) **Post-treatment:** After the desired number of layers has been deposited, the thin film may undergo post-treatment steps such as annealing to improve its properties.

However, SILAR methods have several advantages over other thin film deposition methods. Those are-

- SILAR is a relatively simple and cost-effective technique compared to other chemical and physical deposition techniques (**Simple and Cost-effective**).
- The SILAR process has precise control over the thickness and composition of the deposited thin films (**Controlled Film Growth**).
- SILAR typically results in highly uniform thin films over large areas (**Uniformity**).
- The SILAR process is used to deposit thin films of different materials, including sulphides, selenides, oxides and metals (**Versatility**).
- SILAR is a low-temperature deposition technique, which is beneficial for depositing thin films on temperature-sensitive substrates or for integrating with other materials that may degrade at higher temperatures (**Low Temperature Processing**).

- SILAR can be easily scaled up for mass production, making it suitable for industrial-scale manufacturing of thin film devices (**Scalability**).

Above these are the reason, that's why we are using SILAR methods to prepare thin film in our experiment.

Chemical Bath Deposition (CBD):

CBD is a broadly used technique for depositing thin films of semiconductors, metal oxides, and other materials onto substrates. It involves the immersion of a substrate into a chemical bath solution containing precursors that react to form the desired material. Compared to other physical and chemical deposition methods, the CBD (Fig. 1.5) method has commercially exceptional value. Scientists have given it much consideration because of its ease of use, comfort, large-area scaling, reproducibility, and industrial production. However, CBD also has some limitations, such as limited control over film thickness and composition compared to more advanced deposition techniques like ALD or MBE. Despite these limitations, CBD is widely used in applications such as optoelectronics, photovoltaics, sensors, and coatings, where its simplicity and versatility make it a valuable deposition method.

In comparison to other procedures, chemical bath deposition is advantageous since it is incredibly easy to use, doesn't require any specialized equipment, works at low temperatures, and is inexpensive to deposit. The most appealing positive stand of this approach is its capacity to coat large surfaces in a low-cost, repeatable manner.

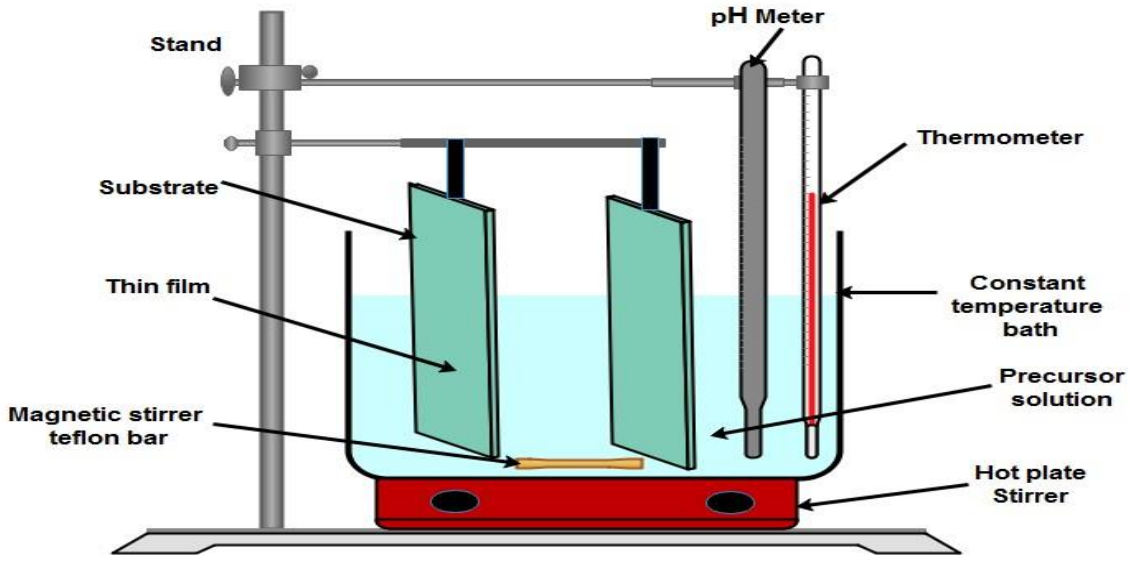

Fig. 1.5 Pictorial representation of the chemical bath deposition process

Other than that, the CBD technique has the following significant advantages over the other methods. Those are:

- CBD is a relatively simple and cost-effective technique for wider industrial applications and the material is used in less amount with minimum loss (**Cost-Effective**).
- CBD is one of the simplest methods (**Simplicity**).
- In CBD, there is no requirement for a high vacuum for chemicals and this can be carried out at room temperature (**Low Temperature Processing**).
- Via CBD the deposition of large area substrate can be obtained by taking certain precautions, for example, lying down the substrate on a shallow tray containing the deposition bath (**Large area deposition**).
- The crystallite size in the films prepared by CBD is very small (**Prepared Small Crystalline Structure**).
- In the CBD method, thin films of well adherent and reproducible with uniform structure can be prepared, which are very useful for photovoltaic applications (**Uniformity and Reproducibility**).
- The CBD technique is a very economical method for broad-scale industrial usages (**Scalability**).

Above these are the reasons to use the Chemical Bath deposition (CBD) method in our experiment.

1.3 Justification for Research on Thin-Film Deposition of ZnO

In today's dynamic and economic world, it is clear that no single Transparent conducting oxide (TCO) thin film can fulfil the diverse demands of every application. However, as different types of Transparent conducting oxide (TCO) thin films continue to advance in efficiency, commercial viability, availability scalability etc.. While ZnO as a Transparent conducting oxide (TCO) thin films may not surpass all other types of TCO's in terms of efficiency or to be suitable for large-scale integration, ZnO possess distinct advantages and potential that make it well-suited for some specific application. One significant advantage of ZnO as a TCO lies in its low materials and processing costs. This cost-effectiveness positions it favourably for integration into consumer goods. By leveraging the affordability, ZnO as a TCO has the potential to revolutionize the way we power everyday products, such as portable electronic devices (touch screens, light emitting diodes, liquid crystal displays or LCDs, solar cells) and some optoelectronic devices.

However, different research works related to ZnO thin films provide the outcomes that the structural, electrical, morphological, and optical properties of ZnO can change extensively by the method of film development. Another noteworthy characteristic of ZnO is, that it is less hazardous. Also, zinc oxide (ZnO) possesses notably good optical and electrical properties in addition to being a cheap and available source in nature. Using ZnO as a TCO have also some other advantages, those are it is non-toxic, great oxidation resistibility, cheap, abundant source of zinc and good thermal stability. ZnO is an element of great interest for use in photonics, electronics, acoustics, and sensing applications. It is essential to many industrialized processes, including those that produce paints, cosmetics, batteries, plastics, tyres, cleansers, fabrics, floor coverings, and more. ZnO single crystals, epitaxial layers, nanostructures, and nanoparticles are all developing at a steady pace.

To name a few, ZnO nanoparticles have revolutionized the development of better sunscreens, paints, and coatings. Furthermore, ZnO is a great candidate for space applications due to its radiation hardness to high-energy proton irradiation. Moreover, zinc oxide possesses oxygenating and antibacterial qualities. As a result, it is used in clinical procedures, such as the application of baby powder and ointments to treat dandruff, various skin irritations, and diaper rashes. It is also used in sunblock due to its reflecting qualities, and lifeguards at the beach frequently wear it on their lips and noses. Likely, ZnO devices will eventually become a necessary component of everyday life.

Considering the availability, lower cost and reduced environmental impact with non-toxicity, ZnO holds promise as a sustainable and environmentally friendly Transparent conducting oxide (TCO). By researching ZnO, scientists and engineers aim to further optimize the performance, efficiency and stability of the Transparent conducting oxide (TCO) thin film, ultimately contributing to cleaner and more sustainable development.

1.4 The Objective of the Study

Wide bandgap (~3.1-3.37 eV) semiconductor ZnO (II-VI) is made from earth-abundant, non-toxic constituent materials with a wide range of applications from optoelectronics to solar photovoltaic to photo-catalytic hydrogen generation to dye removing abilities and solving global water pollution problems. The State of West-Bengal could be benefited from Indigenous, low-cost fabrication technologies in the renewable energy sector namely solar photovoltaic in this scenario, as well as form foundational work in native optoelectronic device-grade material fabrication like that in transparent TFTs. The current project hopes to contribute to ideation and

knowledge building in this regard for the future scope of transition from laboratory prototype to industrial manufacturing for the state w.r.t. TCOs for photovoltaic cells and transparent TFTs. The aims, objective and primary challenge of the current work revolves around the fabrication of nano-structured ZnO thin films using a combined process of SILAR and modified CBD method. The objective is to initially create good quality, as-deposited and later annealed, possibly mono or poly-crystalline, transparent, ZnO thin-films and observe their consequent optical (transmittance and bandgap), electrical and morphological and compositional features. The focus of this work is largely on standardizing a novel no-heat fabrication method during the initial growth process of the films via an aqueous chemical route along with the generation of specular, well-adherent and non-abrasive films. SILAR stands for successive ionic layer adsorption and reaction. In this process, pre-etched substrates are dipped subsequently in cationic and anionic precursor solutions with intermediate water baths. The idea is to facilitate the nucleation and growth of concerned film layers very slowly, layer by layer, with the loosely-held ions being lost or removed when being dipped in the intermediate pure water-baths. The process can be used to give rise to very thin films and can act as seed layers for subsequent chemical bath deposition (CBD) to generate thicker films. In our work, we hope to implement a combined SILAR and modified CBD method to develop quite transparent, nanostructured, ZnO thin films. The observations made and inferences drawn from the analysis of the results are hoped to be published in Peer-Reviewed Journals.

1.5 Conclusion

The introduction chapter has provided an overview of Zinc Oxide (ZnO) as a promising material for Transparent Conductive Oxides (TCOs). We have explored its unique features such as a high degree of visible spectrum transparency, excellent electrical conductivity, and compatibility with flexible substrates, making it a desirable candidate for a broad range of applications, from solar cells and displays to sensors, various optoelectronic devices and transparent electrodes. Additionally, different types of thin film deposition methods and justification for research on this topic have been discussed in this chapter. As we move forward, the subsequent chapters will explore its usage, application and some limitations in greater detail and discuss the latest research efforts aimed at addressing them. By synthesizing existing knowledge and pushing the boundaries of innovation, we aim to unlock the full potential of ZnO as a TCO, paving the way for next-generation optoelectronic devices with enhanced performance and functionality.

In conclusion, the introduction serves as the gateway to the research topic, providing a brief overview of the study's purpose, objectives and significance. To fulfil the objectives, the

literature review critically examined in the next chapter, existing scholarly works to establish the research gap and theoretical foundation for the study. Together, these sections lay the foundation for the research by setting the context, highlighting the knowledge deficit and justifying the need for further investigation.

Chapter-2
Literature Review

2.1 Introduction

Zinc oxide (ZnO) is a non-toxic, cheap and inorganic substance. It usually appears as a whitish powder that is nearly not soluble in polar solvents such as water. It is widely used as an additive in powder form for a variety of products and materials, such as plastics, glass, cement, rubber (like car tyres), oils, paints, balms, sealants, batteries, ferrites, fire retardants, and nourishment (source of zinc supplement). Although zinc oxide (ZnO) exists in the crust of the Earth as the mineral zincite, the majority of ZnO that is used commercially is created artificially. ZnO is commonly referred to as an II-VI semiconductor in materials science because it is a member of the 2^{nd} and 6^{th} groups of the modern periodic table, respectively. Several favourable characteristics of this semiconductor include its broad band gap, high electron mobility, incandescence, stable and high room temperature, and superb transparency.

In this chapter, we will delve into the extensive research conducted by scholars, scientists, and engineers worldwide, spanning various aspects of ZnO's properties, synthesis methods, characterization techniques, and applications in optoelectronic devices. By synthesizing and critically evaluating the literature, we aim to identify the gaps, challenges, and opportunities that exist within the current state of research on ZnO-based TCOs. Moreover, this literature review will serve as a foundation for the subsequent chapters of this thesis/dissertation, providing valuable insights and context for the experimental work, analysis, and discussions presented therein. Through this chapter, we endeavour to contribute to the collective knowledge and understanding of ZnO as a TCO, ultimately paving the way for future advancements and innovations in the field of optoelectronics and solar photovoltaics.

2.2 Review of Earlier Works

A Review of Earlier Works serves as a critical examination and synthesis of existing literature, research, or creative endeavors relevant to a particular topic or field. By analyzing previous contributions, this review aims to identify key insights, trends, gaps, and methodologies, providing a foundation for further exploration and advancement. Here we have divided this review of earlier works section in two parts, one is chemical route method and the another one is physical vapor deposition (PVD) method. Also, reviewed literature based on these two different parts. By critically analyzing and synthesizing existing sources, a literature review helps researchers establish the context for their own study, clarify research questions, and identify avenues for further investigation.

2.2.1 Chemical Route Method

Tahir Saeed et al. **[1]** carried the experimentation by CBD (chemical bath deposition) on the growth of ZnO thin film deposition and characterization. For depositing films of zinc oxide, an easy solution growth method is used here in this study and their following characterisation was shown, as well as two different morphologies of ZnO were seen by SEM. Here Zinc acetate (0.0188 M) and ethylene diamine (0.0340425 M) solutions were used to produce ZnO thin films on glass microscope slides. A tiny amount of base (0.5 M NaOH) was added to elevate the bath. With constant stirring, the reaction mixture was kept at the appropriate temperature for deposition. Glass microscope slides were thoroughly cleaned (rinsed with water and acetone after being scrubbed with trichloroethylene) and submerged in the reaction bath. After varying amounts of time, the substrates were removed, cleaned with distilled water, and dried. Many techniques were then used to evaluate the thin films that had been deposited. This study demonstrates the similar sensitivity of the morphology of ZnO thin films deposited via the CBD method. Interestingly, distinct morphologies are observed even with a single ligand, which could indicate various film properties such as the degree of super saturation and the ligand's surface binding to the oxide.

Mauricio Ortega-Lo ´pez et al. **[2]** researched increasing the CBD method's efficiency while ZnO thin film growth is occurring. To limit both the unwanted homogenous response in the bulk solution and the material deposition on the walls of the CBD reactor, this research provides an effective method for depositing ZnO thin films by CBD. The first step involves the crystallization of zinc peroxide (ZnO2) into cubic structures. The optical bandgap of 4.2 eV and good average transparency (90%) are displayed by this compound. Following annealing, the ZnO2 changes into polycrystalline ZnO with an optical bandgap of 3.25 eV and a hexagonal structure. Starting with NH4(OH) (5.3 M), NH4Cl (0.1 M), ZnCl2 (0.4 M), and H2O2 (30%) aqueous solutions, the solutions utilized in this experiment were successively mixed while being constantly stirred until complete dissolution. The entire process results in high growth rates and ZnO films that are transparent in the visible spectrum. Neither uniform precipitation nor film deposition on the reactor walls is achieved with this method. Therefore, the same solution can be utilized once more for a future deposition operation after developing a film to the appropriate thickness and halting the development process by removing the substrate. The researchers concluded that their approach is efficient in producing high-quality ZnO films with enhanced growth efficiency because the thin films were produced entirely on the substrate surface through heterogeneous growth.

Speciation and the nature analysis of ZnO thin films fabricated by CBD was executed by Paul O'Brien et al. **[3]**. The purpose of the above study is to check and compare the deposited film on glass slides or on the tin oxide substrate, which one is of better quality. In this experiment, thin films of monophasic crystalline hexagonal ZnO were produced onto glass microscope slides and tin oxide-coated glass using solutions of zinc acetate in the presence of sodium hydroxide and ethane-1, 2-diamine. Depending on the conditions surrounding the deposition, two distinct morphologies of ZnO were seen using scanning electron microscopy. In comparison to the films on the tin oxide substrate, films made on glass slides had better morphology and were more adherent. Solutions that are kinetically unstable in terms of zinc hydroxide generation deposit the highest quality ZnO films. The super saturation of zinc hydroxy species is a crucial feature that regulates bath deposition, as demonstrated by calculations on zinc speciation in the solution. These films' bandgap were determined to be 3.15 eV on both substrates based on optical absorption.

Woo-Gwang Jung et al. **[4]** experiments focused on ZnO nanorod development at low temperatures by CBD. In this paper, Chemical bath deposition at standard atmospheric pressure was used to create aligned ZnO nanorod arrays without the use of a metal-based catalyst. ZnO nanorods were produced using a simple two-step process on a PET substrate at 90–95 °C. A sol-gel reaction was used to create the ZnO seed precursor. ZnO seed-coated substrates were used to create ZnO nanorod arrays. To ensure that ZnO nanorods grew in alignment, ZnO seeds were essential. The ZnO nanorod's growth direction is [0001] or the c-axis, and it is a single crystal with a wurtzite structure, as confirmed by HR-TEM and XRD analysis. At ambient temperature, ZnO nanorod photoluminescence tests showed a high UV peak at 378.3 nm (3.27 eV). The growing process proposed in this work enables the large-scale manufacture of oriented ZnO nanorod arrays at affordable prices, which eliminates the need for costly and precise vacuum equipment.

Zinc oxide nanorods were applied to nanoplates in an experiment by Bingqiang Cao et al. **[5]** utilizing CBD growth and surface-related emissions. This work showed how to manufacture one-dimensional ZnO nanorods and two-dimensional ZnO nanoplates using a low-temperature controlled CBD approach. Temperature-dependent cathodoluminescence spectra were used to examine the emissions associated with the surfaces of the nanorods and plates. Moreover, it also illustrates that altering the concentration of the precursor causes the ZnO morphology to change

from nanorods to nanoplates. Consequently, the average aspect ratio (high/width) of ZnO nanorods decreases when the OH-concentration increases. ZnO nanoplates in two dimensions are finally created. These ZnO nanostructures exhibit low-temperature cathodoluminescence spectra with donor-bound exciton emission and surface-state-related exciton emission due to surface impurities. Due to the ionization of donors, the bound exciton emission rapidly declines with temperature and eventually disappears when the temperature rises above 130 K. According to the article, findings indicate that at room temperature, surface-related exciton emission dominates the near-band-gap UV emission.

Structured ZnO thin films produced by CBD were the subject of experiments conducted by A. Drici et al. **[6]** for solar applications. In this experiment, to produce the deposition of porous but adherent thin films, the bath's pH and temperature have been altered during the deposition process. It was found that ZnO films with a hexagonal shape crystallized after half an hour of air annealing at 300°C. They have a small oxygen deficit but are otherwise almost stoichiometric. Because the grains are columnar and the films are porous, huge surface area films can be produced. The films have n-type conductivity and are semi-conductor. It is demonstrated here that in longitudinal structures as opposed to transversal structures, the influence of the grain boundary on conductivity is larger. These ITO-deposited films have been employed in ITO/ZnO/absorbent/aluminium micro-structured solar cells. This paper demonstrated that the absorber has a significant impact on the device efficiency, it might be enhanced by employing a better absorber. The absorbent was either an organic layer of zinc-phthalocyanine or a combination of poly (N-vinylcarbazole) and diaminoanthraquinone. At last, a photovoltaic effect has been achieved.

