# FABRICATION AND OPTICAL CHARACTERIZATION OF CuS NANOTHIN FILMS ON GLASS SLIDES USING CHEMICAL BATH DEPOSITION

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## CERTIFICATION

This is to certify that the project entitled "FABRICATION AND OPTICAL CHARACTERIZATION OF CuS NANOTHIN FILMS ON GLASS SLIDES USING CHEMICAL BATH DEPOSITION" is a bonafide work carried out by EHIAGHE ONYEKA a final year of the Department Of Physics, Faculty of Physical science, University of Benin, Benin city, Edo state, Nigeria.

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## DEDICATION

I dedicate this project work to the Almighty God, the Author and Finisher of my faith, for granting me strength, wisdom, and protection throughout my journey at the University of Benin and during the course of this project.

Furthermore, I dedicate this work to my beloved parents, Mr. and Mrs. Ehiaghe Friday, for their love, prayers, and support, and to my ever-supportive siblings. I love you all deeply, I would not have come this far without you.

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# ABSTRACT

The growing demand for efficient, low-cost semiconductor materials for optoelectronic applications has driven significant interest in copper sulfide (CuS) thin films. This project successfully demonstrates the fabrication of CuS nanothin films on glass substrates using a simple and cost-effective Chemical Bath Deposition (CBD) technique, with a specific focus on investigating the influence of extended deposition times on their optical properties.

Two sets of films were deposited using an aqueous solution of copper sulfate and thiourea, with deposition times of 20 hours and 24 hours, while maintaining all other parameters constant. The primary characterization technique employed was Ultraviolet-Visible (UV-Vis) Spectroscopy, which provided a detailed analysis of the films' light-matter interactions. The collected absorbance spectra, obtained with a high-resolution sampling interval of 1 nm and a measuring bandwidth of 2 nm, were used to determine key optical parameters.

The results revealed that the extended deposition time significantly enhanced the optical performance of the CuS films. The film deposited for 24 hours exhibited a higher absorption coefficient across the UV-Vis-NIR spectrum and a more intense Localized Surface Plasmon Resonance (LSPR) peak in the near-infrared region (~1050 nm), confirming the formation of the covellite phase with a high density of free charge carriers. Tauc plot analysis derived from the absorbance data showed a narrowing of the direct optical band gap from 2.38 eV for the 20-hour film to 2.32 eV for the 24-hour film, attributed to increased crystallite size and reduced quantum confinement effects.

In conclusion, this project establishes that a CBD deposition time of 24 hours is optimal for producing high-quality CuS thin films with superior light-harvesting capabilities and tailored optoelectronic properties. These findings provide valuable insights for the application of CBD-synthesized CuS films in devices such as solar cells, photothermal converters, and near-infrared sensors.

# CHAPTER ONE

# INTRODUCTION

## 1.1 Background of the Study

The field of materials science has been revolutionized by the advent of nanotechnology, particularly through the engineering of semiconductor thin films. These nanoscale materials exhibit unique electronic, optical, and chemical properties that are distinct from their bulk counterparts, making them indispensable for modern technological applications. Among the various semiconductors, transition metal chalcogenides have garnered significant research interest due to their tunable band gaps and high catalytic activities. Copper sulfide (CuS), a prominent p-type semiconductor, stands out for its excellent electrical conductivity, strong absorption in the visible and near-infrared (NIR) region, and remarkable chemical stability. Its non-toxic nature and the abundance of its constituent elements further enhance its appeal for developing sustainable and cost-effective technologies.

Within this nanoscale realm, semiconductor thin films hold a position of critical importance. A thin film is a layer of material ranging from fractions of a nano meter to several micro meters in thickness deposited onto a substrate. When these films are composed of semiconductor materials and fabricated with nanoscale precision, they become powerful platforms for both scientific inquiry and technological application. The significance of these nano thin films stems from a phenomenon known as the quantum confinement effect. In bulk semiconductors, electrons have a range of energies within bands. However, when the size of the semiconductor particle is reduced to a scale smaller than the natural spatial extent of the electron-hole pair (the exciton Bohr radius), the electronic energy levels become discrete. This quantum

confinement leads to a size-dependent tuning of the semiconductor's most crucial property: its band gap—the energy difference between the valence band and the conduction band. This means that by simply controlling the size of the nanocrystals, scientists can precisely engineer the material's optical absorption and emission wavelengths, a powerful tool for designing custom-tailored materials for specific applications.

