SOLUTION GROWTH AND CHARACTERISATION OF ZINC SULPHIDE(ZnS) THIN FILMS AT DIFFERENT MOLAR CONCENTRATIONS AT 50°C FOR 3 HOURS USING CHEMICAL BATH

BY

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CERTIFICATION

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DEDICATION

This project work is dedicated to My Heavenly father for His protection, guidance, provisions, divine health and giving me understanding throughout my four-year educational span in the University of Benin, and to my family for their prayers, advice, love and support.

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ABSTRACT

Zinc sulphide (ZnS) thin films were successfully deposited on glass substrates using an improved solution growth technique (SGT) at a constant temperature of 50 °C for three hours, with bath molarity varied between 0.03 M and 0.15 M. The optical and solid-state characteristics of the films were systematically investigated to evaluate the influence of precursor concentration on their structural and optoelectronic performance. Spectral analyses revealed that absorbance increased while transmittance generally decreased with rising molarity, indicating enhanced light absorption due to improved film density.

The absorption coefficient (α) and refractive index (n) exhibited molarity-dependent variations consistent with changes in surface uniformity and crystallinity. Calculated optical band gaps (Eg) ranged between 3.47 eV and 3.77 eV, signifying direct allowed transitions typical of ZnS semiconductors. Notably, films prepared at 0.12 M displayed optimal optical properties, balancing high transmittance with suitable band gap energy for potential application in solar cells and other optoelectronic devices.

The results confirm that controlled bath concentration in SGT offers a simple and effective route to tailoring ZnS thin films with desirable optical and solid-state characteristics for functional material applications.

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CHAPTER ONE

1.0 INTRODUCTION

Modern society has advanced technologically because of the material science and engineering community's capacity to employ Earth's materials, which have a special combination of mechanical, Electrical and physical capabilities, to create items that facilitate and enhance everyday life.

The need for fossil fuels is rising worldwide, and it is getting more difficult to identify fresh reserves. The ones that are found are substantially smaller than those that have previously been discovered. One notable example is oil reserves: Since 16 of the world's 20 largest oil fields are too small to meet demand worldwide, their production has peaked. We must leave up to 80% of our fossil fuel reserves in the ground in order to keep average global temperature increase below 1.5°C, while worldwide fossil fuel consumption is still rising.

We currently use the equivalent of nearly 11 billion tons of oil per year from fossil fuels worldwide. If things continue the way they are, our known oil deposits could run out in just over 53 years, since crude oil stocks are depleting at a rate of more than 4 billion tons per year.

Only 52 years remain in our known gas reserves, if we boost gas production to make up for the energy gap left by oil. That we have enough coal for hundreds of years is a common misconception, but it ignores the fact that we will need to produce more if our oil and gas supplies run out. Our known coal deposits may disappear in 150 years if we increase production to compensate for gas and oil reserves that are running low.

The advent of environmentally friendly and pollution-free non-conventional energy resources has become a feasible alternative as the demand for power and energy grows at a rapid rate and natural resources are being depleted at the same rate.

Since alternative energy sources are the most affordable, safest, and environmentally friendly way to produce energy for technological advancements that raise living standards, finding them should be the top priority for the entire globe. As a result, thin films applications are incredibly widespread and impactful in our daily lives, even if we don't always realize it. Solar panels, converting sunlight into electricity, rely heavily on thin film semiconductors. Even the scratch-resistant coatings on your eyeglasses or the reflective layers in architectural windows are examples of thin film technology at work. In the realm of electronics, thin films are fundamental to making microchips smaller, faster, and more efficient, driving the digital revolution.

In essence, thin film technology is a powerful tool for materials scientists and engineers. By carefully manipulating materials at the nanoscale, we can engineer new functionalities and improve existing ones, leading to innovations across a vast array of industries. It's a field where the smallest details lead to some of the biggest advancements.

1.2. CHOICE FOR SOLUTION GROWTH TECHNIQUES (SGT)

- It can spread without the use of any kind of electricity
- There are fewer casualties during the experiment
- It is easy to operate, inexpensive, and handy
- Low temperature processing
- Environmentally friendly
- It may be used to deposit points and irregularly shaped objects in a consistent form

1.3. AIM AND OBJECTIVES

1.3.1 AIM

The aim of this work is to grow zinc sulphide (ZnS) thin films at different molar concentrations using a chemical bath at 50°C for 3 hours.

1.3.2 OBJECTIVES

Objectives of this work are to:

1. ascertain the optical and solid-state characteristics of the developed films.
2. determine potential uses for the thin films based on their attributes.

CHAPTER TWO

LITERATURE REVIEW

A thin film is a layer of material with a thickness that can range from several micrometers to fractions of a nanometer (monolayer). In many applications, the controlled synthesis of materials as thin films, or deposition process, is an essential first step. A common example is the household mirror, which usually includes a tiny layer of metal coated to create a reflective surface on the back of a glass sheet. Mirrors were originally made via the silvering method, but more recently, sputtering has been utilized to deposit the metal layer. Throughout the 20th century, developments in thin film deposition techniques have made it possible to achieve several technical advancements in fields including integrated passive devices, magnetic recording media, electronic semiconductor devices, LEDs, hard coatings on cutting instruments, optical coatings (such antireflective coatings), and thin-film solar cells and thin-film batteries for energy production and storage. Thin-film drug delivery is another area in which it is being used in pharmaceuticals.

Materials formed by any other process, no matter how thin in size, are called thick films because the microstructure and physical properties of thin films depend on their mode of creation (Chopra & Kaur, (1983). These films are less than 100 nm thick, made from dielectric transparent materials and have refractive indices less than that of the substrate (Chopra, 1969). The industrial applications of thin films include decorative finishing of plastics, optical coatings of various kinds (mainly anti-reflection coatings, reflection increasing films, multi-layer interference filters and fluorescent coatings). In electronics, thin films are used in photo-emissive surfaces, piezoelectric transducers, radiation detectors, passive and active electronic

components from transistor or resistor capacitor network to such specialized devices as magnetic storage bits, photo sensors and cryotrons (Ilenikhena, Harding, & Chiedu, 2008).

Zinc sulphide (ZnS) is a prominent II–VI semiconductor material with a wide direct bandgap of approximately 3.6 eV in its cubic phase and about 3.9 eV in its hexagonal phase. These properties make ZnS highly desirable for a range of optoelectronic applications, including photodetectors, electroluminescent devices, light-emitting diodes, and buffer layers in solar cells. Additional advantages of ZnS thin films include good chemical stability, non-toxicity, and excellent adhesion to various substrates. These features have motivated the exploration of reliable, cost-effective, and environmentally friendly techniques for the growth of ZnS thin films.