The annealing impact of hydrophobic and textured ZnO films produced by chemical bath deposition was studied by V.R. Shinde et al. **[7]**. The objective of the paper is to reveal the change in properties of textured ZnO cones, grown onto glass substrates after the heat treatment. The structural, optical, and electrical properties of the textured ZnO cones grown onto the glass substrates were examined after they were heat-treated for two hours at 623 K in the air. The findings demonstrated that following heat treatment, the generated ZnO film, which displayed high orientation along the c direction (0 0 2), remained low intensity. Following heat treatment, the size of distinct cones that were nearly perpendicular to the substrate surface decreased dramatically. The hydrophobic surface with a contact angle of 152.84±1.5º was achieved following heat treatment, while the as-deposited ZnO films showed a contact angle of 72.28±1.5º

according to a water wettability analysis. When ZnO was deposited, its electrical resistivity measurement revealed that it was semiconducting, with a room temperature resistance of 10^4 ohms. When ZnO was annealed, its resistivity dropped to 10^3 ohm. Following heat treatment, a shift in bandgap energy from 3.7 to 3.2 eV was noted.

L.L. Yang et al. **[8]** carried out a size-controlled development of well-oriented Zno nanorod arrays using a two-step CBD process. This study looks at how the growth period (t), pH, angle () between the substrate and beaker bottom, and spin coating pretreatments to create a layer of ZnO nanoparticles affect the ZNAs' structure. Among the other pre-treated methods, spin-coating is a very simple and economical process which is why this technique is used to introduce seeding layer on substrates in this study. The findings demonstrate that theta, t, pH, and substrate pre-treatment do have a significant impact on ZNA development. The results show that substrate pre-treatment, pH, theta, and t do have a significant impact on ZNA development. Not only does it help reduce the diameter of ZNAs, but it also significantly affects their orientation when a ZnO nanoparticle layer is added to the substrate. The results show that substrate pre-treatment, pH, theta, and t do have a significant impact on ZNA development. Furthermore, well-aligned ZNAs with a 50 nm diameter developed on the Si substrates that had been pre-treated at growth conditions of pH ∼6, theta = 70◦, and t = 2 h. In this research they concluded that this low-temperature growth could offer a way to create nano-devices on a variety of low-temperature-resistant surfaces and also, because the growing process doesn't require precise or costly vacuum equipment, it can be fabricated on a big scale at a comparatively low cost.

Qingwei Li et al. **[9]** conducted experiments on the low-temperature wet CBD approach for the controlled development of well-aligned ZnO nanorod arrays. This study produced ZnO nanorods on Si substrate using the wet CBD approach, with special attention paid to analyzing the effects of precursor concentration, growing temperature, and time on the as-grown ZnO nanorod shape. Here it is shown that by easily modifying the preparation parameters, well-aligned ZnO nanorods can develop in a controlled manner. The findings show that by varying the precursor concentration, growth temperature and time, ZnO nanorod aspect ratios on the substrate are possible to control. This study highlights the fact that the room-temperature photoluminescence spectra of the ZnO nanorod arrays on all substrates only displayed a prominent near-band edge UV emission peak. In contrast, the deep-level emissions associated with defects were almost completely absent, suggesting that this low-temperature chemical method could produce ZnO nanorod arrays with high optical quality.

Mahshid Poornajar et al. **[10]** carried out the physicochemical factor analysis during the synthesis of ZnO nanorods using CBD. The purpose of this work is to evaluate the effects of relevant variables on the synthesis of ZnO nanorods using CBD, including seed layer thickness, temperature, initial Zn concentration, and poly-ethylenimine (PEI) level. Additionally, it has been observed that the HMTA/Zn molar ratio and precursor concentration can be adjusted to control the growth rate of ZnO nanorods. The outcome demonstrated that a 50 nm seed layer thickness was the ideal starting point for producing ordered vertical ZnO nanorods with the highest density. From the SEM images, we got to know that at a concentration of 0.025 M for Zn ions and 0.015 M for PEI, ZnO nanorods that are uniform and aligned can be produced. From the result, it was made clear that the length of the ZnO nanorods was more significantly affected by temperature than the diameter.

Ravi Shankar Rai et al. **[11]** experimented to quickly synthesize ZnO nanostructures on woven carbon fibre via microwave-treated chemical bath deposition and characterize them. This work described the use of the microwave-assisted chemical bath deposition (MACBD) technique to propagate ZnO on woven carbon fibre (WCF) under varied microwave power and growth periods. Several morphologies of ZnO NSs, such as nanopetals, twinned nanospheres, nanoflowers and nanoflakes, were created on WCF fabric using an aqueous solution of tetra ammonium zinc complex. Several precursor solutions were applied to ordinary WCF fabric samples before they were heated in a microwave. ZnO NSs have a 2-4-minute formation period, which is less than that of traditional CBD. Using FESEM to analyse the processing of ZnO NSs on carbon fibre strands, it was found that changes in precursor solution and microwave duration are the main factors influencing the development of ZnO shape. The oxygen-deficient character of the produced ZnO nanostructures is revealed by the EDS analysis, which accounts for the n-type nature of the intrinsic ZnO. Epoxy resin was employed as a matrix material in conjunction with five layers of ZnO-grown WCF for a variety of applications.

Z.N. Urgessa et al. **[12]** examined the patterned development of ZnO nanorods using chemical bath deposition [12]. This work showed how ordered ZnO nanorods can grow via chemical bath deposition on a patterned seed layer, and it suggests a way to regulate the donor-acceptor layers at the nanoscale. The influence of patterning settings on the density and distribution of the rods is shown on a patterned substrate. It is suggested that bulk heterojunction solar cells' absorber layer could be controlled at the nanoscale morphology by employing such ordered ZnO nanorods. In this experiment, a patterned mask made of polymethyl methacrylate (PMMA) was built over the

ZnO seed layer using electron beam lithography (EBL). This experiment's morphology causes exciton dissociation exclusively at the interfaces, which lowers the photocurrent efficiency. However, It has been demonstrated that low-temperature chemical bath deposition on a substrate with pre-patterning can be used to generate ordered nanorods. In conclusion, this study gives a method for managing the nanoscale distribution of donors and acceptors in a bulk heterojunction (BHJ) solar cell.

The impact of flaws in ZnO nanocrystals produced by chemical bath deposition on photocatalytic activity was studied by Z. Sh. Shaymardanov et al. **[13]**. This study examined the impact of different native defects on the photocatalytic activity of ZnO nanocrystals that were produced using chemical bath deposition and possessed uniform morphological features. They found that the as-grown sample's PL spectrum shows a yellow emission band at around 565 nm, which is indicative of the oxygen atoms in the interstitial space, indicating a volume defect. After that, they annealed the ZnO nanocrystals in the air at a temperature of 200ºC and then found that there is only a single NBE emission band in the PL spectrum, and the defect concentration is very low. And, lastly, they annealed the ZnO nanocrystals in air at a temperature of 500ºC, then they found a green emission band associated with an oxygen vacancy (surface defect) at a wavelength of about 510 nm. Their experimental findings lead them to the conclusion that, in ZnO nanocrystals, the effects of surface and volume defects on photocatalytic activity at nearly equal concentrations differ because of the nature of the defects, with surface defects having a twofold greater effect than volume defects. This study also showed that the rate of dye degradation increased with an increase in the concentration of these flaws and the appearance of surface defects.

The effect of bath temperature on the characteristics and efficiency of Cu2O/ZnS/ZnO hetero-junction thin film made by chemical bath deposition and electro-deposition techniques was investigated by Halima Benathmane et al. **[14]**. The purpose of this experiment was to investigate the effects of bath temperature on ZnS layer thicknesses and ZnO/ZnS heterojunction characteristics. First of all, they prepared a novel p-Cu2O/n-ZnS/n-ZnO hetero-junction thin film by combining electrodeposition and CBD techniques. The ZnS buffer layers reduced in optical band-gap from 3.46 eV to 3.35 eV as the bath temperature increased from 75 °C to 90 °C. Furthermore, the results showed that when the bath temperature rose, ZnS buffer layer thicknesses and surface roughness increased. Their results showed that at 75ºC bath temperature, ZnO/ZnS structure had the smoothest surface, the largest electron density (ND = 1.926 × 1020 cm− 3), and the best crystalline quality (n-type conduction). This study finds that the band gap

value of 3.46 eV will be very effective for solar cells and that the insertion of a ZnS buffer layer in the Cu2O/ZnO hetero-junction would boost the photocurrent responsiveness up to 0.730 mA.

The morphology and orientation-regulating of ZnO nanofibers via CBD were explored by Jinze Zhu et al. **[15]**. In this paper, a synthetic technique that is effective has been used to create ZnO nanostructures with specific crystal orientations. ZnO seed fibres were first made via electrospinning and the sol-gel technique. The second phase involved growing ZnO nanofibers using the CBD technique on the pre-seeded fibres in several chosen orientations. At this point, the volume fraction of isopropanol (IPA) had a major impact on the growth of ZnO fibres generated along the semipolar and nonpolar crystal planes. The solvent's steric hindrance effect and polarity were identified as the growth mechanisms. The result showed that ZnO crystal formation shifts from polar to nonpolar orientations with increasing isopropanol (IPA) volume fraction. At 40% of the IPA volume fraction, ZnO nanofiber's growth orientation shifts from polar to semipolar and When the IPA volume fraction reaches 70%, ZnO nanofibers' growth orientation shifts from semipolar to nonpolar. This work offers a simple way to create ZnO nanofibers with particular morphologies.

Muzaffar Ahmad Boda et al. **[16]** carried out the simple synthesis of hybrid ZnO nanostructures by combining electrodeposition and CBD for enhanced dye-sensitized solar cell performance. In this work, uniquely 1-D ZnO nanorods were fabricated by cathodic deposition of ZnO nanorods over fluorine-doped tin oxide (FTO) coated glass. The goal was to create a photo-anode for DSSCs with effective charge transport dynamics and a reduction in the number of recombination centres. This experiment is carried out with the aim of improving the photocurrent density of the photo-anode to be placed in DSSCs, nanorods of ZnO were worked appropriately with ZnO nano-spindles on employing hexamethylenetetramine (HMT) in order to expand the surface area even more. The experimental analysis showed that, Compared to bare ZnO nanorods, the resultant hybrid photo-anode delivers a 43% increase in photocurrent density. Lastly, it can be concluded that this work describes the easy, quick, and economical method of creating an effective DSSC photo-anode using the straightforward hexamethylenetetramine (HMT) tool to couple CBD and ED.

The ultraviolet photo-response characteristics of bush-like ZnO nanorods produced by CBD were examined by Abhishek KJ et al. **[17]**. This paper presents the UV photo-response properties of MSM-structured bush-like ZnO nanorods (NRs) in air and nitrogen (N2) atmospheres. First of

all, On a soda-lime glass substrate, bush-like zinc oxide nanorods (ZnO NRs) were produced using a deposition process involved in two-step: first, a seed layer was deposited using atmospheric chemical vapour deposition (APCVD), and then the NRs were grown using chemical bath deposition (CBD). X-ray Diffraction and scanning electron microscope results helped to get know about the formation of ZnO and bush-like aggregation of ZnO NRs. Photoluminescence spectroscopy indicated the presence of primarily oxygen vacancy (VO) linked defect states centred at 2.32 and 2.0 eV on ambient temperature. The specimen had a sluggish photo-response but good photosensitivity, measuring 2233% in air and 3166% in N2. It has been concluded from this study that the lack of oxygen molecules has been linked to the increased sensitivity and PPC under N2.

A unique UV photodetector (PD) based on ZnO nanorods (NRs) was fabricated by Salah M. Saleh Al-Khazali et al. **[18]** utilizing chemical bath deposition (CBD) onto a flexible polypropylene carbonate (PPC) substrate. The ZnO NRs onto PPC substrates surface using the CBD technique for UV detecting application has been demonstrated in this study. After ultrasonically cleaning the PPC substrate with ethanol, acetone, and deionized water for five minutes each, the Spin-Coating method was utilized here to deposit the ZnO seed layer. When applying a bias voltage of 5 V, The outcomes showed a high photocurrent at exposure to 385 nm, robust stability over time, excellent sensitivity (52.48%), and quantum efficiency (1088.8%). Additionally, when exposed to 405 nm, they displayed a response time of 66.4 s and a recovery time of 97 s. A flexible high-performance photodetector appears to be promising based on the findings.

Venkata Manthina et al. **[19]** examined the applicability of single-pot ZnO nanostructure production by chemical bath deposition. A variety of ZnO nanostructures have been produced in this work and discussed how their size, shape, and surface area make them suitable for various applications. CBD is used to create ZnO fibres, nanorods, cauliflowers, nano-rod balls, nano-forests, nano-pencils, ellipsoids, and nanotubes by adjusting the growth conditions and additions that affect the ZnO nanostructures. From this study, we got to know that Apart from how it affects the surface-to-volume ratio, the morphological change can affect stability, electron transport, optical characteristics, amount of defects, and other electronic properties. And also how the additives affect the ZnO nanostructure growth was analysed. So from this experiment, we can conclude that the assortment of structures provides a wide range of uses in various devices.

Abdulwahab Salem Zaroug Lahewil et al. **[20]** worked with the synthesis of ZnO nanoclusters micro active area employing continuous wave blue laser-assisted chemical bath deposition based on UV photodetector. In this work, ZnO nanoclusters (NCs) were produced on a glass substrate at a low temperature using the straightforward catalyst-free hydrothermal approach of laser-assisted chemical bath deposition (LACBD). Afterwards, metal–semiconductor–metal (MSM) structured ultraviolet (UV) photodetectors were made using these zinc oxide (ZnO) thin films. In the case of LACBD, ZnO thin-film growth and crystallinity were improved by the application of a 460 nm continuous wave laser with a 30-minute laser irradiation time. The evaluation of a thin film of (Fe-ZnO NCs-Fe)/Glass as a basis for a high-quality UV photodetector demonstrates unequivocally, that ZnO NCs offer low-cost nanostructures that could be used to produce UV sensors. ZnO thin films and nanostructures' UV photodetection properties were ascertained by current-voltage (I-V) and current-time (I-t) measurements. The researchers concluded that UV photodetectors could be used on human skin in the future to prevent cancer and skin ageing when they are incorporated into the Internet of things. It has been demonstrated that ZnO NCs play a significant role in the quick detection of UV radiation.

The experiment on characterizing CBD-grown ZnO films with high c-axis orientation was conducted by S. Kahraman et al. **[21]**. In this study, we investigated the impact of the deposition period and the SILAR-generated seed layer on the properties of ZnO nanostructures created on glass substrates by the CBD method. Here Grain size, lattice strain, dislocation density, morphology, and conductivity activation energies were among the structural factors that were changed and examined. To identify the change of structural parameters: morphological, XRD analysis, SEM observations, and electrical tests were performed. These morphologies provide a large surface area, which is essential for area-dependent applications such as solar cells, gas sensors, photo-electrochemical (PEC) hydrogen generation, and solar energy-to-hydrogen conversion devices, according to the SEM pictures. The ZnO films were discovered to have hexagonal wurtzite-type structures, with a preferential orientation along the C-axis, based on the XRD patterns. It was discovered that while grain size increased, the structures' microstrain and dislocation density values decreased. In the 300–500 K temperature range, the films' activation energy values were found to be between 0.12 and 0.15 eV based on the dark electrical resistivity–temperature relationships.

S. Roy et al. **[22]** executed an experiment by CBD technique to develop ZnO hexagonal nanorods based on an ethanol sensor. In order to effectively detect ethanol vapour (in air),

hexagonal nanorods with Pd nanoparticle sensitization were studied in this work. The effect of different noble metal catalytic contact (Au/Pd–Ag) with palladium surface sensitization on the effectiveness of ethanol sensing has also been studied. On a p-Si substrate coated with SiO2, nanorods were deposited. It was discovered that the nanorod's average length and diameter were, respectively, 500 nm and 70 nm. Every sensor was tested in the 27–300°C temperature range to see if it could detect ethanol vapour. They discovered that the ethanol sensing capability was enhanced by the surface modification of nanorods by Pd nanoparticles and the 70% integration of Pd–Ag catalytic electrode. With a tendency toward saturation above 1530 ppm ethanol (in air), the dynamic range of the sensor was found to be notably high (190–1530 ppm ethanol in air) for both modified and unmodified nanorods.

Son Nguyen et al. **[23]** examined the function of ZnO thin film in the CBD-induced vertically oriented growth of ZnO nanorods. This work uses room-temperature RF magnetron sputtering to produce ZnO seed layers on a Si substrate, with the thickness of the layers being varied. CBD was used to produce ZnO nanorods on the thin film at 90 °C. They investigated the effects of the thickness-dependent surface form of the seed layer on the vertical growth of ZnO nanorod arrays. The average diameter of ZnO nanorods was found to be highly close to the average grain size of ZnO thin film, confirming ZnO film's role as a seed layer for the vertical growth of ZnO nanorods. According to these outcomes, a thin film of ZnO serves as a good seed layer for the vertically oriented development of ZnO nanorods during the Synthesis phase of solutions that follows. ZnO nanorods produced vertically have demonstrated good optical and crystallographic properties.

Maria Elena Fragalà et al. **[24]** experimentation with Application in water treatment, to produce ZnO nanorods onto ultrathin ZnO seed layer. In this experiment, ZnO nanorod arrays that are dense and lengthy are created by chemical bath deposition (CBD) using ultrathin and ultra-smooth ZnO films that are generated via atomic layer deposition (ALD) as seed layers. Dense and long ZnO nanorod arrays were produced by chemical bath deposition (CBD) using ultrathin and ultra-smooth ZnO films that were formed via atomic layer deposition (ALD) as seed layers. Specifically, under UV light irradiation, the thinnest layer of ALD ZnO fosters the growth of dense and perfectly aligned ZnO nanorod arrays that efficiently degrade phenols and methylene blue dye. The resultant ZnO NRs-based photocatalytic substrates are stable across aging and various photo-degradation cycles; Reused samples, in reality, perform comparably even after several cycles that are repeated within a few months of manufacturing.