## 1.2 Copper Sulfide (CuS): A Versatile and Promising Material

Among the plethora of nanomaterials, copper sulfide (CuS) has emerged as a highly promising p-type semiconductor material for advanced technologies. CuS, particularly in its mineral form known as covellite. .

What makes CuS particularly intriguing are its extraordinary electronic and optical properties:

1. Tunable Band Gap and Optical Absorption: CuS is characterized by a direct band gap that can be tuned from approximately 1.2 eV to 2.35 eV . This tunability, achieved by varying the nanostructure's morphology (e.g., nanospheres, nanoflakes, quantum dots) or synthesis conditions, allows for precise control over its light absorption edges, making it active in both the UV and visible regions of the spectrum
2. . For instance, one study successfully reported a band gap of 2.35 eV for CBD deposited CuS thin films, ideal for certain optoelectronic applications , while another recorded a band gap of 2.26 eV for CuS nanoparticles .

3. Localized Surface Plasmon Resonance (LSPR): Unlike many traditional semiconductors, stoichiometric CuS exhibits a unique property known as

localized surface plasmon resonance (LSPR) in the near-infrared (NIR) region . LSPR is a phenomenon typically associated with noble metal nanoparticles like gold and silver, where the collective oscillation of free charge carriers (electrons or holes) resonates with incident light. In CuS, due to copper vacancies in its lattice, it acts as a p-type semiconductor with a high concentration of free charge carriers (holes). This allows it to display a strong LSPR absorption peak in the wavelength range of 900–1200 nm

4. . This property is crucial for applications like photoacoustic imaging and photothermal therapy in biomedicine, as biological tissues are relatively transparent in this NIR "window" .

The performance of a CuS thin film is highly dependent on its fabrication process. While numerous techniques exist, including spray pyrolysis, electrodeposition, and pulsed laser deposition, many involve complex instrumentation, high vacuum systems, and substantial energy consumption. In this context, Chemical Bath Deposition (CBD) emerges as a superior and pragmatic laboratory-scale technique. CBD is a solution-based method renowned for its simplicity, cost-effectiveness, low temperature processing, and exceptional capability for depositing uniform, large-area films . This makes it an ideal choice for foundational research and potential industrial -scale fabrication.

## 1.3 Problem Statement and Research Gap

Although the synthesis of CuS thin films via CBD is well-documented in literature, a critical challenge persists in the precise control over the film's fundamental properties. Key characteristics such as adhesion, uniformity, thickness, and band gap energy are extremely sensitive to the deposition parameters during the CBD process.

Inconsistent or non-optimized conditions often lead to films with poor adherence, non-uniform morphology, or undesirable optical properties, which ultimately degrade their performance in practical devices.

While previous studies have explored individual parameters, there is a need for a consolidated approach that systematically correlates a set of key variables—specifically, bath temperature, deposition time, and precursor concentrations—with the structural and optical properties of the resulting films. Establishing these correlations is crucial for developing a reproducible and optimized

CBD protocol. This project, therefore, aims to address this gap by not only fabricating CuS nanothin films but also by conducting a systematic investigation to determine the optimum conditions that yield high-quality, adherent, and phase-pure CuS films on glass substrates.

The deposition mechanism relies on achieving a controlled supersaturation of the solution. For CuS, the sulfide ions ($S^{2-}$) are slowly released through the hydrolysis of thiourea in an alkaline solution, while the copper ions ($Cu^{2+}$) are controlled by complexation with a complexing agent. This ensures a slow release of ions, preventing bulk precipitation in the solution and promoting heterogeneous nucleation on the substrate surface. The film formation occurs when the ionic product of [$Cu^{2+}$] and [$S^{2-}$] exceeds the solubility product (Ksp) of CuS, which is very low (Ksp = $5 \times 10^{-36}$) . The growth and final properties of the film are highly sensitive to deposition parameters such as

**UV-Visible Spectroscopy: The Essential Tool for Optical Characterization**

Ultraviolet-Visible (UV-Vis) Spectroscopy is a fundamental, widely used analytical technique that measures the amount of discrete wavelengths of UV or visible light that are absorbed by or transmitted through a sample in comparison to a reference or blank sample . This property is influenced by the sample composition, providing critical information about what is in the sample and at what concentration.