Among the various methods available for ZnS thin film fabrication, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), spray pyrolysis, and successive ionic layer adsorption and reaction (SILAR), solution growth techniques — particularly chemical bath deposition (CBD) — stand out due to their simplicity, low cost, and suitability for large-area coatings. In the CBD process, the ZnS thin film is formed through precipitation of ZnS from a supersaturated solution containing zinc ions and sulphide ions, with the use of a complexing agent to moderate the release of metal ions. This method allows for the deposition of adherent, uniform, and well-crystallized thin films on substrates under relatively mild conditions.

The chemical bath typically involves zinc salts (such as zinc acetate or zinc chloride) as sources of Zn^{2+} ions, and sulphur precursors such as thiourea or thioacetamide to supply S^{2-} ions. Complexing agents like ammonia or triethanolamine are introduced to control the free Zn^{2+} concentration and prevent rapid precipitation, allowing thin film growth on the substrate rather

than in the bulk of the solution. The fundamental chemical reaction leading to ZnS formation can be expressed as:

$$Zn^{2+}_{(aq)} + S^{2-}_{(aq)} \rightarrow ZnS_{(s)}$$

This reaction is driven by supersaturation, while the nucleation and growth processes are largely influenced by bath parameters, including molar concentration, pH, temperature, and deposition time.

A critical factor in the CBD process is the molar concentration of the precursors. The molar concentration directly affects film thickness, grain size, crystallinity, optical transmittance, and even electrical resistivity. At higher molar concentrations, there is generally a greater availability of Zn^{2+} and S^{2-} ions, which increases nucleation rates and film growth. However, excessively high concentrations can result in rapid precipitation, leading to loosely adherent or porous films with increased surface roughness and pinholes. Therefore, precise control of precursor concentration is essential to achieving high-quality ZnS films with uniform and dense microstructure. Studies have shown that varying the molar concentration can slightly shift the optical bandgap, which may be attributed to quantum confinement effects or the presence of defects introduced during growth. Similarly, electrical resistivity of ZnS films often decreases with increasing concentration due to a higher carrier concentration within the films.

In addition to molar concentration, bath temperature and deposition duration significantly influence the film characteristics. Operating at a moderate temperature of 50°C for a period of 3 hours is considered favourable for achieving good quality ZnS thin films. At this temperature, there is sufficient thermal energy to facilitate ion mobility and promote controlled nucleation on the substrate surface while minimizing undesirable homogeneous precipitation in the solution. A deposition time of three hours generally provides enough duration for complete and uniform film growth without resulting in overly thick layers that might crack or peel from the

substrate. Literature sources such as (Pathan, H. M., & Lokhande, C. D. (2004) have documented that moderate bath temperatures yield compact, well-adherent, and highly transparent ZnS films suitable for optoelectronic applications.

Characterization of ZnS thin films synthesized under these conditions is essential to evaluate their suitability for device applications. X-ray diffraction (XRD) is typically employed to identify the crystalline structure (whether cubic or hexagonal) and estimate crystallite size. Scanning electron microscopy (SEM) provides insight into the surface morphology, grain distribution, and film uniformity. Optical properties, including the bandgap and transmittance, are usually assessed through UV-Visible spectrophotometry. Additional techniques such as energy dispersive X-ray spectroscopy (EDX) can confirm the elemental composition and stoichiometry of the films, while four-point probe or Hall effect measurements reveal their electrical properties.

2.0 THEORY

2.1 SOLAR RADIATION

Solar radiation is the primary source of energy that sustains life on Earth and drives its weather, climate, and environmental systems. It refers to the electromagnetic energy emitted by the Sun, which travels through space and reaches the Earth's atmosphere and surface. This energy is essential not only for natural biological processes such as photosynthesis but also for technological applications including solar power generation.

The Sun emits radiation across a broad range of wavelengths, including ultraviolet (UV), visible light, and infrared (IR). The solar spectrum that reaches the Earth's surface consists of approximately 5% ultraviolet radiation (100–400 nm), 43% visible light (400–700 nm), and 52% infrared radiation (700 nm–1 mm). While ultraviolet radiation is largely absorbed by the

Earth's ozone layer, visible and infrared radiation make up the majority of solar energy that reaches the surface (Liou, 2002).

At the outer edge of Earth's atmosphere, the average solar irradiance is about 1,361 watts per square meter (W/m^2), a value known as the solar constant (Duffie & Beckman, 2013). However, not all this energy reaches the ground. As solar radiation passes through the atmosphere, a significant portion is absorbed, scattered, or reflected by air molecules, dust particles, clouds, and gases such as ozone and water vapor. On average, about 30% of incoming solar radiation is reflected back to space, and 20% is absorbed by the atmosphere. Only approximately 50% reaches the Earth's surface, making it available for heat generation, photosynthesis, and solar energy systems (NASA Earth Observatory, 2020).

Several factors influence the amount of solar radiation received at any given location. These include the latitude of the location, time of day, season, altitude, and atmospheric conditions such as cloud cover and air pollution. Solar radiation is most intense at the equator and decreases towards the poles. It also varies throughout the day, peaking at solar noon when the sun is at its highest point in the sky.

Solar radiation interacts with the Earth's surface and atmosphere in complex ways. Reflection, absorption, and scattering determine how much radiation reaches the surface and how it is distributed. The scattering of shorter wavelengths of light (blue and violet) by atmospheric particles is what gives the sky its blue color, while red sunsets occur due to the scattering of shorter wavelengths and the dominance of longer red wavelengths at low solar angles.

Solar radiation plays a critical role in renewable energy production, particularly in solar photovoltaic (PV) systems that convert sunlight directly into electricity, and solar thermal systems that use solar heat to produce hot water or steam. The efficiency of these systems depends on the intensity and duration of solar radiation available. Accurate measurement of

solar radiation is essential for the planning and operation of solar energy projects. Instruments such as pyranometers and pyrheliometers are used to measure global and direct solar irradiance, respectively (IRENA, 2021).

Beyond its role in energy, solar radiation is essential for maintaining Earth's climate and supporting ecosystems. Plants depend on it for photosynthesis, which forms the base of the food chain. It also influences atmospheric and oceanic circulation patterns, making it a key component of the Earth's climate system.

2.1.1 SOLAR RADIATION INTERACTION WITH THE EARTH'S ATMOSPHERE

Solar radiation, also known as insolation, is the energy emitted by the Sun in the form of electromagnetic waves. It is the primary source of energy for the Earth and drives all weather, climate, and biological processes. As this solar energy reaches Earth, it interacts with the atmosphere in various ways, which significantly affect how much radiation reaches the Earth's surface and how it influences the environment.