S. Aksay et al. **[25]** carried the experimentation by chemical bath deposition assisted by microwave (MW-CBD) to study the ZnO: Sn nanostructured film's optical and structural characteristics. In this experiment, they describe how MW-CBD deposits Sn-doped ZnO and how the amount of Sn dopant affects the doped nanostructures' structural, morphological, and optical characteristics. XRD, SEM, AFM, and UV–Vis spectra were used to examine the impact of Sn doping on ZnO films. The XRD results revealed that every film has a hexagonal wurtzite structure. It came to light that the peak density of the ZnO film decreased with increasing Sn levels. The film's surface was found to have hexagonal nanorods based on the SEM data. It was discovered that as the concentration of Sn doping increased, the surface roughness changed. It was found that when the amount of Sn dopant increased, the film's T% values increased from 70% to 80%. It was noticed that the ZnO's E_g value was 3.27 eV, while for ZnO: Sn 3% film, it was found to be increase up to 3.37 eV. These results indicate that ZnO films doped with Sn are perfect materials for use in optoelectronic devices.

R. Chandramohan et al. **[26]** conducted research on the impact of annealing temperature on the morphology, optical characteristics, and structural characteristics of Al-doped ZnO thin films produced by CBD on the glass substrate. The heat treatment, which was carried out at 300°C and 400°C, had some effect on the physical properties of the formed structures, according to the optical and structural characterization of these films. When the films are annealed below 300ºC, no noticeable changes in the surface morphologies are seen. The XRD data show that the deposited thin films have a polycrystalline hexagonal structure. It is found that the films that are not annealed have smaller crystallite sizes than those that are annealed at 300 °C and 400 °C, respectively. The direct band gap energy was found to increase from 3.25 to 3.32 eV during 30 minutes of air-medium annealing at 300 and 400 degrees Celsius. They suggest that the sample surface's low oxygen content following thermal treatment could be the cause of this rise in band gap energy. The refractive index, extinction coefficient and the size of the grains showed some variation with the rise in annealing temperature. These polycrystalline films based on ZnO doped with Al are meant to be used as electrodes in optoelectronic devices and gas sensors.

Tae-hyun Lee et al. **[27]** executed an experiment via modified chemical bath deposition (M-CBD) for ZnO nanorod's fast vertical growth. This study employed the Modified-CBD technique to examine the impact of changes in temperature of growth, growth duration, and concentration of solution during the ZnO nanostructures growth on Si (100) seeded substrates. Using M-CBD

alone, they were able to create vertically grown ZnO nanorods in this experiment that had a strong structural XRD property and a fast growth rate without the need for extra annealing. According to the FEG-SEM measurement, they found that under every circumstance, vertically grown ZnO nanorods with good morphological characteristics were produced. All samples had low FWHM values, 0.18–0.23, and strong (002) peak intensities, according to the XRD measurement results, although no thermal annealing was carried out following development. This indicates that the ZnO nanorods have excellent crystal structure. The results of this study indicate that processing flexible substrates that need to be processed at low temperatures can be greatly facilitated by the M-CBD process.

The impact of varying pH values on growth solutions for ZnO nanostructures was examined by Ahmed F. Abdulrahman et al. **[28]**. The ZnO nanostructures used in this work were created via the modified-CBD technique. To achieve the best possible pH conditions and yield a better - quality ZnO nanostructure, scientists have investigated how different pH values in the aqueous growth solution, ranging from 6.4 to 12, affect the synthesized ZnO nanostructure surface morphology, growth rate, defects, elemental chemical compositions, crystal quality, lattice parameters, and optical properties. As the initial pH values increased, so did the average transmittance. According to the outcome of the XRD, the nanostructures of ZnO were aligned along the peak of diffraction c-axis (002) and had good crystal quality up to a pH of 9.4. However, the FE-SEM photos demonstrate that the crystal quality declined beyond that point. In conclusion, this research implies that the morphological, structural, and optical features of ZnO nanostructures were significantly and remarkably affected by varying the aqueous growth solution's pH from 6.7 to 12 under a method of injection by an air bubble.

Jinze Zhu et al. **[29]** examined the morphology and orientation-regulating of ZnO nanofibers using CBD. This work presents the application of an efficient synthetic method for the growth of ZnO nanostructures with desired crystal orientations. ZnO seed fibres were first made via electrospinning and the sol-gel technique. The second phase involved growing ZnO nanofibers using the CBD technique on the pre-seeded fibres in several chosen orientations. It has been identified that at isopropanol (IPA) volume fractions of 40% and 70%, respectively, ZnO nanofibers grow from polar to semi-polar and from semi-polar to non-polar, depending on the growth orientation. Also, several preferred orientations are used to synthesis ZnO in a variety of morphologies, including wedge forms, discoid shapes, equiaxed shapes, and hexagonal prisms. The polarity and the solvent's steric hindrance effect were identified as the growth mechanisms

and also this work offers a simple way for creating ZnO nanofibers with specific morphologies.

2.2.2 Physical Vapour Deposition (PVD) Method

Y. F. Lu et al. **[30]** analyzed how the growth of thin film deposition of ZnO through PLD is effected by thermal annealing. Using STS (scanning tunnelling spectroscopy) and STM (scanning tunnelling microscopy), this work investigated the changes in the surface characteristics of ZnO thin films with thermal annealing. To look into how thermal annealing affected the chemical bonding and composition of the film, XPS (X-ray photoelectron spectroscopy) of ZnO thin-film surface measurements were carried out. The distinctive vibrations of the ZnO thin-film crystal structure can be measured by Raman spectroscopy. After annealing, the ratio of oxygen in ZnO increases, which was shown in the results of XPS. This might be a factor in the increased resistivity of ZnO thin-film upon annealing. It is also found that the adsorption and dissociation of water on the ZnO film surface cannot be inhibited by annealing. ZnO film surfaces STS spectra showed that no empty states were detected above the surface Fermi level. They also identify that the surface states band gap may be reduced by annealing. The intensity of E2 mode, which is related to the enhancement of crystal quality can be enhanced by annealing that indicated by Raman spectra.

V. Craciun et al. **[31]** discussed the Characteristics of high-quality ZnO thin films deposited by PLD (pulsed laser deposition). On silicon and glass substrates ZnO thin films have been formed by PLD (pulsed laser deposition), and for that, a 248 nm wavelength KrF laser was used. Research has been done on how deposition factors such as oxygen pressure, substrate temperature, laser fluence etc. affect the grown film properties. They identify the optimized conditions for the growth of high-quality ZnO thin film is approximately $5x10^{-2}$ ohm-cm electrical resistivity, reflection line (FWHM value of the (002)) of XRD less than 0.15° with the orientation of the film is c-axis, more than 85% optical transmittance in the visible spectrum at 350 °C substrate temperature. High-quality ZnO thin films carried some valuable characteristics, which are around 3.26 eV band gap and approximately 1.98 refractive index. The produced ZnO thin films exhibited exceptional quality, as evidenced by their band gap of 3.26 eV and refractive index of around 1.98. In conclusion, for ZnO films formed at such low temperatures, using any process, these are some of the best attributes that have been documented so far.

The optical applications of Al-doped thin films of ZnO deposited by PLD were discussed by

Gurpreet Kaur et al. **[32]**. Al-doped ZnO (Al: ZnO) thin films with high transparency and conductivity were produced on glass substrates. In this study, they have examined the impact of Al: ZnO thin film thickness on the optical, structural, and electrical characteristics, with a special focus on the optical uses of these films. They have chosen 2% Al-doping by weight in ZnO and found that with no impurity phase, the formed thin films are extremely crystalline and aligned along a certain plane. They found that Particle size, shape, and distribution change as the number of layers increases, hence altering the thin film stress and characteristics morphologically. The surface roughness and the distribution of grain affect the Al: ZnO thin film's optical and electrical characteristics and the film thickness also influences the optical band gap and determines the optical transparency (T) and refractive index (n). In the visible range, they have higher optical transmittance. The band gap is lowered by Al-doping ZnO. In conclusion, Al: ZnO thin films are a good choice for the transparent window layer of solar cells because of their high optical transmittance value and are applicable for optoelectronic applications such as LEDs(as photoluminescence spectra give sharp visible emission peaks) and laser diodes.

J. B. Franklin et al. **[33]** synthesized the ZnO thin films on transparent conducting substrates as Indium tin oxide (ITO) using Optimised pulsed laser deposition(PLD).In this paper, the investigation was done on ITO, to check the influence of extended range (50–650º C) of deposition temperature. Also, the investigation of 120–250 nm thickness deposited films, crystallinity, optical properties and the influence of temperature and pressure of oxygen on substrate conductivity was done, determining the ideal circumstances for producing highly crystalline ZnO while maintaining the basic characteristics of the substrate. This study shows that, by increasing the oxygen pressure to 50 mTorr at as low as 50°C, films can be produced with a transparency greater than 85%. Also, by adjusting the pressure of oxygen within the deposition chamber enables the low-temperature production of ZnO with higher crystallinity. It can be concluded that the ability to modify the deposition parameters (such as temperature, oxygen pressure etc.) for controlling crystallinity makes it possible to control ZnO deposition on functionalized organic and flexible substrates (In particular, those that shouldn't be exposed to extreme heat).

B. Chakraborty et al. **[34]** experimentation on electron beam evaporated thin films of ZnO and surface defects influence on its FET bio-sensing features such that selectivity, sensitivity and longevity towards reliable PSA detection. In this case, thin films of ZnO have been fabricated via

EBE (electron beam evaporation), with the defect state density and surface roughness being adjusted by varying the current and time (such deposition parameters). To examine defect state density and roughness of the surface, a lot of characterization methods have been studied. It has been found that the antibody binding density exhibits non-monotonic behavior, despite the sensors' trans-conductance decreasing monotonically as defect density increases. Moreover, a lifespan of 4 months has been maintained by a sensor with an initial 0.1 fM detection limit of PSA which was non-optimized, whereas the sensor with the best sensitivity maintains its function for up to 2 months. Therefore, it can be concluded that fine-tuning the ZnO FET biosensor's surface defect state is a crucial need for guaranteeing both a low detection limit and high sensitivity as well as a dependable long-term performance.

S.J. Lim et al. **[35]** researched on thin films of ZnO as an active layer for TFT means thin film transistor, fabricated by ALD and RF Sputtering. First of all at growth temperatures of about 100 to 250 °C, using a metal precursor as diethyl Zn (DEZ) and water as a reactant, ZnO thin films have been deposited by ALD. To focus on the application as TFT's active channel layer, some vital film features such as chemical, microstructure and electrical were measured for the film fabricated by ALD and compared these features with the Rf sputtering generated ZnO thin film. Without the O–H bond there is no carbon contamination as shown by the results of XPS for the films of ZnO generated by ALD. (002) is the preferential orientation for both the thin films of ZnO generated by ALD and sputtering, according to microstructure investigations performed using X-ray diffraction. From their result, it can be concluded that ALD ZnO has substantially lower resistivity than sputtered ZnO films under the majority of the growth circumstances examined and because ALD ZnO has relatively high carrier concentrations, proper modification is required during the deposition process to be used as TFT's active channel layer.

S. Flickyngerova et al. **[36]** studied the optical and structural properties of ZnO thin films generated by Rf sputtering. By varying the deposition conditions, using RF diode sputtering first of all they prepared the thin films of Zinc oxide (ZnO) and aluminium-doped zinc oxide (ZnO: Al). Investigations were conducted to check how the structural and optical characteristics were influenced by negative bias voltage and RF power. The polycrystalline and hexagonal wurtzite structure of both un-doped and Al-doped ZnO films was confirmed by X-ray diffraction measurements (XRD). Both bias voltage and RF power showed no effect on the high optical transmittance (>90%) of the sputtered ZnO and ZnO: Al films in the 400–800 nm wavelength range. It can be concluded that the un-doped and Al-doped ZnO thin films optical band gaps

exhibited a tendency to narrow (due to partial ionization of the carrier impurities) and were dependent on negative bias and RF power.

Jamilah Husna et al. **[37]** researched thin films of ZnO deposited onto soda-lime glass substrates with ITO coated by RF magnetron sputtering and the influence of annealing temperature between 250 to 450°C on its structural and optical properties are investigated. This study's primary goals are to develop thin films of ZnO that can be used as a thin-film solar cell buffer layer and to enhance the film quality through carefully managed annealing. The polycrystalline annealed ZnO film orientations are (002), (101), and (001) with hexagonal wurtzite structure of crystallites, according to the X-ray diffraction measurement. After annealing, it was discovered that the films' crystalline properties and grain size increased. annealed at 400°C, optical band gap ZnO films first blue-shifted (3.1–3.23 eV) and when annealed at 250–450°C, optical band gap ZnO films then red-shifted (3.23-5.23 eV). In the optical bandgap spectrum, the ZnO thin films showed over 85% transmittance and based on all the findings, annealing after deposition can enhance the quality of the film by reducing roughness and improving characteristics of the crystalline, which will be very superior to use as buffer layer in the thin film solar cells based on CIGS or CdTe.

Wei Gao et al. **[38]** analyzed the thin films of ZnO deposited by magnetron sputtering onto glass substrates. The effects of processing factors on thin-film structural, electrical, and optical properties were examined and briefly reviewed. From the result of SEM and XRD, we understood that working pressure, oxygen partial pressure, working distance, bias, plasma excitation, type of mode of deposition and doping have a great influence on the microstructure and quality of the films. It was also found that the crystal structure, chemical composition, microstructure, and deposition technique (dc or rf) all have a significant impact on the electrical conductivity of ZnO films and the thin films of ZnO deposited with rf power carried quite better quality than the films generated by dc deposition. Also, it can be concluded that thin films with an ideal microstructure and excellent conductivity are thought to be achievable with careful control of processing parameters including doping, target to substrate distance, bias voltage, type of plasma excitation, total and partial pressure, and other factors.

2.3 Gap of Knowledge

From the above literature review and to the basis of our knowledge, a relatively lesser amount of work has been done with low-temperature or room-temperature applications during the aqueous chemical route method for the growth of ZnO thin films. As the aqueous chemical route provides a better scope for large-area substrate fabrication of such thin films, it is a more viable option for low-infrastructure labs to achieve low-cost commercial growth techniques. In this regard, a further improvement such as relatively very low-temperature or room-temperature application during the growth method will not only reduce the operating cost but can also lead to parallel novelty in such thin film nucleation and growth processes. The current work is a humble attempt to bridge this apparent gap of knowledge.

2.4 Probable Solution

A combined method of SILAR and modified CBD can achieve this low-temperature or room-temperature feature during the aqueous chemical route method. As SILAR helps to nucleate a very thin seed layer, it can later help the primary CBD process in the growth of well-adherent and specular ZnO thin films. The whole as-deposited process can thus be possibly achieved without any heat application during the aqueous growth and nucleation process, along with simultaneous fabrication of novel nanostructure. The CBD process can further be modified by novel intermediate cleansing steps to achieve a finer and smoother film. In this regard, the following chapters on Material and Method and Result and Discussion will shed more light in detail.

2.5 Scopes of the Present Work

This thesis presents a comprehensive and formalized description of the systematic process involved in the fabrication of ZnO thin films. This work aims to provide a clear and concise framework for researchers and practitioners in the field, facilitating the replication and understanding of the ZnO thin film fabrication procedure. The described process encompasses the key stages, materials and equipment involved in the successful fabrication of ZnO thin films.

In this current work, an attempt is made to fabricate ZnO thin films via combined SILAR and modified CBD method at room temperature. The primary effort is directed to nucleate and grow ZnO as-deposited film without any external application of heat at room temp. The as-grown films were further subjected to post-deposition treatment at varying times and the final sample was eventually subjected to optical, morphological, compositional and electrical analysis. The idea was also to achieve novel nanostructure in these as-grown films and further improvement of these structures under post-treatment conditions. Finally, a comparative analysis of the results from all the samples is hoped to be discussed. In this study, the work based on the proposal is executed through the following steps.

The whole work is presented in the form of a thesis. Where the first chapter of the thesis provides an introduction and background of ZnO thin films, and different types of deposition techniques such as physical and chemical route methods and also establishes the objective and Justification for Research on Thin-Film Deposition of ZnO. This chapter sets the stage for the thesis by presenting the research goals, outlining the significance of transparent conducting zinc oxide and justifying the importance of the research.

The second chapter delves into the previous work done on ZnO thin film, particularly focusing on the different methods used and the fabrication processes employed. It examines the existing literature and studies related to ZnO thin film to provide an ample understanding of the progress and limitations in the field. The chapter also reviewed previous literature related to ZnO thin films to find the gap in the knowledge as well as possible solutions.

The third chapter describes the experimental setup and methodology used in the research. It outlines the apparatus, instruments, and materials utilized for the experiments conducted throughout the thesis. The chapter provides a comprehensive explanation of the experimental procedures, ensuring the reproducibility of the results. It includes details on sample preparation, and measurement techniques followed during the experimentation.

The fourth chapter focuses on presenting the results obtained from the experiments conducted in the study. The chapter includes graphical representations, images, and calculated data to present the findings effectively. The results are discussed in light of the research objectives, and the implications and significance of the obtained results are analyzed. Characterization

techniques employed to evaluate the performance and the ZnO thin film features are discussed, along with the corresponding instruments used.

The final chapter of the thesis summarizes the entire research and provides a conclusive assessment of the findings. It highlights the key outcomes, discusses the implications of the research, and evaluates the extent to which the research objectives were achieved. Additionally, the Fifth chapter offers insights into the future scope of the work, suggesting potential avenues for further research and development in the field of transparent conducting zinc oxide thin film. It provides recommendations for enhancing the performance, stability, and efficiency of ZnO thin film and explores the broader implications of the research.

2.6 Conclusion

In this chapter, a review of previous work is presented. From the reviewed section the actual problem is identified and a probable solution is proposed. Next, the objective of the present work and the step through which the proposed work is implemented are summarized. The next chapter will give us a proper overview of the materials, and apparatus involved in this experiment and their usage, Also, the step-by-step experimental procedure or methods of this experiment.

Chapter-3 Experimental Setup & Methodology for Fabrication of ZnO Thin Film

3.1 Introduction

The experimental setup and methodology for the fabrication of the ZnO thin film chapter provides a comprehensive description of the procedure and equipment used in the fabrication of the ZnO thin film. This section outlines the step-by-step process involved in creating the ZnO thin film on glass substrates, from the cleaning of glass substrates to drying it, preparation of precursor solution, and process involved in the deposition and testing of the final output product. By detailing the experimental setup and methodology, this chapter serves as a guide for researchers and technicians interested in replicating or modifying the fabrication process. The experimental setup for thin film deposition of ZnO typically includes various equipment and tools necessary for the preparation of precursor solution, cleaning and drying of glass substrates, film deposition etc. The following sections provide a comprehensive description of the major components used in the fabrication process of ZnO thin film.

3.2 Material List

Table 3.1 Required material for precursor solution

Sl No	Material Name	Specification	Manufacturer
1	Zinc chloride ($ZnCl_2$)	Molar mass:136.30 g/mol, Purity:≥95%,Chloride(as ZnO):≤5%,Heavy metals(as Pb):≤0.005%,Water:≤2%	Merck Life Science Pvt. Ltd.
2	Sodium hydroxide (NaOH)	Molar mass:40.0 g/mol, Purity:≥97%, Carbonate(as Na_2CO_3):≤1.0%	Merck Specialities Pvt. Ltd.
3	Potassium hydroxide (KOH)	Molar mass:56.11 g/mol, Purity:≥84%, Carbonate(as K_2CO_3):≤2.0%, Heavy metals(as Pb):≤0.002%	Merck Life Science Pvt. Ltd.
4	Deionized Water	Purity:99.99%	Generic
5	Ethanol	Purity:99%,Lab grade	Generic
7	Concentrated Hydrochloric acid (HCl)	Purity:99%,Lab grade	Generic

3.3 Experimental Apparatus

Instruments and apparatus used in scientific studies to measure, observe, or manipulate variables of interest are referred to as experimental apparatus. For precise data collection and reliable results, apparatus design and selection are essential. When choosing them, factors including sensitivity, precision, and suitability for the experimental setup are considered. To preserve the integrity of the experiment, equipment needs to be calibrated and maintained regularly. In the below section, the experimental apparatus used throughout the present work is mentioned and their purpose is described.

3.3.1 Magnetic Stirrer

The Magnetic stirrer (Fig. 3.1) is used to process and stir the precursor solution. Here we used Zinc Chloride ($ZnCl_2$) as cationic and sodium hydroxide (NaOH) as anionic solution sources, which was stirred carefully by a magnetic stirrer. This is manufactured by REMI and input wattage is around 160W only for the stirrer part of the instrument.

Fig. 3.1 Magnetic Stirrer

3.3.2 Piezo-U-Sonic Ultrasonic Cleaner

This ultrasonic cleaner (Fig. 3.4) is used to ensure the complete cleanness of the soda-lime glass substrates (75 mm x 25 mm). The input power is around 120W. First of all the soda-lime glass substrates are dipped into the mixed solution of ethanol and deionized water, which was stirred carefully by the magnetic stirrer. Then few times later it was withdrawn from the solution of ethanol and deionized water. The soda-lime glass substrates, which

were taken out from the ethanol and deionized water solution, were then put into the chamber of the piezo-u-sonic ultrasonic cleaner. A few times later it was removed from that particular chamber and proceeded further for air drying. After all these processes, we got an edged and cleaned glass substrate which was ready for the next step (deposition) of the experiment.

Fig. 3.2 Ethanol & deionized water solution

Fig. 3.3 Chemical Bath Chamber

Fig. 3.4 Piezo-U-Sonic Ultrasonic Cleaner

3.3.3 Air Furnace

The air furnace (Fig. 3.5) utilizes heated air circulation within a chamber to maintain a consistent and precise temperature, ensuring uniform heat distribution and efficient drying of the substances being tested. It is used to facilitate accurate and reproducible experimental procedures for allowing samples to be dried, heated or annealed.

In our experiment, after the cleaning process, it is crucial to ensure that the glass substrates are completely dry before proceeding to the next fabrication steps. Excess moisture can negatively affect subsequent layers and their adhesion. To dry the substrates, they were placed in the air oven set at a temperature of 40ºC. The controlled heat facilitates the evaporation of any remaining liquid, ensuring a dry and clean surface.

The thorough cleaning of glass substrates through a multi-step process using DI water, the solution of ethanol and acetone, followed by controlled drying, provides a clean and pristine surface for subsequent deposition and fabrication steps in ZnO thin film deposition. This meticulous cleaning procedure ensures the removal of impurities and enhances the overall performance and reliability of the fabricated ZnO thin film.

Fig. 3.5 Air Furnace

3.4 Experimental Procedure

Nucleation and growth of ZnO thin films were carried out on soda-lime glass substrates (75 mm x 25 mm) using two different growth techniques in the union of Successive Ionic Layer Adsorption and Reaction and Chemical Bath Deposition methods, with no application of heat (room-temperature) during the deposition process. The as-deposited films, so grown, revealed uniform specular films without any spotted, powdery or abrasive features. A pre-deposition cleansing of the substrates was done by ultrasonic cleaning of the glass substrates in a 1:1 solution of ethanol and deionized water in the bath sonicator for 30 minutes. Following that the glass substrates were washed in deionized water and then immersed in concentrated hydrochloric acid (35 %) for one hour and then heavily rinsed in deionized water. The idea was to etch the

glass substrates so that the etched rough surface acts as nucleation centres for easy migration of ionic species during the actual growth process. In the review of previous works, it was observed that an initial seed layer of $ZnO/Zn(OH)_2$ helps in the subsequent quick and stable growth of the requisite films through the CBD method. To achieve this, the SILAR method was carried out first on the glass substrates from individual cationic and anionic precursor solutions. Zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH) solutions were used as individual cationic and anionic sources and glass substrates were successively dipped in these solutions for some 100 cycles. Between every cationic and anionic solution, there were beakers placed with plain deionized water and every dipping in ionic solution was followed by a dipping in deionized water to wash away the loosely held ions on the substrates. After some 100 cycles, a slight whitish colour change was observed over the glasses and suggested growth of minimum thin seed layer formation. The substrates were then air-dried and then followed by the CBD method. In the case of CBD, the intended heterogeneous reaction for film deposition on the substrate surface faces competition from the homogeneous reaction inside the bulk solution which leads to colloidal particle formation. Loosely adherent films with porous appearance occur because of the adsorption of the colloidal particles that are formed inside the solution. Also, a competing heterogeneous reaction leads to the unwanted deposition of films on the CBD reactor wall. In actuality, in these scenarios, only a small percentage of the reactance is utilised in the desired film generation over the substrate. $ZnCl_2$ solution (0.5 M) was first mixed with excess $NH_4(OH)$ (9M) inside a beaker for the formation of necessary complex ions. It is because the solubility product constant of $Zn(OH)_2$, a possible precipitate formed because of the addition of $ZnCl_2$ in water, is easily exceeded by its ionic product in the above solution in the absence of NH_3. However, in the presence of NH_3, the concentration of the Zn^{2+} is reduced because of the formation of complex ions type of $Zn(NH_3)n^{2+}$. 'n' here is the coordination number and can take values from 1-4, of which 4 is the most stable number. Besides that, NH_3 also helps in maintaining the pH of the solution. As the solution now had a greater concentration of NH_3 because of the excess addition of $NH_4(OH)$, it now had greater stability so far as precipitation of solid phases was concerned. The solution was now stirred using a magnetic stirrer and the glass substrates were dipped inside the solutions using a clamp and stand (Fig. 3.6). The pH value 10 was found in the experimental solution. After one hour, a further low-concentration solution of NaOH (0.1M) was added to raise the pH of the bath to 11. It is because in our review work it was noticed that in the presence of NaOH, zinc hydroxide precipitated and led to the formation of ZnO. The idea was to use the concept of the presence of colloidal particles in the solution to be adsorbed on the substrate surface and some degree of possible direct deposition of ZnO on the

substrate. Also at pH values of 10.5 or 11.0, it was observed in previous works that the best quality of uniform specular films adhered to the glass surface. The glass substrates were continued to be stirred in this final mixed solution for another 2 hours every 30 minutes, the samples being taken out of the solution and dipped and cleansed for 10 seconds in a pure KOH (0.1 M) solution, and then re-inserted inside the mother solution over the magnetic stirrer. This modified step of cleansing the substrates for a few seconds in KOH solution, in between the deposition process, was because to eliminate the large loosely-held particles over the substrate surface and lead to the formation of a much smoother, uniform film. After 2 hours, the samples were removed from the mother solution and air-dried for 24 hours. The entire process (SILAR and CBD) was repeated under similar conditions for 7 samples (from now on S_1, S_2, S_3, S_4, S_5, S_6 and S_7). The approximate thickness of the films was determined by the weight-difference method, by dividing the obtained weight of the deposited samples length, breadth and density of deposited material ($Zn(OH)_2$ or ZnO) and were all kept around 300 nm. Sample S_1 was left at its as-deposited conditions, while samples S_{2-4} were annealed under open-air conditions inside a air furnace at 350 ℃ for 30, 60 and 90 minutes respectively(Fig. 3.7). Samples S_{5-7} were annealed under similar open-air conditions inside the air furnace at 400 ℃ for 30, 60 and 90 minutes respectively. The prepared samples (Fig. 3.8) were then subjected to corresponding optical, morphological compositional and electrical analysis furthermore. Fig. 3.9 shows the representative images of carbon-coated deposited film samples used for SEM. The results and analysis so obtained are discussed in detail in the next chapter.

Fig. 3.6 Representative Image of Chemical Bath Deposition

Fig. 3.7 Representative Image of Air-Furnace Annealing

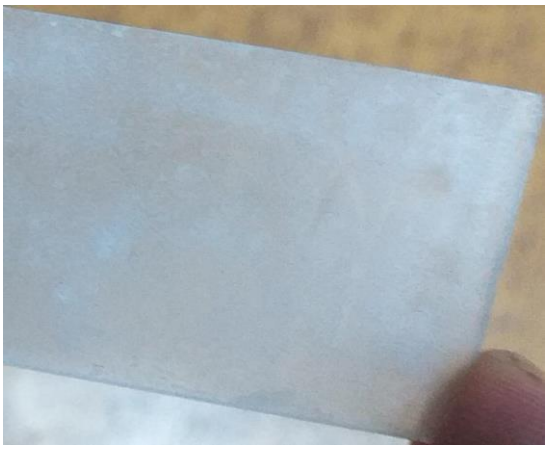

Fig. 3.8 Representative Image of the Prepared Samples

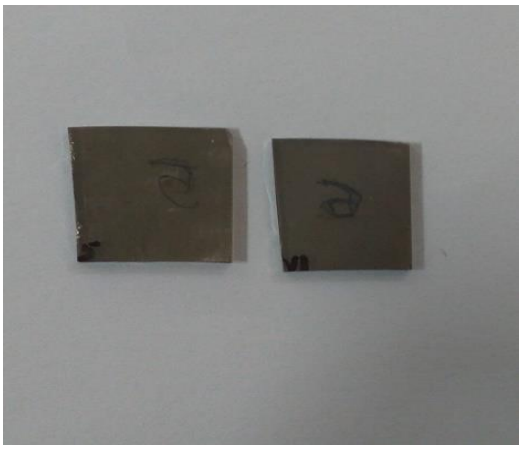

Fig. 3.9 Representative images of carbon-coated deposited film samples

3.5 Conclusion

The fundamental objective of this chapter was to study and enhance the fabrication process of ZnO thin film without the application of heating and to achieve improved efficiency, stability and reliability. A key focus is placed on the preparation of precursor solution and the fabrication process, starting with the thorough cleaning and drying of the glass substrate, ensuring its suitability for the deposition process. The methodology adopted ensured the precise fabrication of ZnO thin film as a TCO, resulting in optimized performance.

The process followed by Chapter 3, where the utilization of appropriate characterization techniques in this research allows for the comprehensive analysis of key performance parameters, economical side and material properties. By following the experimental setup and methodology, with the obtained results and subsequent discussion, this study aims to provide valuable insights and contribute to the understanding and improvement of ZnO as a transparent conducting oxide (TCO).

Chapter-4 Characterization Techniques, Results & Discussions

4.1 Introduction

ZnO thin films as a transparent conducting oxide (TCO) have earned great attention in current years due to their higher efficiency, stability, scalability and low cost. Among various transparent conducting oxide (TCO) thin films, ZnO thin films have emerged as a promising alternative to traditional indium tin oxide(ITO) thin films. ZnO as a TCO offers several advantages, including cheap, non-toxic, plentiful source of zinc. Consequently, it has a wide bandgap (~3.1-3.37 eV), also ZnO as a TCO provides very good optical and electrical properties. In this study, we employed a comprehensive characterization approach, which involved various analytical techniques, namely scanning electron microscopy (SEM), current-voltage (I-V) characteristics and spectrophotometry analysis and measurement. By utilizing these techniques, we aimed to gain insights into the morphological, electrical and optical properties of ZnO as a TCO.

Through this comprehensive study, we aim to compare the alternative samples of ZnO thin film and evaluate their performance based on various characteristics such as optical, electrical and morphological. The findings of this study will contribute to the understanding of the factors influencing the efficiency of ZnO as a TCO and aid in the development of a more efficient and cost-effective ZnO-based transparent conducting oxide (TCO) thin film.

4.2 Characterization Techniques

In scientific research, characterization techniques are crucial instruments for analyzing and comprehending the characteristics and behaviour of materials, compounds, or systems. These techniques involved different approaches to the analysis of a sample's morphology, optical, composition, electrical and other important features. The particular characteristics of the material or system being studied, as well as the goals of the study, will determine which characterization technique is best. In the below section, the various techniques used throughout the present study to determine the different characteristics as per our objectives are described.

4.2.1 Spectrophotometry

Spectrophotometry is a widely used method for quantifying the absorption or transmittance of light through a chemical element or substance. It involves evaluating the light's intensity as it passes through a sample to determine the extent to which the substance absorbs or transmits light across a range of wavelengths. This technique is

valuable in several fields, including material science, chemistry and chemical engineering, physics and electrical engineering, and medical applications, for quantitative analysis.

There are two primary laws by which spectrophotometry works, the law of Lambert's and the law of Beer's. As per the law of Lambert's, the solution's thickness (length of the path through which the light passes) which is being analyzed is directly correlated with the absorption of light. The equation is expressed as $A= \log_{10} (I_0/I) = ai * b$, where the intensity of the incident light is denoted as 'I_0', the intensity of the transmitted light is denoted as 'I', the solution's absorbency index characteristic denoted as 'ai', absorbance and the medium's thickness is denoted as 'A' and 'b' respectively.

The law of Beer's explains that the solution's concentration is directly proportional to the amount of the absorbed light. The equation is expressed as $A= \log_{10}(I_0/I) = ai * c$, where the solution's concentration is denoted as 'c'. By uniting these two laws, the equation becomes $A = \log_{10} (ai* b*c)$. In spectrophotometers, the internal diameter or width of the cuvette is typically maintained at exactly 1 cm to simplify calculations.

The light energy received at the phototube after it has passed through the solution is given as a percentage known as transmittance (% T). By comparing this particular with the source light intensity, the amount of absorbed light (not the light that is transmitted) can be measured. This is represented by the equation $I / I_0*100= \%T$, where the sample amount of light that passes is denoted as 'I', and the source light intensity is denoted as 'I_0'. The absorbance (A) is calculated using the equation $\log_{10}(I/I_0)$. By measuring the absorbance or transmittance, the determination of the concentration of the absorbing molecule in the solution can be possible. If the molar absorptivity of the molecule (the amount of light absorbed at a specific wavelength by a specified concentration of solute in moles/litre) is known, the concentration can be directly calculated.

In this project, the ZnO thin films play a crucial role as it absorbs the incident light spectrum. To determine the absorbance spectrum range for various ZnO thin films used in TCOs (Transparent conducting oxide), Spectrophotometry is employed with the Lambda 35 UV/VIS Spectrometer manufactured by Perkin Elmer (Fig. 4.1). The details of the Spectrophotometry analysis will be discussed in the subsequent chapter, specifically in the section dedicated to Optical characterization and analysis.

Fig. 4.1 Spectrometer (Model: Perkin Elmer Lambda 35, UV/VIS Spectrometer)

4.2.2 I-V Characteristics

The relation between the current passing through a component, material, or circuit and the difference of potential across that particular component or material is known as the current-voltage characteristics (I-V characteristics). This relationship is usually shown as a chart or graph. The current-voltage relationship at one pair of terminals of an electronic component with more than two terminals—such as a vacuum tube or transistor—may be dependent upon the third terminal voltage or current. The most basic I–V curve is that of a resistor, which shows a relationship that is linear between the generated electric current and the voltage applied in correlation with Ohm's law. As we know from Ohm law the current is proportional to the voltage, so the I–V characteristics curve of a resistor is a simple straight line with a +ve slope that passes through the origin. The reciprocal of the slope indicates the actual resistance. The electrical characterization (Current-Voltage) was carried out under dark and light conditions, using 150W UV Source (253.7 nm) and Keithley 2602B (IV Machine).

A nonlinear circuit element is shown by a curved line, whereas a linear circuit element is represented by a straight line through the origin. Transistors and diodes, for instance, are nonlinear components, whereas resistors, capacitors, and inductors are linear. The most prevalent kind of resistance found in circuits is the linear or ohmic resistor. Shampa Mondal et al. **[40]** reported a current ratio from forward to reverse is ~15 at 3.0 V for SILAR deposited films on their experimentation, growth of ZnO thin films via SILAR and its I-V characterization. They described that the SILAR-deposited films have very high resistivity,

which is the actual cause of this low value of the current ratio from forward to reverse. The low donor defect density and the abundance of chemically absorbed oxygen species that are integrated into the grains and surface of these films during film preparation account for the chemically deposited (SILAR) film's superior resistivity when compared to films produced using alternative techniques. This is to be expected as the deposition is done in ambient air that's why on the surface and at the grain boundaries, a significant amount of molecules of oxygen are chemically absorbed. Also, they showed that the heterojunction of n-ZnO/p-Si displays rectifying and nonlinear I-V Characteristics. The I-V characteristic is studying to check whether the contacts of the film are ohmic or rectifying, by calculating or taking the value of the voltage at room temperature (T ~ 25 ºC) with changing the current. By knowing the relation between current (I) and voltage (V), we can able to understand that the contacts of the film are whether ohmic or rectifying. If the characteristics between current and voltage showed a linear relation, then that means the contact has an ohmic character.

4.2.3 Scanning Electron Microscopy

3-D images with very high resolution of a sample's surface have been generated using a focused beam of electrons by a strong imaging process called scanning electron microscopy (SEM). We can get the Sample's morphological, topographical, and compositional information from this SEM technique. Images with magnification from 20X to 30,000X approximately, spatial resolution of 50 to 100 nm and width of 1 cm to 5 microns can be processed in a scanning mode by traditional SEM techniques.

SEM's accelerated electrons have a lot of kinetic energy, which is released during interaction with the sample and produces a range of signals. The surface of a specimen or sample is illuminated by a focused beam of electrons, resulting in the generation of high-resolution images with magnifications around 10x to 100,000x or more. The fundamental principle of SEM involves scanning the electron beam across the specimen or sample's surface in a raster pattern. When the electron beam interacts with the sample or specimen, different kinds of signals are emitted, including backscattered electrons, secondary electrons, and characteristic X-rays. Secondary electrons are responsible for providing information about the sample's morphology and topography, while sample compositional information is revealed by the backscattered electrons.