When solar radiation enters the Earth's atmosphere, it undergoes three major processes: scattering, absorption, and reflection. Each of these interactions influences the quality, intensity, and distribution of sunlight on the Earth's surface.

Scattering occurs when sunlight strikes small particles and molecules in the atmosphere. The gases in the atmosphere, such as nitrogen and oxygen, scatter shorter wavelengths of light (like blue and violet) more effectively than longer wavelengths (like red and yellow). This selective scattering, known as Rayleigh scattering, is the reason why the sky appears blue during the day. Larger particles such as dust and water droplets cause Mie scattering, which is not wavelength-specific and contributes to the whiteness of clouds and the hazy appearance of the sky in polluted areas.

Absorption is another crucial process. Some of the incoming solar radiation is absorbed by atmospheric components. The ozone layer, found in the stratosphere, absorbs much of the harmful ultraviolet (UV) radiation, protecting living organisms from genetic damage. Water vapor and carbon dioxide, two major greenhouse gases, absorb significant portions of infrared radiation. This absorption of energy helps to warm the atmosphere and plays a vital role in regulating the Earth's temperature.

Reflection occurs when solar radiation is bounced back into space without being absorbed. This reflection is due to clouds, atmospheric particles, and the Earth's surface itself. The proportion of reflected radiation is called albedo. Bright surfaces like snow and ice have high albedo, reflecting most of the sunlight, while darker surfaces like forests and oceans absorb more and reflect less.

Despite these interactions, about 50% of the incoming solar radiation manages to reach the Earth's surface. Once it arrives, it is absorbed by land, water, vegetation, and built surfaces, converting it into heat. This absorbed energy drives weather patterns, ocean currents, and enables processes like photosynthesis in plants. The Earth, in turn, emits some of this energy back into the atmosphere as infrared radiation.

A portion of this outgoing infrared radiation is absorbed and re-radiated by greenhouse gases in the atmosphere. This is known as the greenhouse effect. It helps to keep the Earth's surface warm and habitable. Without this natural effect, the Earth would be too cold to support life as we know it.

2.2 SOLAR RADIATION INCIDENT ON SURFACES

Solar radiation incident on surfaces refers to the sunlight that directly or indirectly reaches the Earth's surface in the form of electromagnetic waves. It is the primary energy source driving weather, climate, and biological processes. The total radiation a surface receives consists of

direct radiation (from the sun's rays), diffuse radiation (scattered by atmospheric particles), and reflected radiation (bounced off nearby surfaces).

The intensity of solar radiation on a surface depends on several factors: solar angle, time of day, season, latitude, and atmospheric conditions. When the sun is directly overhead, radiation is most intense; when it is lower in the sky, the rays strike at a slant and cover a larger area, reducing intensity. Atmospheric elements like clouds, dust, and pollution scatter or absorb solar energy, affecting how much reaches the surface.

Surface characteristics also play a key role. Dark surfaces absorb more radiation and heat up faster, while light-colored surfaces reflect more sunlight—a property known as albedo. This influences surface temperature and contributes to local and global climate regulation.

Solar radiation incident on surfaces is vital in agriculture, solar energy systems, architecture, and climate studies. Accurate understanding of this radiation helps optimize crop growth, improve energy efficiency, and assess environmental impacts.

The interaction between solar radiation and Earth's surfaces is a crucial part of the planet's energy balance, affecting both natural ecosystems and human technologies.

2.2.1 SELECTIVE SURFACE

All things emit energy into their surroundings as their temperature rises above absolute zero, or -273.15°C. Electromagnetic waves, which propagate at the speed of light, are the energy's equivalent in radiation. There are a wide variety of known radiation kinds. Its wavelength characterizes each of these kinds. EMF radiation can have wavelengths that are indefinitely short or endlessly long. Sunlight falls inside the electromagnetic spectrum between about 0 and 4.0 micrometres. This is how one can characterize the nature of solar radiation. Vibrant light, ultraviolet light, near- and far-infrared radiation make up this spectrum. Between 0.40 to 0.71 micrometres (um) is the wavelength of light.

Approximately 7% of the Sun's radiation occurs in this wavelength range. Approximately 48% of the Sun's energy falls in the range of 0.71 to 4.0 micrometres. This range is known as the near (0.71 to 1.5 micrometres) and far infrared (1.5 to 4.0 micrometres).

2.3 OPTICAL AND SOLID-STATE PROPERTIES

The optical properties that are measured or calculated in this work include;

- Transmittance(T),
- Absorbance(A),
- Reflectance(R)
- Absorbing power or coefficient of absorption(a).
- Refractive index(n)

The solid states properties are;

- Bandgap (Eg)
- Film thickness(t)

2.3.1 TRANSMITTANCE (T)

The transmittance of a specimen is the ratio of transmitted light to the incident light, often expressed in percentage.

$$T = \frac{I}{I_0} \times 100\% \quad (2.1)$$

Transmittance and absorbance are related by $T = 10^{-A}$ (2.2)

2.3.2 ABSORBANCE (A)

Absorbance(A) quantifies how much light is absorbed by the thin film. It is the common logarithm of the reciprocal transmittance $A = -\log_{(10)}(T)$ (2.3)

The absorbance(A), is usually determined directly from measurements of absorption spectra and instrument scales are often calibrated in this unit (Cothian, G. F. 1958). Other properties are obtained from calculation based on them.

The reflectance(R) is obtained from the relation $A + T + R = 1$ (2.4)

2.3.3 ABSORBING POWER OR COEFFICIENT OF ABSORPTION(A)

The absorbing power or coefficient of absorption (a) is a qualitative measure of the ability of a material to absorb light and is measured in unit of reciprocal distance. When applied to electromagnetic radiation, Atomic and Subatomic particle.