. Although, SEM offers several advantages over other microscopy techniques, including

- Much higher magnifications and resolutions can be achieved by SEM, which allows the detailed imaging of surface structures and features at the nanoscale.

- When used in conjunction with energy-dispersive X-ray spectroscopy (EDS), SEM can provide details about the sample or specimen's elemental composition.
- Sample preparation for SEM offers flexibility in terms of sample size, shape, and composition. To reduce charging effects and get improved image quality, the samples of SEM can be coated with conductive materials.

In the following section, we have presented a comprehensive analysis of the SEM, focusing on the particle size and shape of the thin films of ZnO. Visual representations from the Inspect F50 model (Fig. 4.2) in the form of appropriate images are included to support our findings.

Fig. 4.2 Instrument of SEM (Model: Inspect F50)

4.3 Results and Discussions

Results and Discussions represent the heart of research findings and their interpretation. Following this, the Discussions section delves into the significance of the results, contextualizing them within existing literature, addressing limitations, and offering interpretations and implications for future research. Together, these sections elucidate the study's findings, providing insights, interpretations, and avenues for future research, thereby contributing to the advancement of knowledge in the field.

4.3.1 Optical Characterization and Analysis

All the samples S_1-S_7 revealed relatively moderate transmittance (Fig. 4.3-4.4) values in the visible spectrum region. Experiments were carried out in Perkin Elmer Lambda 35, UV/VIS Spectrometer (Fig. 4.1). For all the annealed samples (350 and 400 ℃), a prominent red-shift in absorption band edge was observed suggesting an increase in band-gap for all the annealed samples compared to the as-deposited sample. For the samples annealed at 400 ℃ , a relatively higher transmittance was observed compared to those obtained at 350 ℃ in the same visible spectrum region. This would suggest two things. First, there is an increased formation of ZnO in those annealed at 400 ℃, which is transparent in the visible region, compared to those annealed at 350 ℃. Sample S_7 (annealed at 400 ℃ for 90 mins) as such showed the highest transmittance in the visible spectrum region, suggesting the greater degree of formation of ZnO in that sample. Secondly, the existence of impurities in the semiconductor matrix is known to introduce new quantum states, especially at the forbidden energy gap, and to disturb intrinsic electronic quantum states. These impurities create electronic classes akin to the deep-state active defects found in the forbidden energy gap. The sub-bandgap nature is mutated because of electronic transitions from such charge carrier traps in the forbidden gap. Samples S_2-S_4 reflected a lower transmittance value compared to S_5-S_7 and it is because of electronic transitions in the direct bandgap region, which takes place near the extremum of the conduction band because of those deep-level defect states. The absorption coefficient calculated from equation 1(Transmittance graphs) is then used to derive the bandgap.

$$\alpha = \frac{1}{d}\ln(100/\%T) \quad \ldots. (1)$$

The absorption coefficient (α) is here derived from the thickness (d) of the film deposited and percentage transmittance (%T).

For allowed direct band transitions, Tauc's relation (equation 2) is plotted using the transmittance values obtained in Fig. 4.3-4.4 for S_1-S_7.

$$\alpha h\upsilon = B(h\upsilon - E_{bg})^r \quad .... (2)$$

Here 'h' is Planck's constant, 'υ' is the incident light frequency, 'r' is variable, with the value of r being equal to 1/2 for direct allowed band transitions and 'E_{bg}' is band-gap. The linear section of Tauc's plot is extrapolated to derive the band gap (Fig. 4.5-4.11) of the samples. From the as-deposited sample onwards to the annealed ones, a general increment in bandgap was observed. This implied that a greater degree of improved crystalline lattice-structure formation started taking place for the higher annealed samples, with the as-deposited sample mostly consisting of an amorphous lattice structure. In the event of lower photon energy transitions, direct band-gap

can also decrease because of defects like interstitial, vacancy or antisite, charge trappings and grain boundary disorders. Thus presence of free surface Zn particles in the as-deposited sample could also contribute to the lower bandgap. Table 4.1 shows the approximate bandgaps so derived from Tauc's plot of the concerned samples.

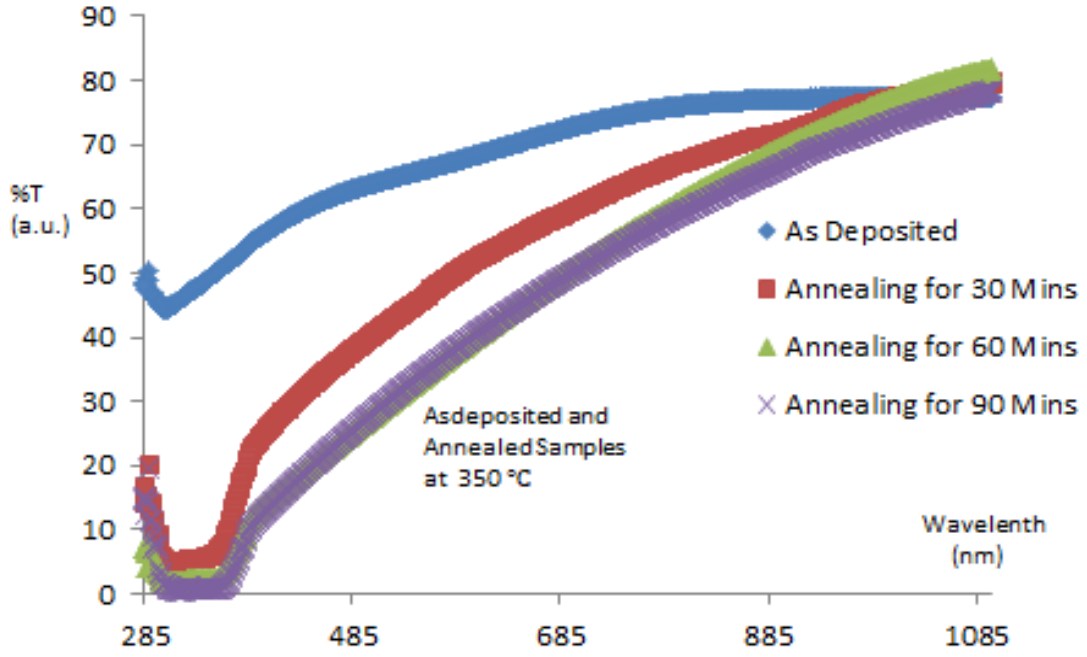

Fig. 4.3 Transmittance Spectrum of Sample S_1, S_2-S_4

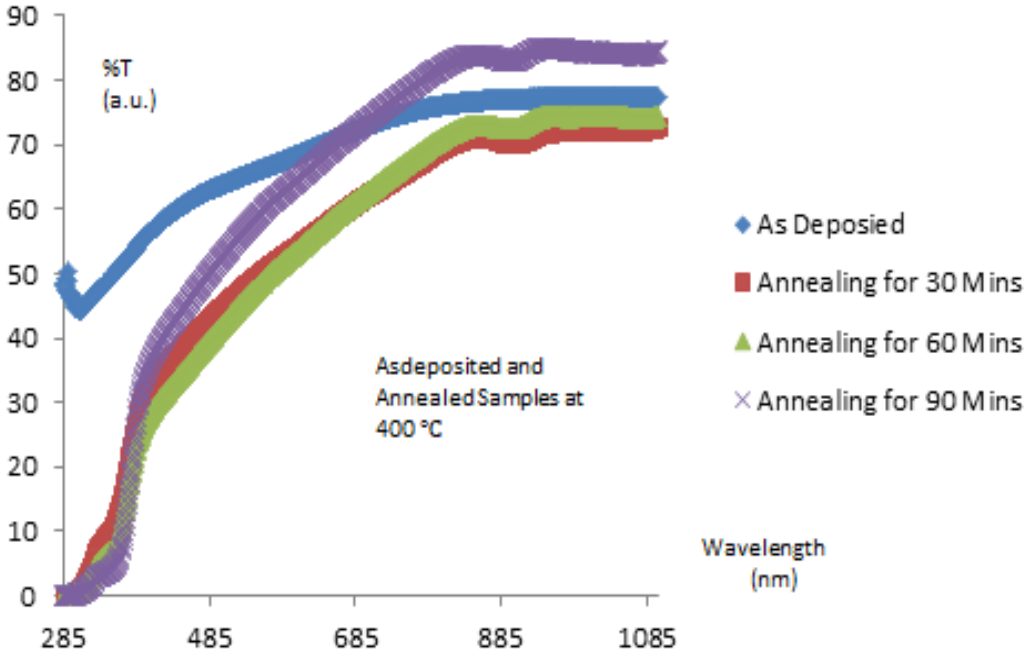

Fig. 4.4 Transmittance Spectrum of Sample S_1, S_5-S_7

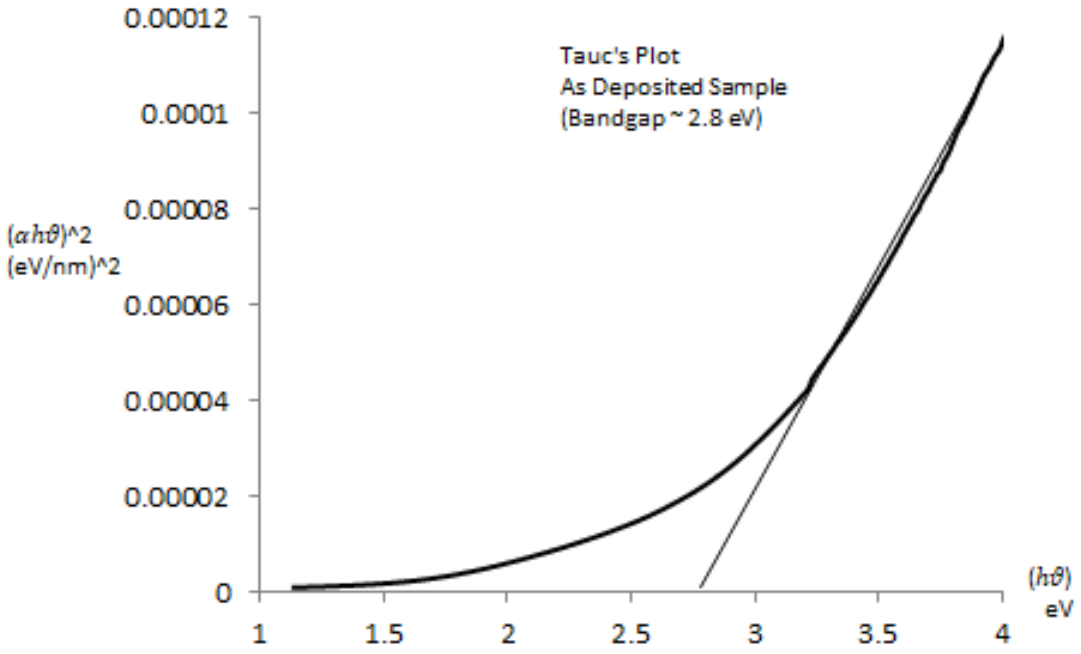

Fig. 4.5 Tauc's Plot of Sample S_1

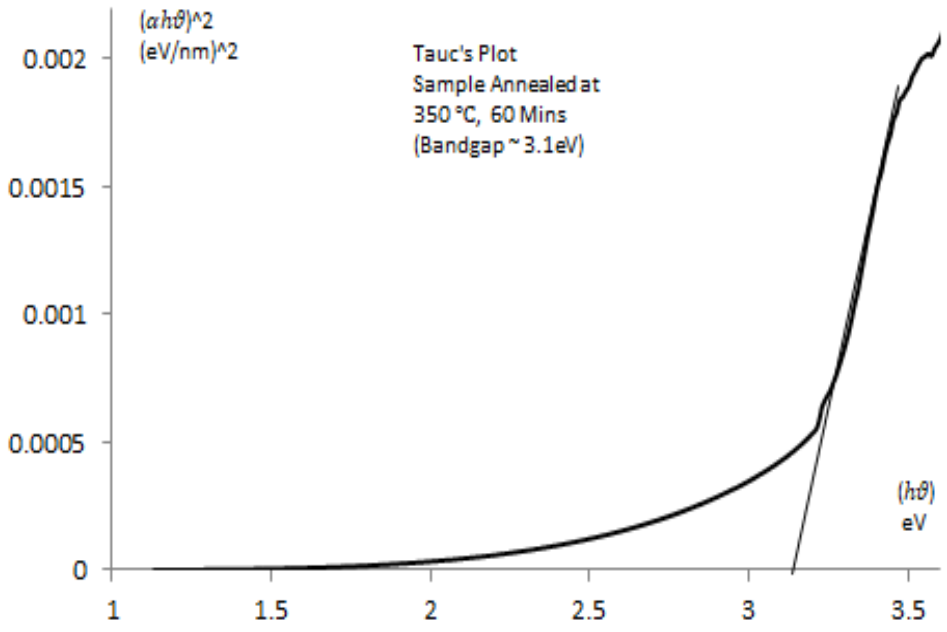

Fig. 4.6 Tauc's Plot of Sample S_2

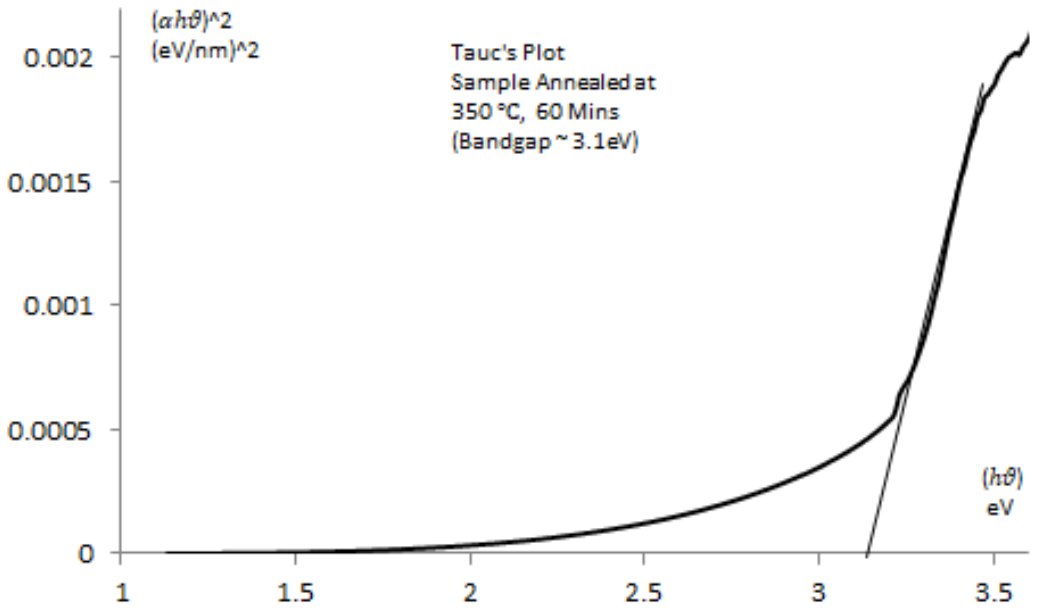

Fig. 4.7 Tauc's Plot of Sample S_3

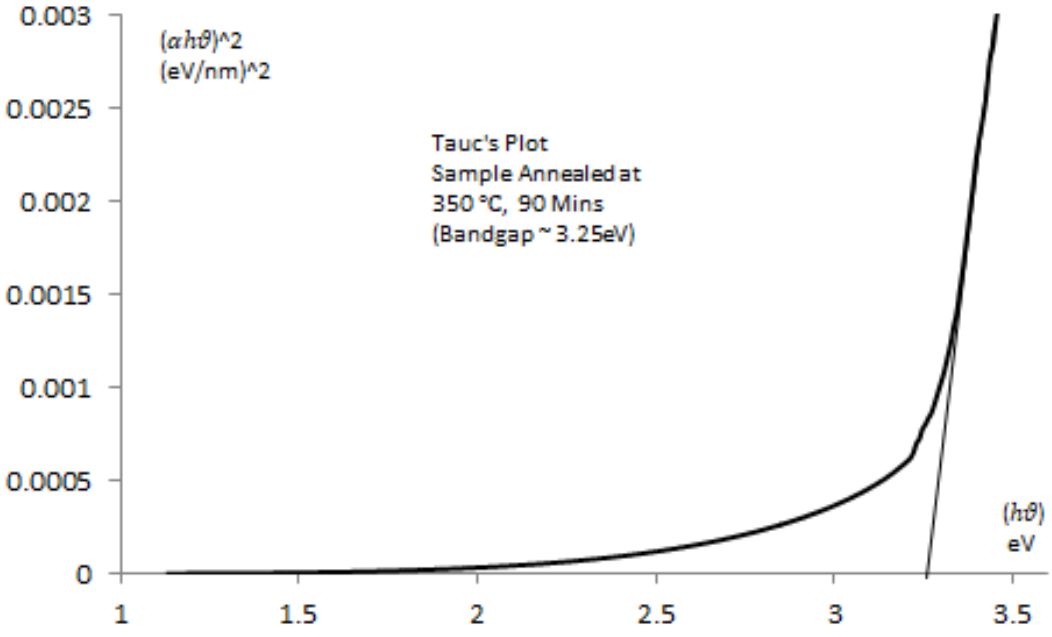

Fig. 4.8 Tauc's Plot of Sample S_4

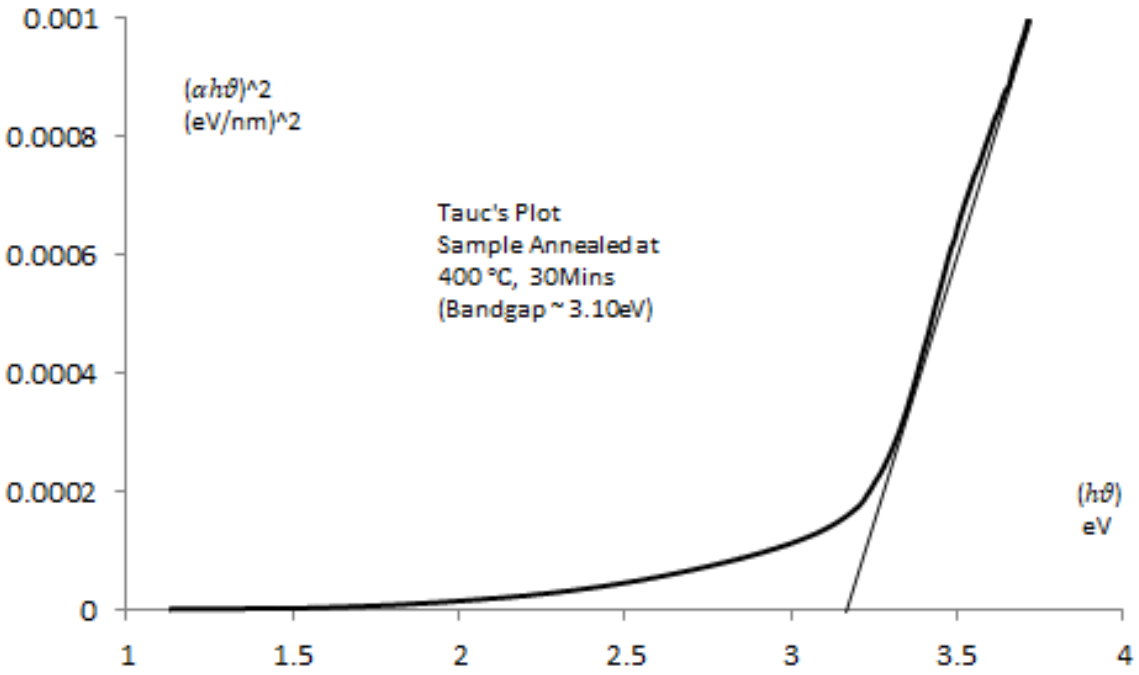

Fig. 4.9 Tauc's Plot of Sample S_5

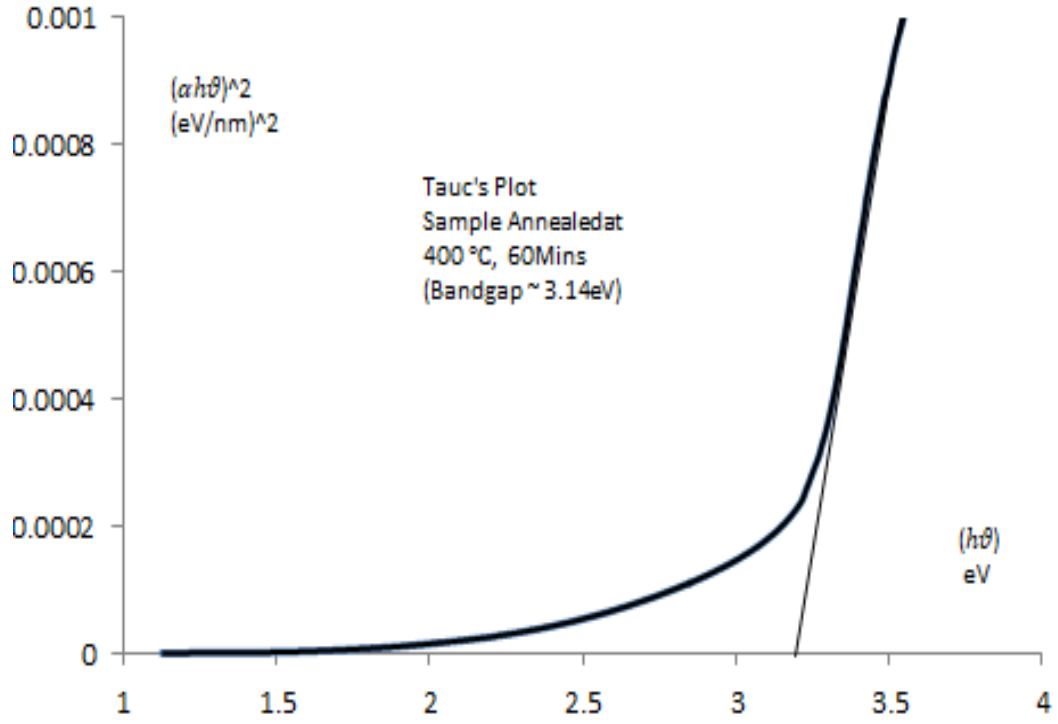

Fig. 4.10 Tauc's Plot of Sample S_6

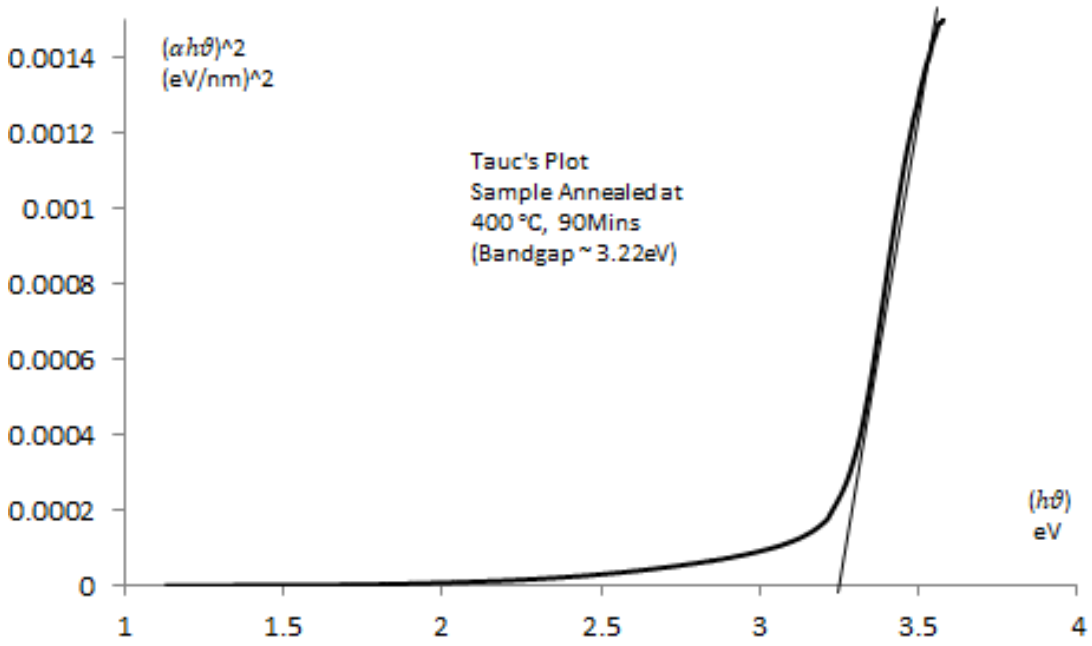

Fig. 4.11 Tauc's Plot of Sample S_7

Table 4.1 Approximate Bandgap of Samples S_1 – S_7

Sample	~ Approximate Band-gap (eV)
S_1	2.8
S_2	3.10
S_3	3.10
S_4	3.25
S_5	3.10
S_6	3.14
S_7	3.22

The value of the bandgap, so obtained, for the annealed samples match well with those found in ZnO thin films, seen in previous literature reviews. The as-deposited sample probably consisted of $Zn(OH)_2$ or $Zn(OH)_2$/ZnO composition, which at higher annealing temperatures decomposed into only ZnO.

4.3.2 Morphological Characterization and Analysis

Scanning Electron Microscopy (SEM) images were obtained for the samples S_1, S_4, and S_7. The results for the as-deposited sample showed a certain degree of growth of wire-like interconnected nanostructures over the sample surface as well as a few ultralong microwires (Fig. 4.12). On higher magnification, such ultralong microwires revealed smaller nanorod-like structures present inside them (Fig. 4.13). It is expected that the thickness of such nanorods is well below 100nm (to be only confirmed with the cross-sectional view). This phenomenon of such smaller nanorods discovered with such ultralong microwires can be explained by the following. The nucleation and growth process of the as-deposited films has a preferred morphological shape orientation where smaller nanorods coalesce with each other to form larger microwires. Also probably a particular structural plane formation is preferred (to be confirmed by HRXRD) during the growth process and results in a particular directional growth. It is to be mentioned, that many incidents of as-deposited nanorods are found for ZnO thin films, which are carried out by PVD methods and usually show good crystallinity. The observed microwires vis-à-vis the nanorods in this as-deposited sample grown by combined SILAR and CBD methods should also suggest good crystallinity of the film. Sample S_4, which was annealed at 350℃ for 90 minutes, showed a similar topography (Fig. 4.14) as S_1, but a more dense network of such nanowire formation on the surface. It is apparent, that application of heat has further facilitated the growth of such preferential morphology, as well as more coalescing of such individual nanowires being also induced. One thing to be noted is that the average width of such nanowires (rods) has slightly reduced (Fig. 4.15), probably caused by the coalescing of the wires to give rise to large coalesced irregular particle shapes as well as ultralong microwires. This is observed in Fig. 4.14, but more for sample S_7 which is annealed at 400℃ for 90 minutes (Fig. 4.16 and 4.17). Here as well a quiet dense network of nanowire formation is seen, but what is more interesting is that the frequency of ultralong microwires has gone up quite high. This suggests, that higher annealing temperature facilitates the preferential morphological growth of structures like ultralong microwires and probably has to do a lot with the inherent directional growth of ZnO based on preferential structural plane formation.

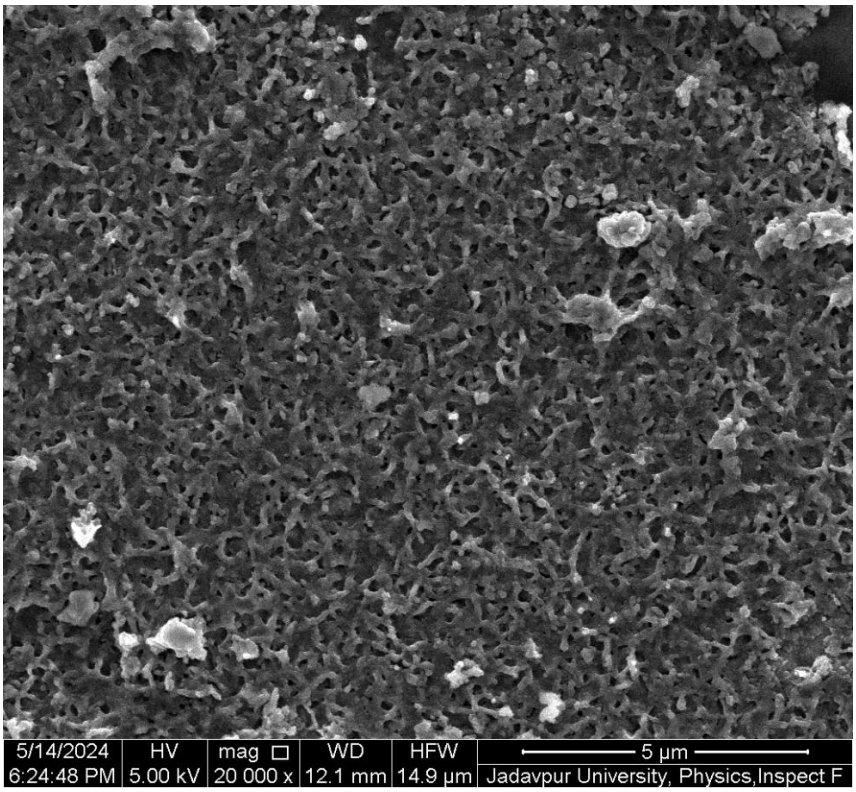

Fig. 4.12 SEM Micrograph of sample S_1

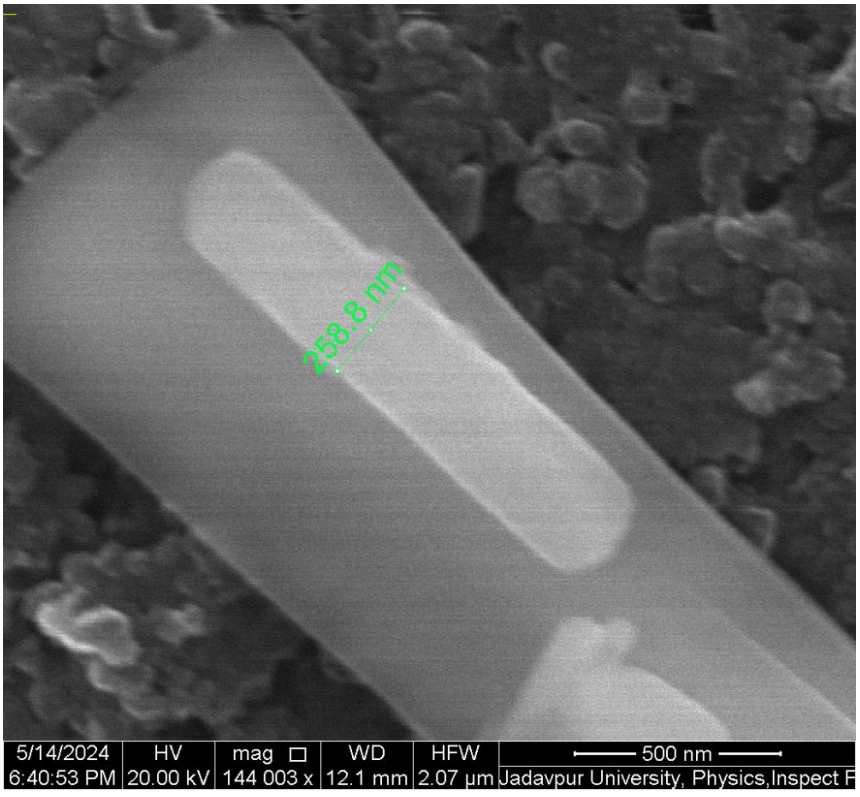

Fig. 4.13 SEM Micrograph of Ultralong Microwires and Nanorods in sample S_1

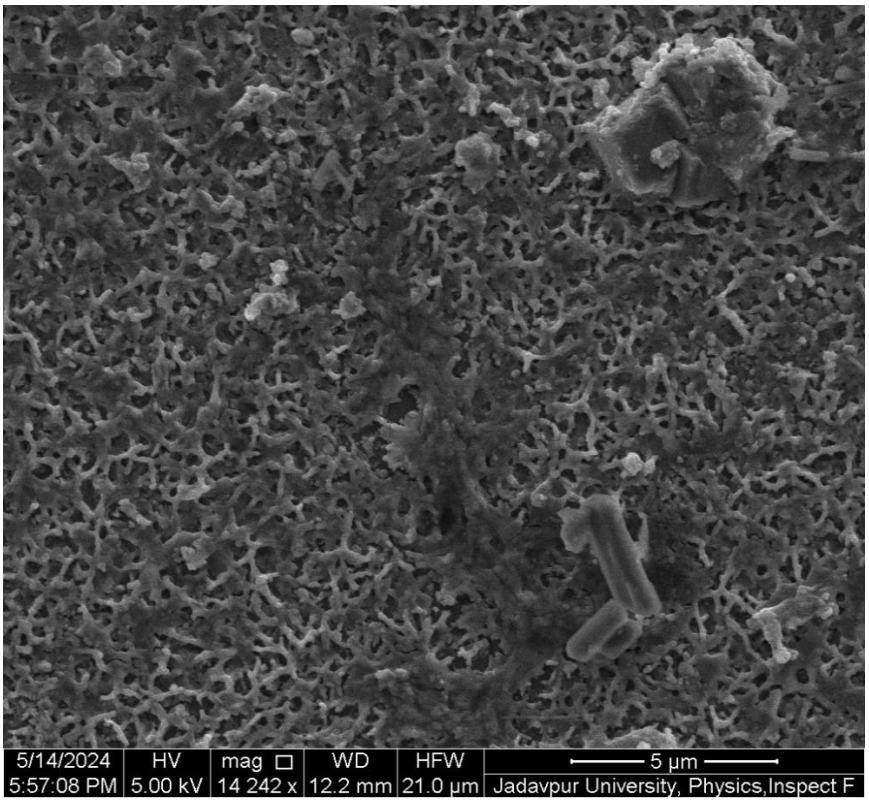

Fig. 4.14 SEM Micrograph of sample S_4

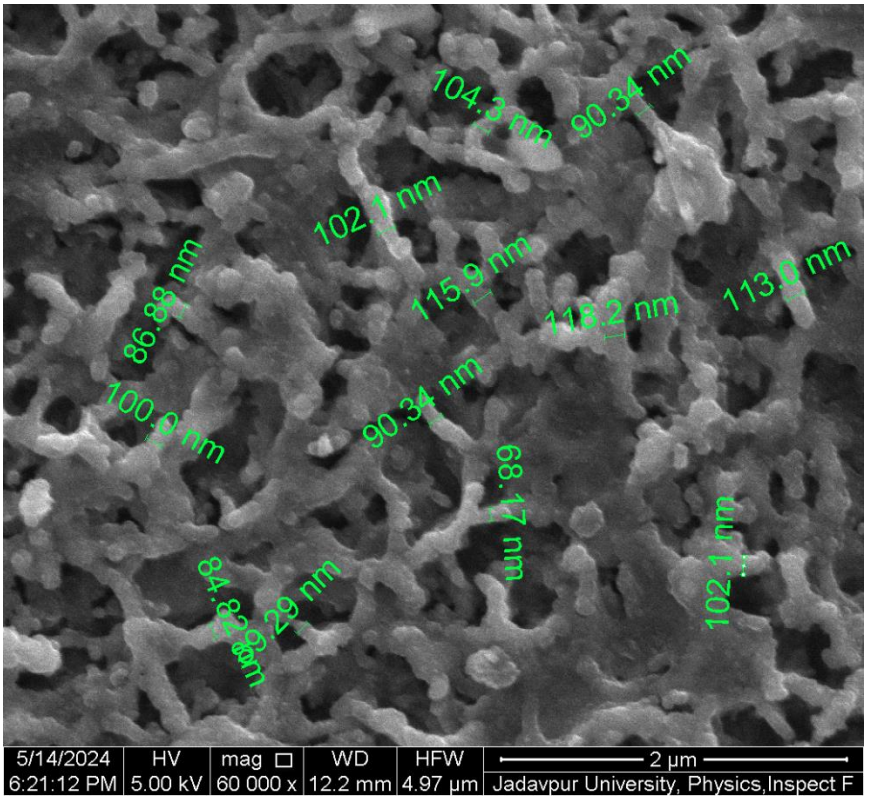

Fig. 4.15 SEM Micrograph of Nanowire or Nanorod Network in sample S_4

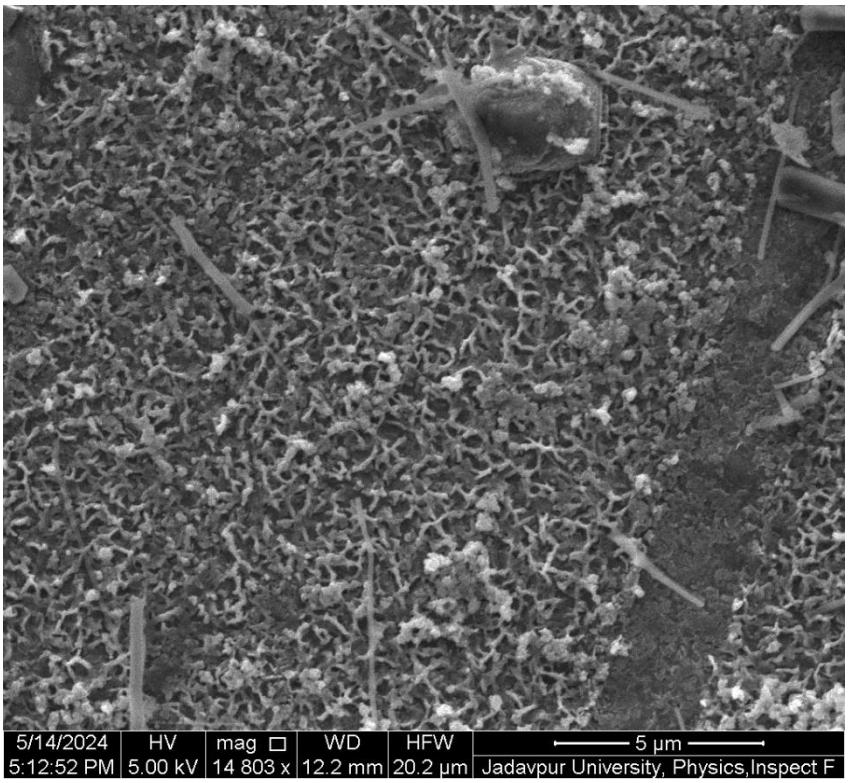

Fig. 4.16 SEM Micrograph of sample S_7

Fig. 4.17 SEM Micrograph of a large number of Ultralong Microwires in sample S_7

4.3.3 Compositional Characterization and Analysis

An energy-dispersive X-ray analysis of the samples revealed the following weight percentage composition of zinc and oxygen according to Table 4.2. The analysis revealed a slight increase in oxygen in weight percentage w.r.t. zinc in sample S_7, suggesting a slight degree of reduction of oxygen vacancies in the sample and consequent probable improved crystallinity. The S_7 sample also had earlier revealed a greater number of formations of ultralong ZnO microwires and higher temperature of annealing for this sample has not only facilitated a preferential morphological growth, it has also induced increased oxidation and vis-à-vis reduced oxygen vacancy and better lattice structure for the grown films. Whether this increased oxidation is in some way co-related with a greater degree of formation of ZnO microwires, can only be established with further in-depth analysis. Usually mass percentage of zinc and oxygen in ZnO is about 80.34 and 19.64 % respectively. The observed data in Table 4.2 reveals the values in a similar range, suggesting some degree of formation of zinc oxide, more or less, in all the samples. Fig. 4.18, 4.19 and 4.20 shows the EDX graphs of samples S_1, S_4 and S_7.