The absorbing power (a) is a measure of rate of decrease in intensity of beam of photons or particles in its passage through a particular substance. If I_0 is the incident flux, I is the emergent flux through a material of thickness t, the absorption coefficient (a) of propagation of the flux through the material is given (Bohren, C. F., & Huffman, D. R. (1983) and (Wooten, F. 1972) as

$$I = I_0 \exp(-\alpha t) \quad (2.5)$$

From equation (2.1) and (2.5), the transmittance (T) and coefficient of absorption are relayed by

And

$$T = \exp(-\alpha t) \quad (2.6a)$$

$$\alpha = (\mathrm{In}T^{-1}) \quad (2.6b)$$

for a unit distance travelled, t=1 Then,

$$\alpha = \mathrm{In}(T^{-1})\ \mu m^{-1} \quad (2.7a)$$

or

$$\alpha = \ln(T^{-1}) \times 10^{6} m^{-1} \quad (2.7b)$$

2.3.4 REFRACTIVE INDEX

The general expression for the reflectance(R) normal to surface in terms of optical constants n and k is given by,

$$R=[(n-1)^2 + K^2]/[(n+1)^2 + K^2] \quad (2.8)$$

Where K is extinction coefficient for semiconductors, $K^2 << (n+1)^2$ The equation (2.8) reduces to

$$R= (n-1)^2 / (n+1)^2 \quad (2.9)$$

From equation (2.9)

$$n= (1+R^{1/2}) / (1 - R^{1/2}) \quad (2.10)$$

2.3.5 BANDGAP (Eg)

The energy of an electron in a crystal falls within well-defined bands (Markvart, 2000). The energy of electron in the valence band is separated from the conduction band by energy bandgap or bandgap. The width of the bandgap Ec - Ev is a very important property of semiconductors and is usually denoted by Eg. The crystalline materials have four (4) types of electron transitions from upper part of valence band to lower part of conduction band. The general expression for direct transition is,

$$\alpha = (hv-Eg)^n \quad (2.11)$$

where n=1/2 for direct allowed transition between extreme of the conduction and valence bands, and n=3/2 for direct forbidden transitions.

The dependence of the absorption coefficient on the energy quanta near absorption edge is given by,

$\alpha = (hv - Eg)^{1/2}$ (2.12a)

$\alpha^2 = hv-Eg$ (2.12b)

where hv = photon energy

the plot of α^2 against hv gives a straight line that deviates from being straight in the region of absorption edge.

The extrapolation of the straight portion of the graph to the point $\alpha^2 = 0$ gives the energy gap(Eg)

The photon energy E(J) for a given wavelength λ is;

$E(J) = hv(J)= hc/\lambda(J)$ (2.13)

Where h = plank's constant = 6.62×10^{-34} Js, C = velocity of light = $3x10^8$ ms^{-1}

λ = wavelength in meters (m)

the equation (2.13) gives

$hv(J) = (6.62x10^{-34} \times 3x10^8)/\lambda(m)J$ But $1(Ev)=1.6x10^{-19}J$

$hv(Ev) = 1.986x10^{-16}/\lambda(nm) \times 1.6x10^{-19}$

This gives $hv(Ev) = 1241/\lambda(nm)$ (2.14)

The equation (2.14) can be used to calculate photon energies (hv) in Ev for various wavelengths (λ) in nm.

2.4 THIN FILMS

Thin film materials are high purity materials and chemicals used to form or modify thin film deposits and substrates. Examples include precursor gases, sputtering targets, and evaporation filaments. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction.

Thin films play an important role in many technological applications including

microelectronic devices, magnetic storage media and surface coatings. A familiar application of thin films is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface.

The performance of optical coatings (e.g. antireflective, or AR, coatings) are typically enhanced when the thin film coating consists of multiple layers having varying thicknesses and refractive indices.

Similarly, a periodic structure of alternating thin films of different materials may collectively form a so-called super lattice which exploits the phenomenon of quantum confinement by restricting electronic phenomena to two- dimensions.

Work is being done with ferromagnetic and ferroelectric thin films for use as computer memory.

It is also being applied to pharmaceuticals, via thin film drug delivery. Thin-films are used to produce thin-film batteries. Thin film application also be adopted on Dye-sensitized solar cell. Ceramic thin films are in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin coating of interest for protection of substrate materials against corrosion, oxidation and wear. In particular, the use of such coatings on cutting tools can extend the life of these items by several orders of magnitude.

2.4.1 THIN FILM DEPOSITION METHODS

Thin film deposition methods are various procedures for forming thin layers of material on a substrate surface. These approaches differ in terms of the deposition process, materials employed, film thickness control, and application. These are some major thin film deposition methods:

1. Physical Vapor Deposition (PVD):

-Evaporation: This approach involves heating a substance in a vacuum chamber

until it vaporizes. The vaporized atoms or molecules condense onto a substrate,

resulting in a thin layer.

-Sputtering: Sputtering involves hitting a target material with high-energy ions

in a vacuum chamber, causing atoms to eject and deposit on a substrate surface.

2. Chemical vapor deposition (CVD):

-Low-Pressure Chemical Vapor Deposition (LPCVD) is a low-pressure process in which precursor gases react on a heated substrate surface to deposit a thin coating.

-Plasma-Enhanced Chemical Vapor Deposition (PECVD) employs plasma to speed up chemical interactions between precursor gases, resulting in the deposition of thin films with better attributes such as higher density and reduced defect density.

3. Atomic layer deposition (ALD):

ALD is a sequential, self-limiting process in which precursor gases are alternatively injected onto a substrate surface, allowing for fine control of layer thickness and composition at the atomic level.

4. Sol-gel deposition:

Sol-gel deposition converts a precursor solution (sol) to a solid thin layer (gel) by hydrolysis and condensation. The thin film is created by applying the gel to a substrate and then curing it to eliminate the solvent and consolidate the material.

5. Spin coating:

Spin Coating is a solution-based process that involves dispensing a liquid precursor onto a substrate and spinning it at high speeds to equally distribute the material. After spinning, the solvent evaporates, leaving only a thin coating.

6. Dip coating:

Dip coating involves dipping a substrate in a solution with the desired material and removing it at a predetermined rate. When the substrate is extracted, a thin coating forms on its surface.

7. Chemical Bath Deposition:

CBD is a solution-based process for producing thin films by immersing substrates in a chemical bath containing precursors. Chemical interactions occur between the precursors and the substrate surface, forming the thin layer.

8. Molecular beam epitaxy (MBE):

MBE is a high-vacuum process that deposits material one atomic layer at a time by directing atom or molecular beams onto a heated substrate surface. These

deposition processes are versatile in terms of material selection, film thickness control, deposition rate, and scalability, making them ideal for a variety of applications in electronics, optics, coatings, and energy storage. Deposition methods are chosen based on desired film qualities, substrate compatibility, and manufacturing constraints.

2.4.2. CHEMICAL BATH DEPOSITION(CBD)METHOD

Chemical bath deposition (CBD) is an economical and low-temperature technology (25-90°C) for depositing huge areas of semiconductor thin films. However, the intended heterogeneous reaction on the substrate surface is limited first by the competing homogeneous reaction, which produces colloidal particles in the bulk solution, and second by material deposition on the CBD reactor walls. As a result, the CBD technique has a low profit-to-starting materials efficiency.