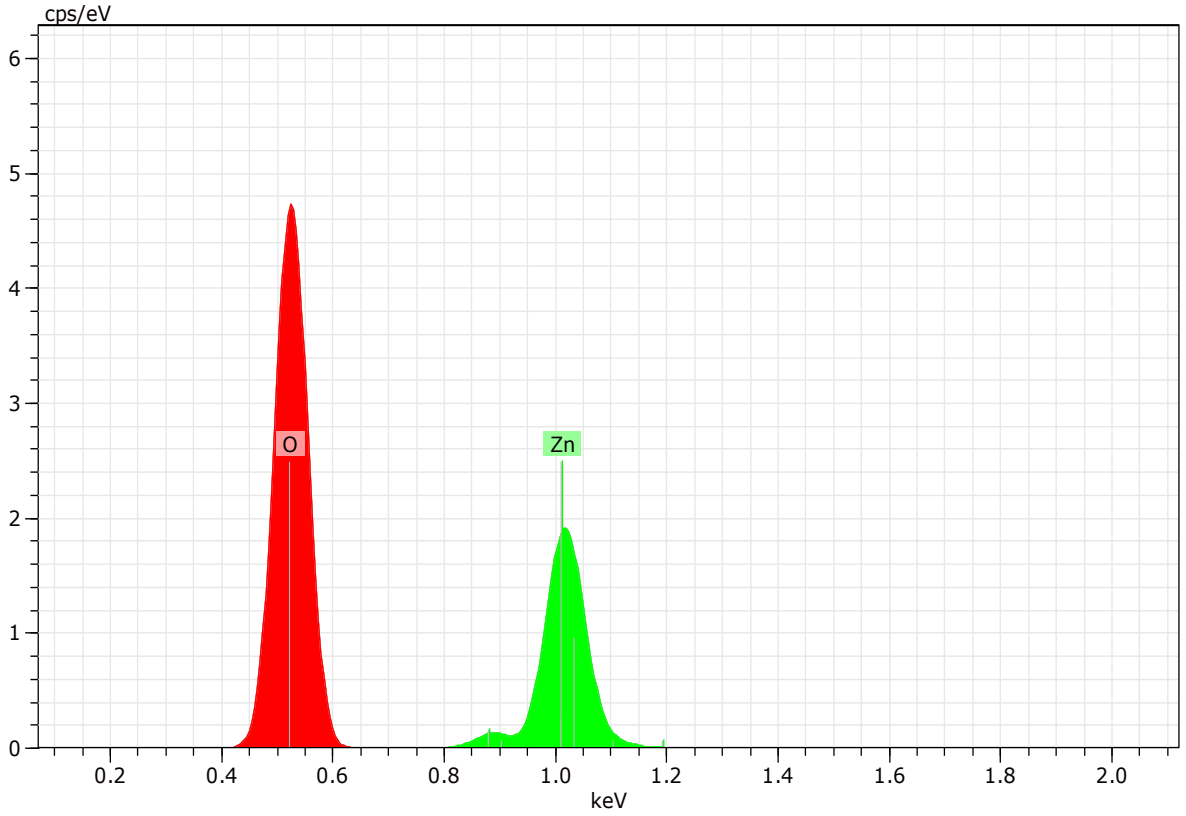

Fig. 4.18 EDX graph of sample

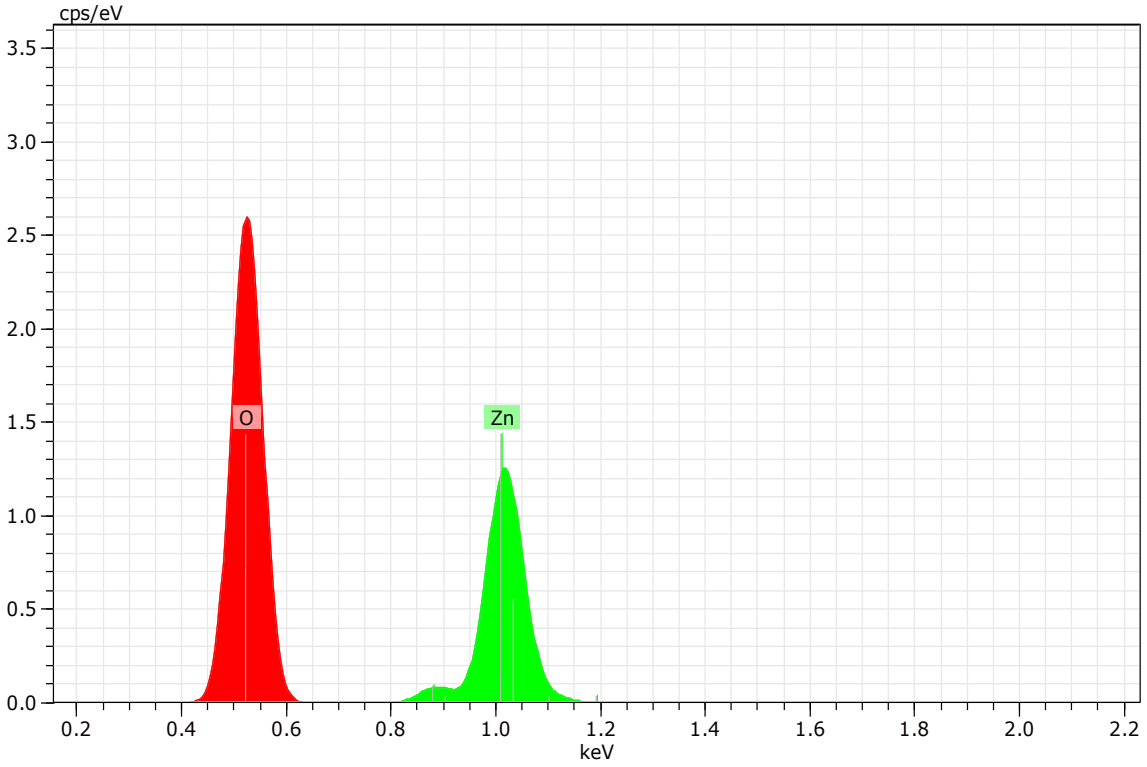

Fig. 4.19 EDX graph of sample S_4

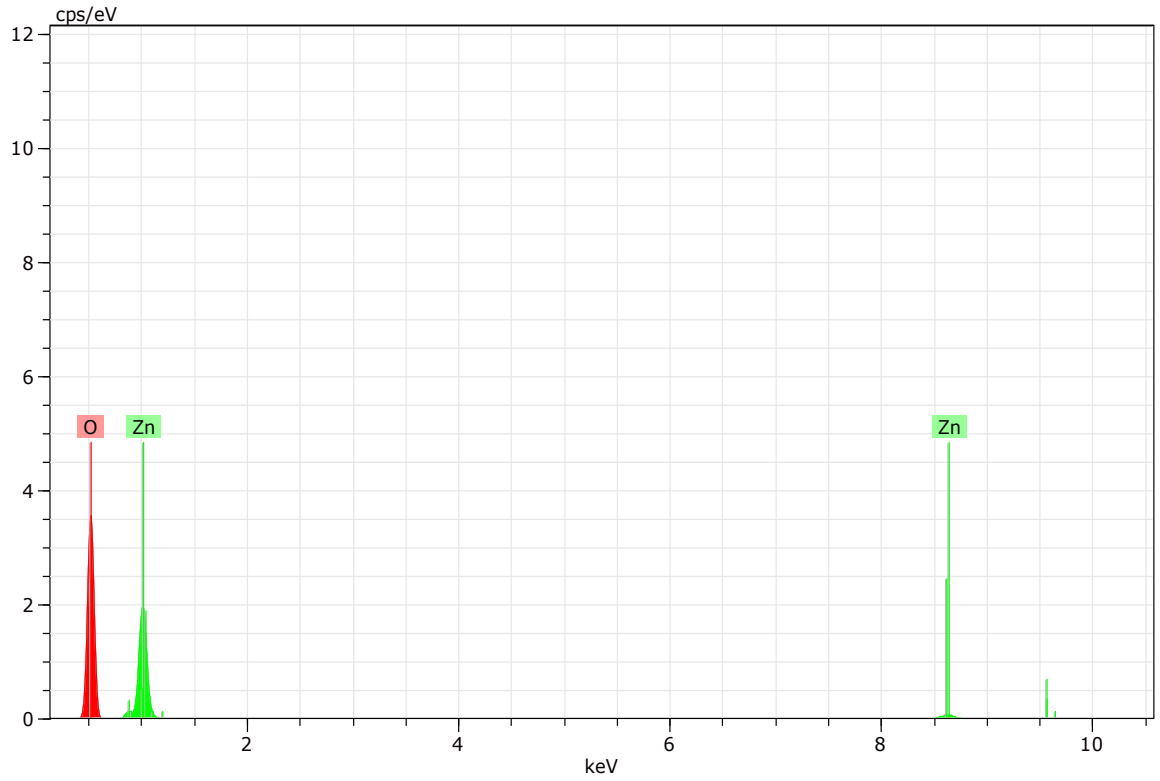

Fig. 4.20 EDX graph of sample S_7

Table 4.2: Compositional Values of Samples S_1, S_4 and S_7

Sample Type	Weight Percentage (Zn)	Weight Percentage (O)
S_1	80.34	19.66
S_4	80.34	19.66
S_7	80.2	19.8

4.3.4 Electrical Characterization and Analysis

The electrical characterization (Current-Voltage) was carried out under dark and light conditions, using 150W UV Source (253.7 nm) and Keithley 2602B (IV Machine). The prepared sample types, as discussed in the "Materials and Method Section", were only provided with two new metal contacts on the top surface via soldering, using a soldering alloy of lead and tin on the concerned samples and subjected to quick heating in air-furnace for 1 min at 75℃. The metal-semiconductor junctions were then subjected to Electrical-Voltage (IV) characterization (Fig. 4.21-4.27). The dark and light characterizations were carried out in an enclosed wooden chamber. The resistance values under dark and a light condition were obtained for the highest current values and are shown in Table 4.3. All the samples revealed broad linear behaviour of the metal-semiconductor junctions. This linear behaviour could be attributed to the easy tunnelling of carriers, which is largely dependent on the doping level of the semiconductor near the metal-semiconductor junction and high doping is expected to narrow the depletion region. Besides, the presence of Zn in p-type compound semiconductors is known to improve the tunnel-contacts. The photo-response (Light current- Dark Current)/ (Dark Current) or $(I_l - I_d)/ (I_d)$ was obtained for the individual samples. The photo-response of the samples revealed low to moderate gains.

Table 4.3 I-V Characteristics of Samples $S_1 - S_7$

Sample Type	Dark Resistance (Ω)	Light Resistance (Ω)	Photo-response $(I_l - I_d)/(I_d)$
S_1	7.56E+06	6.64E+06	0.14
S_2	6.69E+06	5.57E+06	0.20
S_3	6.03E+06	4.25E+06	0.41
S_4	5.28E+06	3.57E+06	0.47
S_5	4.80E+06	2.98E+06	0.61
S_6	3.78E+06	1.86E+06	1.03
S_7	2.70E+06	1.14E+06	1.36