The CBD method is based on controlled precipitation of the material to be manufactured, which results in a coating on the substrate surface. Although precipitation can be regulated by modifying the experimental parameters (chemical composition and process temperature), nucleation in the solution and on the reactor walls cannot be fully eliminated. As a result, only a tiny portion of the reagents in solution are employed to grow the substrate film, while a larger amount of material creates colloidal particles in the solution and a worthless layer on the reactor walls. For example, Ortega-López et al. (2003)s estimated that just 2% of the chemicals in solution are utilized during CdS film development on a substrate.

During CBD film growth, two processes can take place: on the one hand, a heterogeneous reaction upon the substrate surface occurring between adsorbed ionic species and those in the solution; on the other hand, colloidal particles first nucleated in the solution can be adsorbed upon the substrate surface. The first process leads to compact and well-adhered films, constituting good prospects for electronic applications, but the second process yields porous and badly adhered films. Accordingly, there is currently a great interest in optimizing the efficiency of the CBD method, by minimizing both the deposition process upon the reactor walls and the homogeneous precipitation in the bulk solution.

2.4.3. ADVANTAGES OF CHEMICAL BATH DEPOSITION(CBD)

Chemical bath deposition (CBD) is a process for depositing thin films of diverse materials onto substrates using a chemical reaction in solution. Some benefits of CBD include:

-CBD is typically less expensive than other thin film deposition processes such as physical vapor deposition (PVD) or chemical vapor deposition (CVD). It requires little equipment and may be done at moderate temperatures, resulting in lower energy use.

-CBD is suitable for depositing thin films across wide regions of homogeneous

thickness, making it useful for applications requiring substrate homogeneity, such as solar cells or large-scale electrical devices.

-Conformal Coating: CBD can coat complicated and irregularly shaped surfaces with reasonable ease, resulting in conformal coating of three-dimensional structures. This makes it suitable for applications in electronics, optics, and surface engineering.

-Controlled Deposition: CBD offers good control over film thickness and composition by adjusting parameters such as solution concentration, temperature, and deposition time. This control enables the precise tuning of material properties for specific applications.

2.5 THIN FILM MEASUREMENTS TECHNIQUES

Thickness, optical, and solid-state characteristics, among other criteria, are critical in defining the effectiveness and uses of thin films. Thin film measurements involve a wide range of techniques, from simple chemical and mechanical procedures to highly complicated electronic and spectroscopic methods. Other methods used to measure thin films include:

-Simple chemical analysis method,

-Gravimetric method,

-Spectrometric method,

-Spectrophotometric method.

2.5.1 MEASUREMENT OF FILMTHICKNESS

The measurement of film thickness of this work is restricted to two methods namely;

- The gravimetric method
- The optical method

- The gravimetric method is given by:

Density = mass/volume (2.15)

$$\rho = \frac{M2-M1}{2at} = \frac{\mathrm{m}}{2lbt}$$

$$\mathrm{t} = \frac{\mathrm{m}}{2lb\rho}$$

Where; t = film thickness

$m = M_2 - M_1$ is mass of film deposited, M_2 and M_1 are the mass of the glass slides after and before deposition

A = Area of the film on rectangular glass substrate of length I, and width b.

B. The optical method:

Optical techniques are usually the preferred method for measuring thin films because they are accurate, non-destructive, and require little or no sample preparation. The two most common optical measurement types are spectral reflectance and ellipsometry.

Spectral reflectance measures the amount of light reflected from a thin film over a range of wavelengths, with the incident light normal (perpendicular) to the sample surface.

Ellipsometry is similar, except that it measures reflectance at non-normal incidence and at two different polarizations. In general, spectral reflectance is much simpler and less expensive than ellipsometry, but it is restricted to measuring less complex structures.

The optical method based on light absorption coefficient is given by;

$$T=(1-R)^2 \exp(-\alpha t) \quad (2.17)$$

Where R is the reflectance and t the film thickness

Taking the natural logarithm on both sides of equation 2.17 gives;

$$l=In[(1-R)^2/T]/\alpha \quad (2.18)$$

This equation is used to compute film thickness with absorbance $A \geq 0.10$ in this work.

2.5.2 MEASUREMENTS OF THIN FILM OPTICAL PROPERTIES

Spectroscopic method is used to study many film properties which include thickness, film composition, and nature of film. crystallographic orientations, lattice parameters, crystallite size and preferred orientations.

In this research work, a T80+ double beam spectrophotometer was used to determine the absorbance of the coated glass slide in the ultraviolet (UV), visible (VIS) and near infrared (NIR) region of this work. In order to measure the absorbance of the film the coated glass slide was placed on sample holder while the sample beam was made incident on it. The standard or coated glass slide was mounted along the path of the reference beam for compensation. The absorbance was obtained from the absorbance spectral. Other optical properties were obtained from thin based theory.

2.6 APPLICATIONS OF THIN FILMS

Thin films are widely used in a variety of industries due to their unique features and adaptability. Some common applications of thin films are:

-Optical Coatings: Thin films are used to apply anti-reflection coatings to lenses and windows, as well as reflective coatings to mirrors and filters in optical systems. These coatings increase light transmission, minimize glare, and improve optical performance.

-Semi-conductor devices: Thin films are critical components in semiconductor production, used to manufacture integrated circuits (ICs), transistors, and other electronic devices. They serve as dielectric, insulating, and conducting layers in semiconductor production process.

-Solar Cells: Thin films are essential in photovoltaic technology because they create the active layers in solar cells. Materials such as amorphous silicon, cadmium telluride, and copper indium gallium selenide (CIGS) are deposited as thin films to efficiently convert sunlight into energy.

-Displays and Touchscreens: Thin films are used to make liquid crystal displays

(LCDs), organic light-emitting diode (OLED) displays, and thin-film transistor (TFT) backplanes. They provide for high-resolution visuals, low power consumption, and adaptable display designs.

-Protective Coatings: Thin films are used to generate protective coatings that increase surface durability, corrosion resistance, and scratch resistance. They improve the performance and longevity of automobile parts, electrical gadgets, metal components and architectural glass.

-Microelectromechanical Systems (MEMS): Thin films are used in MEMS devices, which combine mechanical and electrical components at the microscale. Accelerometers, gyroscopes,

and micro valves all make use of them as structural layers, sensor elements, and actuation mechanisms.

Thin films are used in medical devices and implants due to their biocompatibility and barrier qualities. They are used as coatings on surgical instruments, medication delivery systems, and biomedical sensors, as well as diagnostic applications such as biosensors and lab-on-a-chip systems.

CHAPTER THREE

3.0 EXPERIMENTAL WORK AND MEARSUREMENT

3.1 PREPARATION OF GLASS SLIDES

Five samples of glass slide typically 75 by 26mm and about 1mm thick where prepared by degreasing them in concentrated hydrochloric acid for three days. After three days, the degreased samples of glass slides where scrubbed in cold detergent solution using rubber sponge to avoid scratching their surfaces thereafter, rinsed in distilled water. The glass slides were dip dried in air, labelled using masking tape and weighed by an electronic balance.

Fig 3.1: Degreased and labelled uncoated glass slide

3.2. PREPARATION OF SOLUTE REAGENTSOLUTION

The mass of each solute reagent was calculated from the following equation

$$M = \frac{m \times W \times Vol}{1000}$$

Where;

M = molar concentration

W= Molecular weight of chemical reagent

V = Volume of distilled water required for the solution

m = mass

3.2.1 PREPARATION OF ZINC NITRATE SOLUTION

The total mass of zinc nitrate needed for the experiment was prepared at once to prevent inconvenience in preparing the zinc chloride solution at separate times. Extra volume of zinc nitrate was also prepared to ensure sufficient amount in the case of error. The total mass of zinc nitrate prepared was calculated as follows;

$m = \frac{0.5 \times 297.52 \times 55}{1000} = 8.18g$

On an electronic balance, 8.18g of zinc nitrate was weighed using a clean, dry measuring beaker. It was transferred into a 100ml beaker. The zinc nitrate is dissolved in the measured 100ml distilled water for dissolution.

3.2.2 PREPRATION OF SODIUM HYDROXIDE SOLUTION

The same technique was applied in the preparation of 20ml of sodium hydroxide

$$m = \frac{3 \times 40 \times 20.0}{1000} = 2.4g$$

2.4g of sodium hydroxide is weighed by using measuring beaker and dissolved in a clean and dry flat bottom flask with distilled water, covered for the night to ensure thorough dissolution.

3.2.3 PREPRATION OF THIOUREA SOLUTION

The same technique was applied in the preparation of 65ml of Thiourea

$$m = \frac{0.8 \times 76.12 \times 65}{1000} = 3.96g$$

3.96g of thiourea is weighed by using measuring beaker and dissolved in a clean and dry flat bottom flask with distilled water, covered for the night to ensure thorough dissolution.

3.3 PREPARATION OF SOLVENT REAGENTS SOLUTION

For solvent reagents, the volume (V) of the solvent for a given molarity M was calculated using the relation,

$$V = \frac{M \times Wt \times 100}{d.p} \times \frac{Vt}{1000}$$

where:

M=Molarity required

V = Total volume of ammonia solution

Wt = Molecular mass

Vt = Total volume required

d = Density and specific gravity

P = Percentage array

$$V = \frac{10 \times 17.03 \times 100}{0.88 \times 33} \times \frac{30}{1000} = 17.59$$

Volume of distilled water was obtained using;

$V_T = V_{H20} + V_{NH3}$

$V_{H20} = V_T - V_{NH3}$

=30 – 17.59 = 12.41ml

3.4 PREPARATION OF DEPOSITION BATHSOLUTION

The deposition bath were five glass beakers of 50ml volumes each. Reagents used for the deposition of zinc sulphide thin films were different volumes of 0.5M Zn $(NO_3)_2.6H_2O$, 10M NH3, used as a complexing agent, 0.8M $(NH_2)_2CS$ and 3M NaOH solutions. Different volumes of distilled water were added to each beaker to raise the volume to the required volume (i.e. 50ml). This was done so that the required molar concentration in each beaker would be achieved as shown in Table 3.1

Table 3.1 Chemical bath constitution for deposition of Zinc Sulphide (ZnS) thin films in different molar concentration of zinc nitrate in solution at 50℃ for 3hours.

No of Glass Slides	Deposition at 50^0C Time(hrs)	Vol (ML) of Zn $(NO_3)_2.6H_2O$ M = 0.5	Vol (ML) of NH_3 M=10	Vol (ML) Of NaOH M=3	Vol (ML) of $(NH_2)_2C_5$ M = 3	Vol (ML) Of Distilled H_2O	Vol (ML) Of Total Solution	Molarity of Zn Nitrate in Solution
1.	3hrs	3.0	3.0	2.0	5.0	37.0	50.0	0.03
2.	3hrs	6.0	4.0	3.0	8.0	29.0	50.0	0.06
3.	3hrs	9.0	4.0	3.0	11.0	23.0	50.0	0.09
4.	3hrs	12.0	5.0	4.0	14.0	15.0	50.0	0.12
5.	3hrs	15.0	5.0	4.0	17.0	9.0	50.0	0.15

3.5 THIN FILM DEPOSITION

A glass slide was suspended vertically in each of the five bath solutions, with the aid of a plastic peg and a hard paper cover at the centre of the beaker (placed in a position that it would have no contact with the bottom or sides of the beaker) for 3hours at different molarity. Thereafter, the glass substrate coated with ZnS was removed, rinsed with distilled water, and dried in open air at room temperature. The thin film obtained at the end of the deposition was well adherent and faint green in colour.

Fig3.2: Zinc Sulphide (ZnS) deposition on glass slides in the deposition bath at 50℃ of different molarity concentration.

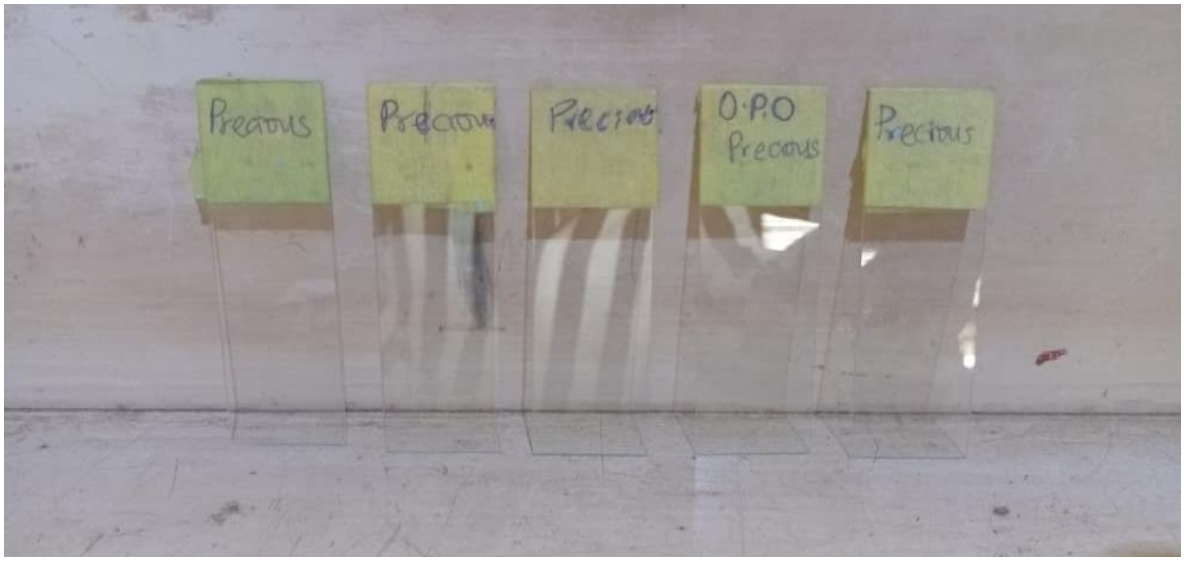

Fig3.2: Glass slides coated with zinc sulphide (ZnS) thin films.