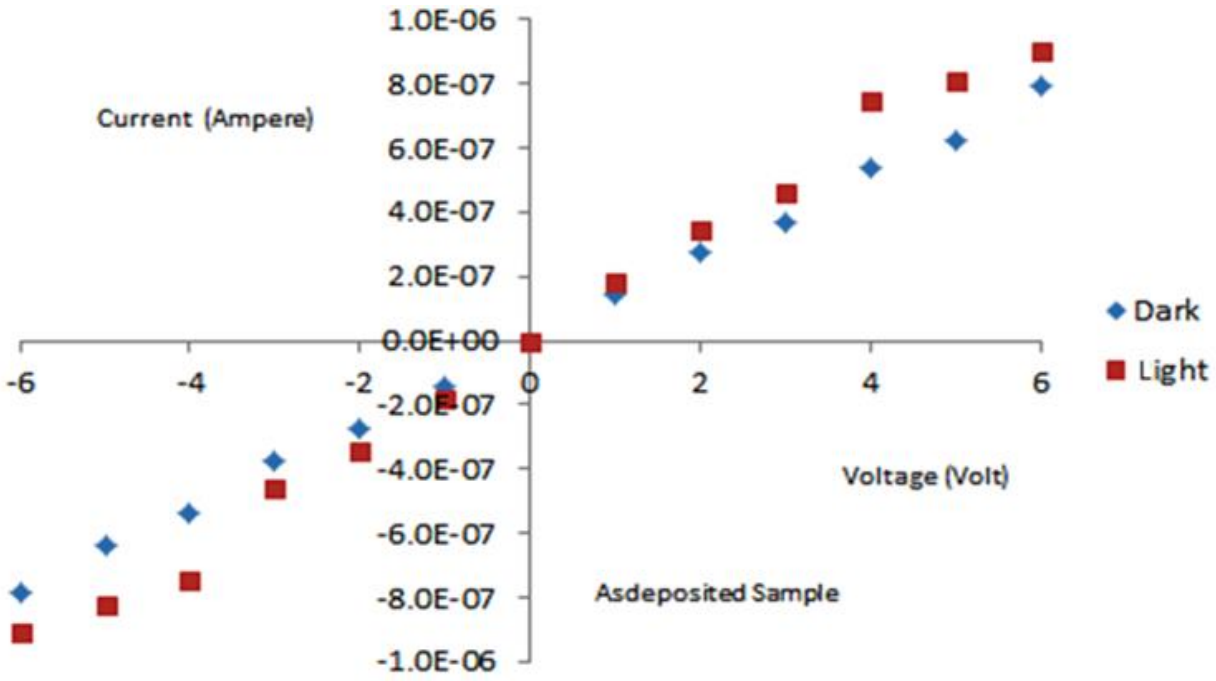

Fig. 4.21 I-V Characteristics of Sample S_1

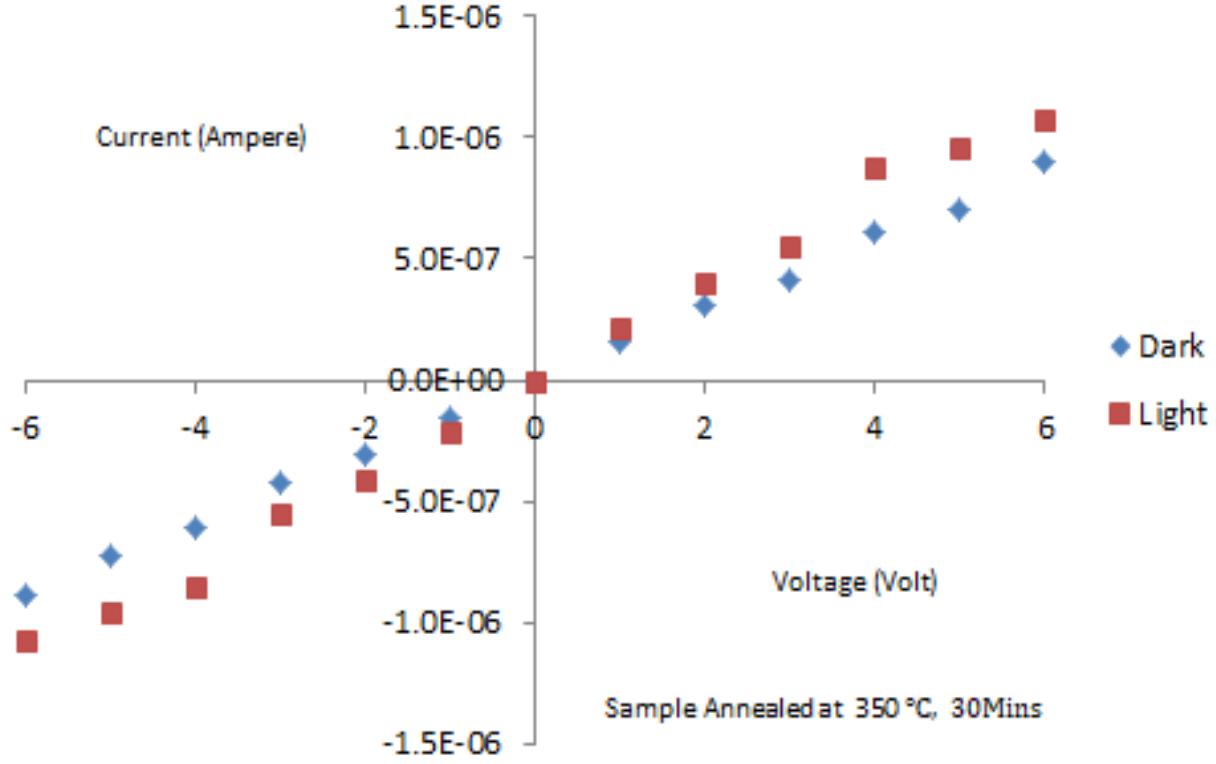

Fig. 4.22 I-V Characteristics of Sample S_2

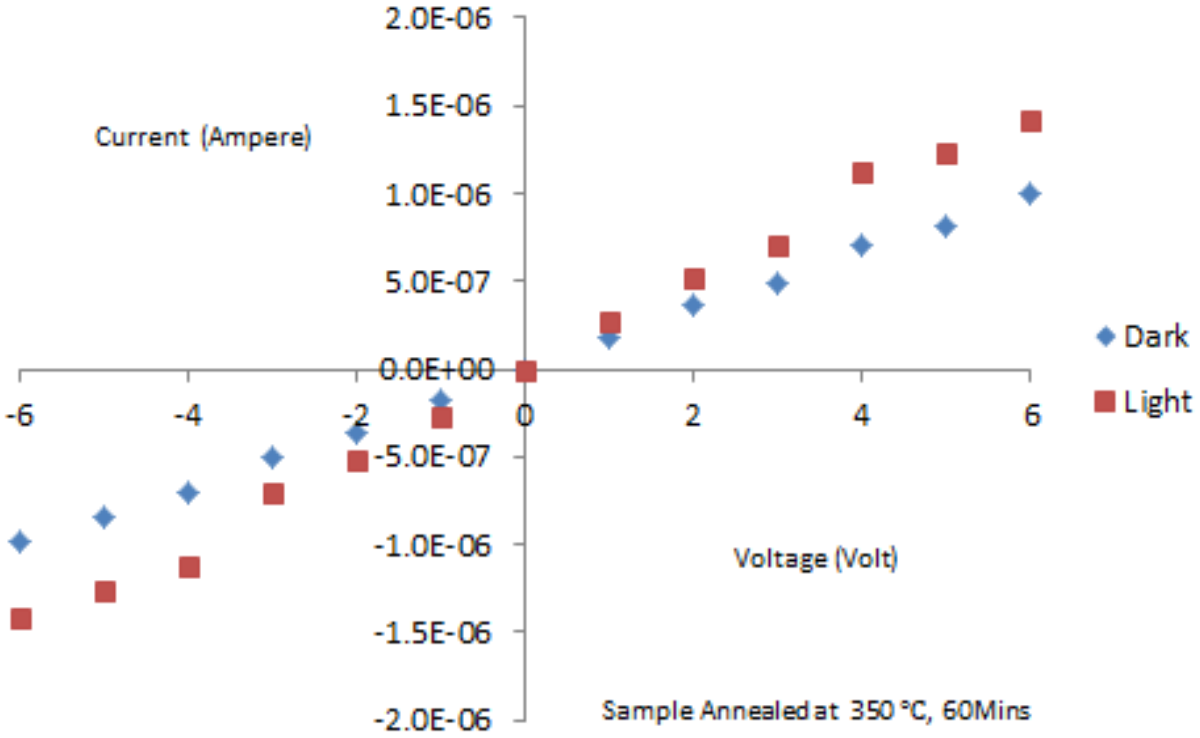

Fig. 4.23 I-V Characteristics of Sample S_3

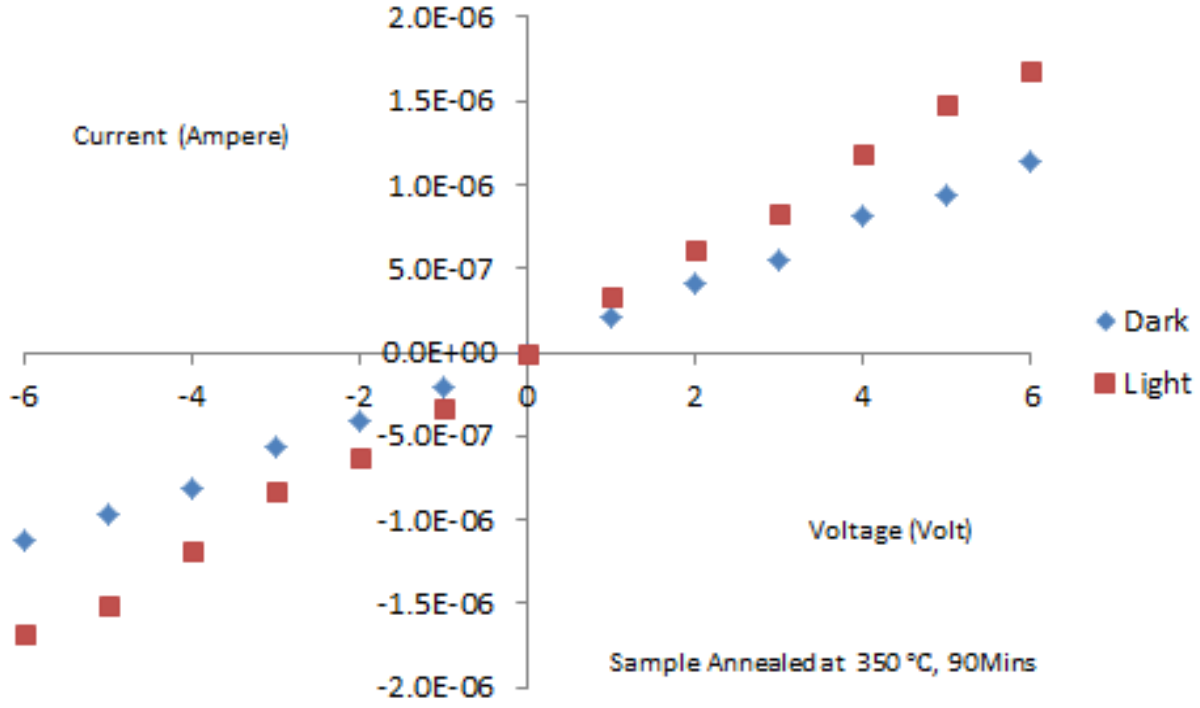

Fig. 4.24 I-V Characteristics of Sample S_4

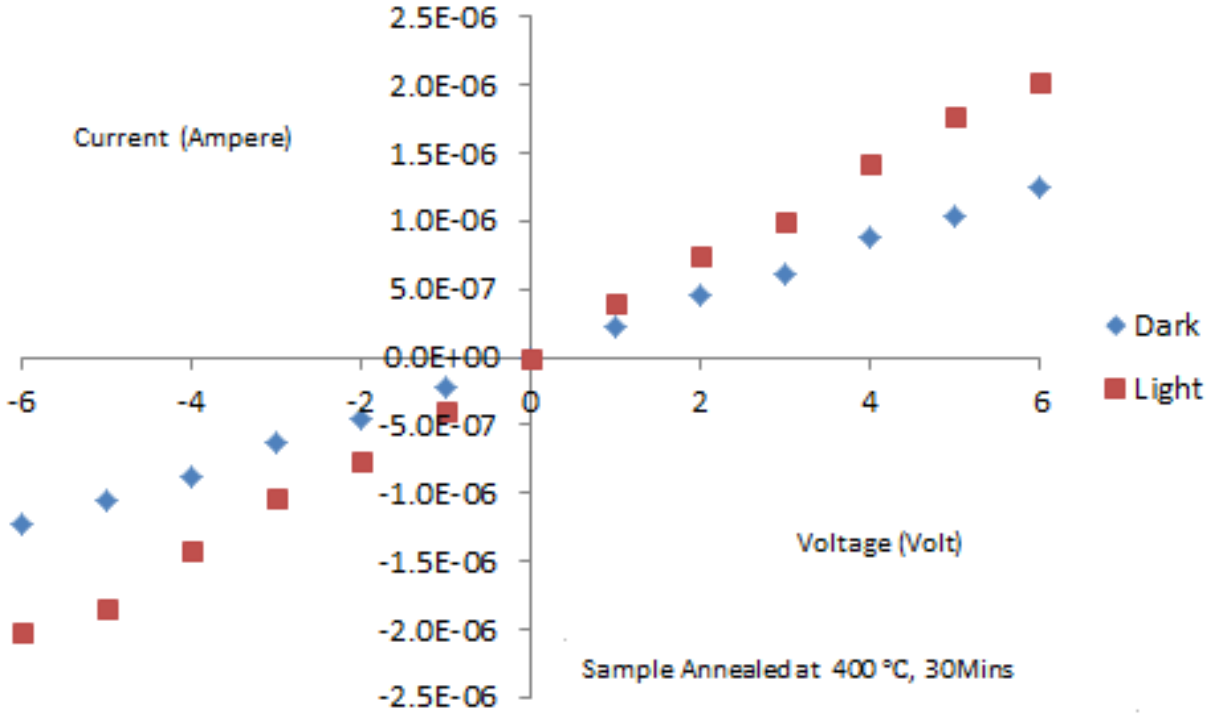

Fig. 4.25 I-V Characteristics of Sample S_5

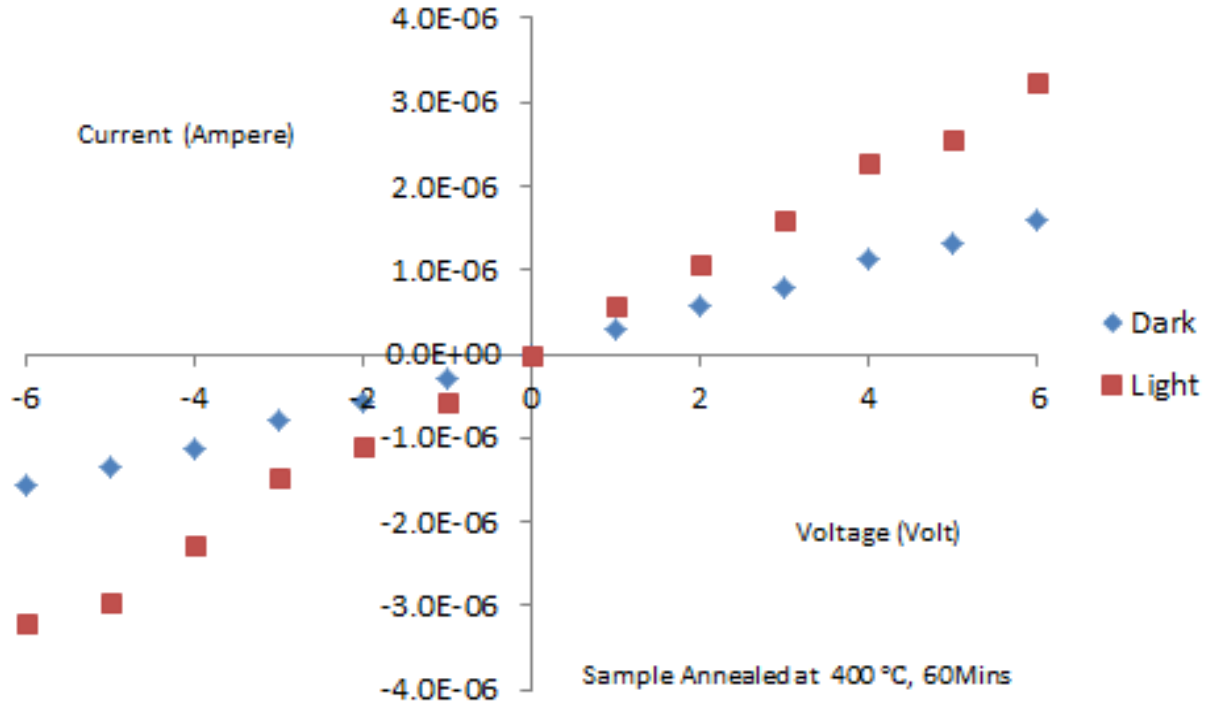

Fig. 4.26 I-V Characteristics of Sample S_6

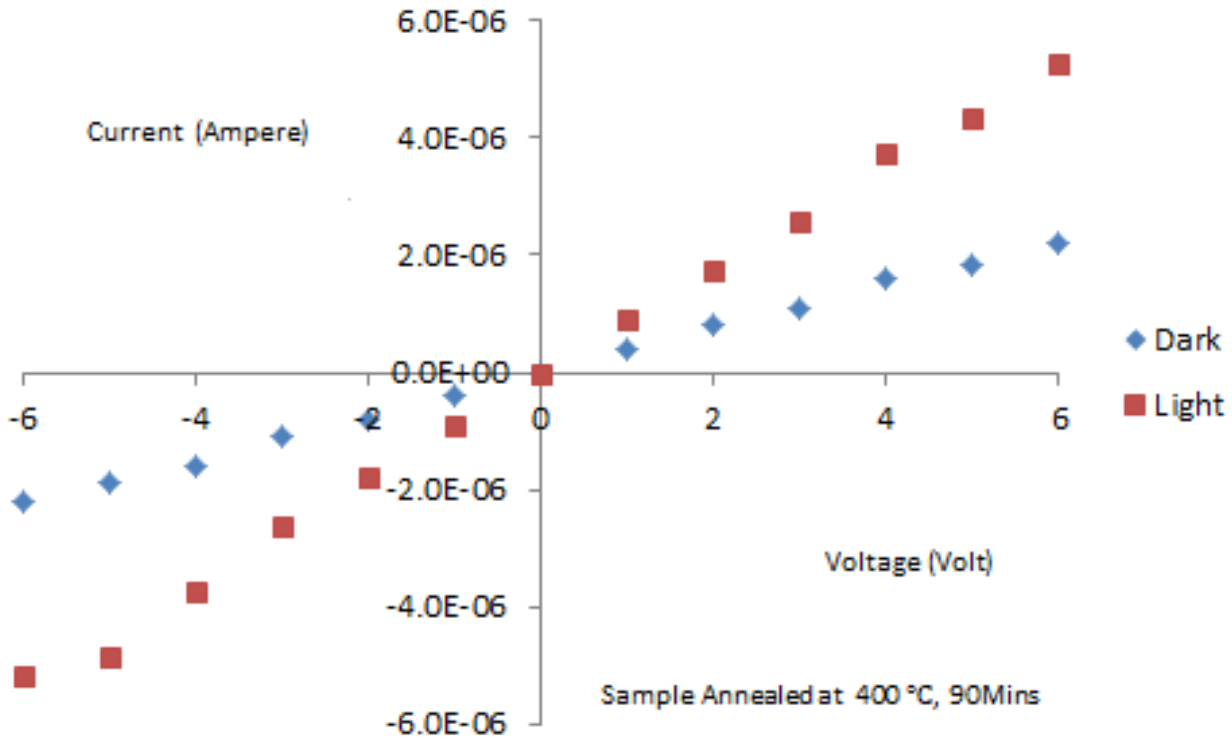

Fig. 4.27 I-V Characteristics of Sample S_7

4.4 Conclusion

The chapter provides us with a detailed calculative and graphical view of the study. In conclusion, the use of SEM, spectrophotometry, and I-V characteristics analysis in the investigation of ZnO as a transparent conducting oxide (TCO) thin film has provided valuable insights into their performance and potential applications.

The utilization of various characterization techniques has facilitated a thorough analysis of the transparent conducting zinc oxide (ZnO) thin film under investigation, leading to the generation of significant results. The interpretation and discussion of these results have provided valuable insights into the performance, efficiency, and potential improvements of zinc oxide-based transparent conducting thin film. By drawing upon the findings discussed, this study concludes with key recommendations and implications for future research scopes in the field of transparent conducting zinc oxide (ZnO) thin film.

Chapter-5
Conclusion
&
Future Scopes

5.1 Conclusion

The current work carried out a modest attempt to fabricate ZnO thin films via SILAR and modified CBD method, without any direct application of heat during the aqueous growth and nucleation process. The fabricated films, post-treatment, on subjection to UV-visible spectrophotometry revealed moderate transmittance in the visible spectrum for all the samples, suggesting a good degree of formation of ZnO in the as-deposited sample as well. There was also a prominent red shift observed in the absorption band edge, suggesting an increase in the band gap for all the annealed samples compared to the as-deposited sample. For the samples annealed at 400 ℃ a relatively higher transmittance was observed compared to those obtained at 350 ℃ in the same visible spectrum region, suggesting a greater degree of formation of ZnO in them. The bandgap values of all the samples were quite within the range of the standard bandgap value of ZnO found in the literature. SEM micrographs of samples S_1, S_4, and S_7 revealed growth of wire-like interconnected nanostructures in all of them, suggesting that the growth process itself has facilitated novel nanostructure formation. Furthermore, in the as-deposited sample itself, nanorods were found to coalesce with each other to form ultralong microwires, suggesting preferential morphological growth orientation. Also with increased annealing, the number of ultralong microwires was found to increase and implied that heat itself has an effect in inducing this preferred morphological growth orientation. The compositional analysis revealed good degree parity with standard weight percentage values of zinc and oxygen in ZnO for all the samples. Also, the highest annealed sample suggested an improved reduction in oxygen vacancies implying that an improved lattice structure and defect-reduction has also taken place. Eventually, the whole range of samples was subjected to IV-characterization and displayed a good range of low to moderate photo-response gains.

5.2 Future Scopes

The research conducted in this thesis lays the foundation for future studies and advancements in the field of thin film deposition of ZnO. The following are some potential areas of future research and development about transparent conducting zinc oxide (ZnO).

- The current work can be extended right away in future to study the comparative structural analysis of all the samples so concerned.

- Furthermore, a Transmission Electron Microscopy of the samples will give us a further idea of the lattice structure of the fabricated films.
- These characterizations along with XPS and ARPES will help us in determining the ultimate electronic band-structure of the deposited films and a possible theoretical band-modelling of the same.
- Understanding the underlying physics of such wide bandgap II-VI semiconductors can help in future innovation and novel application of these materials in transparent electronics.
- Parallel ramifications of such knowledge building can also lead to the improved application of such novel nanostructured thin films in TCO applications of solar cells, hydrogen evolution via solar photocatalysis and dye degradation for wastewater treatment.
- Similar deposition is hoped to be carried out on ITO coated glass and further comparative analysis will be done on those samples.
- An attempt will be made to fabricate memristor-based resistive switching devices using such ZnO thin films for possible application of cross-bar architecture in reservoir computing.

All relevant results and analysis would be the avenue for future research.

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