3.6. MEASUREMENT

3.6.1 OPTICALAND SOLID STATE DETERMINATION

The optical properties calculated in this work includes the absorbance (A), Transmittance (T) and reflectance (R), and absorbing power (a). The solid-state measurements carried out on the films was the energy band gap (Eg), film thickness (t) and refractive index (n).

The measurement of the spectral absorbance was done in the laboratory of Biochemistry department, of the University of Benin, Benin City, Nigeria, A T80+ UV/VIS Double beam UV/VIS Spectrophotometer was used to determine the absorbance of the films in the ultraviolet (UV), visible (VIS), and near infrared regions of the electromagnetic spectrum (i.e. a wide range of wavelength). The spectral absorbance was read directly from the instrument. Other properties such as transmittance, reflectance, refractive index, absorbing power, etc. were calculated from the absorbance spectral. The spectral transmittance was obtained from Eqn(2.3), spectral reflectance was obtained using Eqn(2.4), absorbing power was computed from Eqn(2.9), while the band gap of the deposited thin films were computed using Eqn(2.11), and obtained from extension of linear part of the plots of absorbing power(a^2) against photon energy(hv). The refractive index of the films was computed using Eqn(2.14). The film thickness (1) was computed by optical method using Eqn(2.18) for films with absorbance $A \geq 0.1$.

Fig3.3: T80+UV/VIS Double Beam Spectrophotometer

CHAPTER FOUR

RESULTS

Table 4.1: Spectral absorbance (A), transmittance (T), reflectance (R) and absorbing power (α) of ZnS thin films deposited on glass slides at 0.03 molar bath concentration at 50℃ for 3hours.

0.03M						
λ (nm)	A	T	R	$\alpha \times 10^6 (m^{-1})$	hv	$\alpha^2 \times 10^{10} (m^{-2})$
311	0.393	0.405	0.202	0.904	3.990	8.170
380	0.019	0.957	0.024	0.044	3.265	1.940

Table 4.2: Spectral absorbance (A), transmittance (T), reflectance (R) and absorbing power (α) of ZnS thin films deposited on glass slides at 0.06 molar bath concentration at 50℃ for 3hours.

0.06M						
λ (nm)	A	T	R	$\alpha \times 10^6 (m^{-1})$	hv	$\alpha^2 \times 10^{10} (m^{-2})$
303	0.064	0.863	0.073	0.147	4.095	2.16
305	0.060	0.870	0.070	0.139	4.069	1.93
311	0.227	0.593	0.180	0.523	3.990	2.74
328	0.030	0.933	0.037	0.069	3.784	0.476
336	0.017	0.962	0.021	0.038	3.693	0.144
342	0.012	0.972	0.016	0.028	3.629	0.078
344	0.010	0.977	0.013	0.023	3.608	0.053
347	0.009	0.979	0.012	0.021	3.576	0.044
351	0.007	0.984	0.009	0.016	3.536	0.026
357	0.004	0.991	0.005	0.009	3.476	0.008
361	0.004	0.991	0.005	0.009	3.438	0.008

364	0.003	0.993	0.004	0.007	3.409	0.005
370	0.010	0.977	0.013	0.023	3.354	0.053
378	0.012	0.973	0.015	0.027	3.283	0.073
382	0.011	0.974	0.015	0.026	3.249	0.068
388	0.011	0.974	0.015	0.026	3.198	0.068
391	0.011	0.974	0.015	0.026	3.174	0.068
404	0.010	0.977	0.013	0.023	3.072	0.053
506	0.008	0.982	0.010	0.018	2.453	0.032

Table 4.3: Spectral absorbance (A), transmittance (T), reflectance (R) and absorbing power (α) of ZnS thin films deposited on glass slides at 0.09 molar bath concentration at 50℃ for 3hours.

0.09M						
λ (nm)	A	T	R	$\alpha \times 10^6\,(m^{-1})$	hv	$\alpha^2 \times 10^{10}(m^{-2})$
305	0.063	0.865	0.072	0.145	4.069	2.10
311	0.436	0.366	0.198	1.005	3.990	10.10
383	0.016	0.964	0.020	0.037	3.240	1.369

Table 4.4: Spectral absorbance (A), transmittance (T), reflectance (R) and absorbing power (α) of ZnS thin films deposited on glass slides at 0.12 molar bath concentration at 50℃ for 3hours.

0.12M						
λ (nm)	A	T	R	$\alpha \times 10^6\,(m^{-1})$	hv	$\alpha^2 \times 10^{10}(m^{-2})$
311	0.675	0.211	0.114	1.556	3.990	24.21
365	0.002	0.995	0.003	0.005	3.400	0.025

Table 4.5: Spectral absorbance (A), transmittance (T), reflectance (R) and absorbing power (α) of ZnS thin films deposited on glass slides at 0.15 molar bath concentration at 50℃ for 3hours.

0.15M						
λ (nm)	A	T	R	$\alpha \times 10^6 (m^{-1})$	hv	$\alpha^2 \times 10^{10}(m^{-2})$
311	0.681	0.208	0.111	1.570	3.990	24.65
383	0.020	0.955	0.025	0.025	3.240	0.625

Table 4.6: Average Optical and solid state properties (at wavelength(λ) of 361nm) of ZnS thin films deposited by improved solution growth technique (SGT) in bath solution for different molarity at 50℃ for 3hours.

Average optical state properties	DIFFERENT MOLARITY OF ZnS IN BATH SOLUTION				
	0.03M	0.06M	0.09M	0.12M	0.15M
A	0.206	0.027	0.172	0.339	0.351
T	0.681	0.944	0.732	0.603	0.582
R	0.113	0.028	0.097	0.059	0.068
α X $10^6 M^{-1}$	0.474	0.063	0.396	0.781	0.798
n	2.013	1.402	1.905	1.642	1.706
Average Solid State properties					
t	0.305	0.013	0.272	0.492	0.502
Eg(Ev)	3.628	3.478	3.766	3.695	3.615

DISCUSSION

The absorbance spectra for the deposited zinc sulphide (ZnS) thin films grown in a deposition bath at 50°C for 3 hours under different molar concentrations reveal that the ZnS thin films exhibit high transmittance (T) and low reflectance (R), which are characteristic features of good optical window materials.

The transmittance (T) of the ZnS films was observed to increase with increasing wavelength within the visible and near-infrared regions, indicating that the films allow more light to pass through as the wavelength increases. However, the transmittance decreases slightly with increasing deposition concentration, suggesting that thicker or denser films tend to absorb or scatter more light.

Conversely, the absorbance (A) of the films decreases as wavelength increases but increases slightly with higher molar concentration, showing that more densely packed ZnS layers have higher optical density. The reflectance (R) values remain generally low across all wavelengths, confirming that ZnS films are efficient at minimizing reflection losses, which is vital for antireflection and solar applications.

As the deposition time was fixed at 3 hours, changes in optical properties can mainly be attributed to concentration variations. Films produced at lower molar concentrations showed higher transmittance ($T \approx 0.90–0.98$) and lower reflectance ($R \approx 0.02–0.04$), while those at higher concentrations showed reduced transmittance ($T \approx 0.70–0.85$) and slightly higher absorbance.

The refractive index (n) of the ZnS thin films was found to lie between 1.4 and 2.0, indicating their suitability for use as antireflection coatings and optical windows. The absorption coefficient (α) values, derived from the transmittance and absorbance data, were used to determine the optical band gap (Eg) of the ZnS thin films. The average band gap ranged

between 3.5eV and 3.8 eV, consistent with reported values for ZnS, confirming their semiconducting and optically transparent nature. The optical behavior therefore suggests that the ZnS films grown at 50°C for 3 hours are uniform, well-adherent, and possess desirable optical properties for use in photovoltaic, optoelectronic, and architectural application

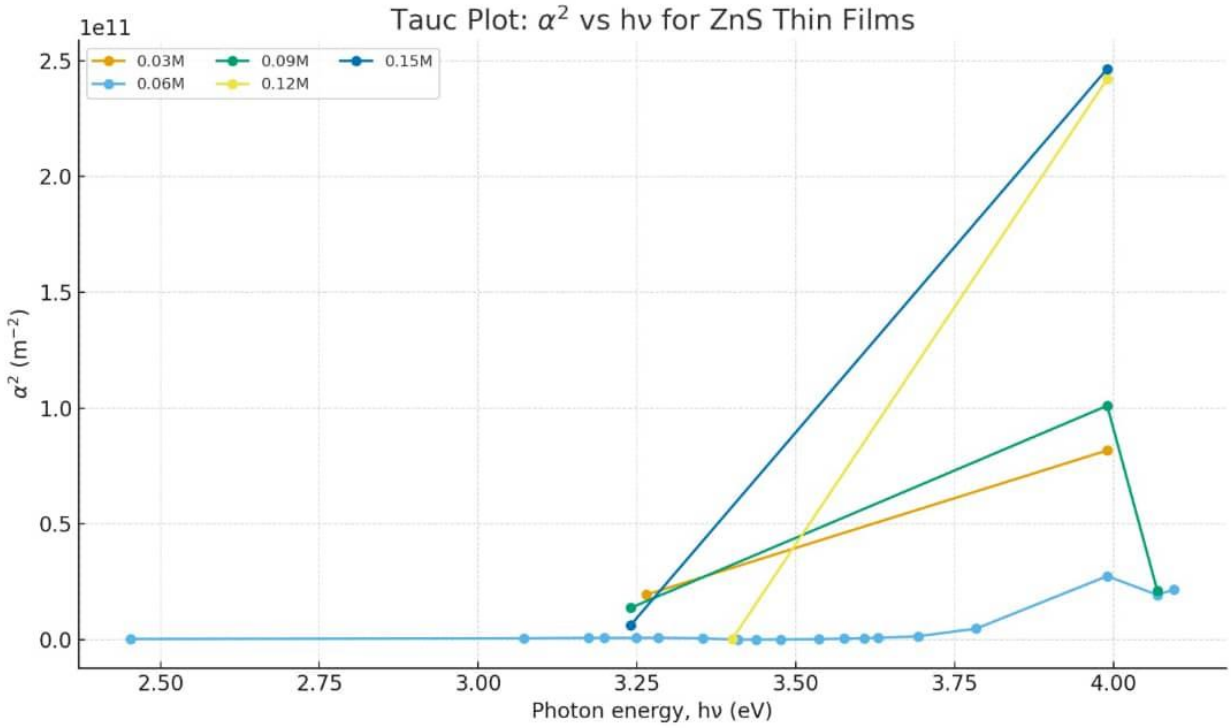

Fig 4.1 Plot of α^2 against hv for ZnS thin films deposited on glass by solution growth technique in a deposition bath concentration of different molarity at 50℃ for 3 hours

CHAPTER FIVE

5.0 FINDINGS, RECOMMENDATION AND CONCLUSION

5.1 FINDINGS

1. ZnS thin films were successfully deposited at various molar concentrations (e.g., 0.03 M, 0.06 M, 0.09 M, 0.12 M, and 0.15 M).
2. Increasing molar concentration likely produced thicker films, leading to slightly higher absorbance and lower transmittance due to enhanced scattering and absorption.
3. Absorbance increased with higher concentration, suggesting thicker and denser films.
4. Transmittance decreased slightly as concentration increased—confirming that more concentrated solutions yield films with greater photon absorption.
5. Reflectance remained low, showing that ZnS films allow substantial light penetration.

5.2 RECOMMENDATION

To optimize the performance of ZnS thin films, the following are recommended:

1. Investigate different molar concentrations (e.g., 0.05–0.20 M) at constant deposition temperature (50°C) to determine their influence on optical band gap and film uniformity.
2. Extend the deposition time beyond 3 hours to study growth kinetics and possible enhancement in crystallinity and optical transparency.
3. Repeat the experiment at higher temperatures (60–70°C) to observe improvements in film adhesion and reduction in surface roughness.

5.3.CONCLUSION

Zinc sulphide (ZnS) thin films deposited at 50°C for 3 hours show excellent optical transmittance, low reflectance, and moderate absorbance, confirming their potential as optical coatings in solar and architectural applications. The band gap values indicate that the films are wide-band-gap semiconductors suitable for transparent electronic devices and antireflection applications. Thus, ZnS thin films synthesized under these conditions demonstrate promise for use in photovoltaic cells, optical windows, and thermal control coatings, aligning with the increasing demand for eco-friendly, cost-effective, and high-performance thin film materials.

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