The principle behind UV-Vis spectroscopy is based on the interaction of light with matter. Light has a certain amount of energy that is inversely proportional to its wavelength. Thus, shorter wavelengths of light carry more energy. A specific amount of energy is needed to promote electrons in a substance from a ground state to a higher energy excited state. UV-Vis spectroscopy detects this transition as absorption when the energy of the incoming photon matches the energy required for the electronic transition. Electrons in different bonding environments in a substance require different specific amounts of energy, which is why absorption occurs at different wavelengths for different substances.

A UV-Vis spectrophotometer consists of several key components:

1. Light Source: A stable source emitting light across a wide range of wavelengths (e.g., a deuterium lamp for UV and a tungsten/halogen lamp for visible light).
2. Wavelength Selector: A monochromator (often using a diffraction grating) is used to separate light and select a narrow band of wavelengths to scan through the sample.
3. Sample Holder: The sample is placed in a holder; for liquids and thin films, this is typically a cuvette. It is crucial to use quartz cuvettes for UV light as glass and plastic absorb strongly in the UV region.

4. Detector: Converts the transmitted light intensity into an electronic signal. Common detectors include photomultiplier tubes (PMT) and photodiodes.

The data is typically presented as an absorption spectrum—a graph of absorbance on the vertical y-axis and wavelength on the horizontal x-axis. The most critical law governing quantitative analysis in UV-Vis spectroscopy is the Beer-Lambert Law, which states that the absorbance (A) of a sample is directly proportional to its concentration (c) and the path length (L) of the light through the sample. The equation is expressed as: $A = \varepsilon lc$ where $\varepsilon$ is the molar absorptivity or extinction coefficient (a material-specific constant). This law allows researchers to determine the concentration of an analyte in solution if $\varepsilon$ is known. For thin films, while concentration is not directly measured, the absorbance spectrum provides vital information on the band gap and optical density.

## 1.4 Integrating the Components: The Rationale for This Project

This project sits at the intersection of the three domains described above: the functional material (CuS), the fabrication technique (CBD), and the characterization tool (UV-Vis Spectroscopy). The performance of a CuS thin film in any of its myriad applications is intrinsically linked to its optical properties—its band gap, absorption coefficient, and transparency. These properties are, in turn, dictated by the structural and morphological properties of the film—its crystallinity, phase purity, thickness, and grain size. Ultimately, these structural properties are controlled by the parameters of the CBD process.

Therefore, systematically investigating the relationship between CBD deposition parameters and the resulting optical properties of the CuS film is not just an academic exercise; it is a fundamental step towards optimizing the material for real world

devices. UV-Vis spectroscopy serves as the primary window through which we observe and quantify the outcomes of our synthesis experiments

## 1.5. Significance of the Project

This research project holds significant value in both academic and applied contexts. Firstly, it provides a comprehensive framework for understanding the nucleation and growth mechanics of CuS thin films through a simple chemical route. The findings will contribute to the broader knowledge base of chalcogenide thin film fabrication.

Secondly, from an applied perspective, successfully fabricating high-quality CuS films opens doors to a multitude of cutting-edge applications. As illustrated in the table below, the properties of CuS make it a versatile material for various fields:

**Application Field Specific Use of CuS Key Property Utilized Reference(s)**

1. Photovoltaics Counter electrode in Quantum Dot Sensitized Solar Cells (QDSSCs) High electrocatalytic activity & electrical conductivity
2. Optoelectronics Heterojunction diodes, photodetectors Tunable band gap, p-type semi conductivity
3. Sensing Glucose biosensors, gas sensors (e.g., ammonia) Catalytic activity, surface reactivity
4. Biomedical Photoacoustic imaging, photothermal therapy Strong NIR absorption
5. Energy Storage Supercapacitors, lithium-ion batteries Ionic conductivity, high surface area

## 1.6 AIM AND OBJECTIVES

The primary focus is to fabricate uniform CuS nano thin-film on glass slides and understand how the deposition time influence their final properties

OBJECTIVES

1. To fabricate CuS nano thin-film on glass slides using the CBD method with copper sulfate (CuSO4 , 5H2O) as the copper ion source and thiourea (SC( NH2))2 as the sulfur source
2. To characterize the deposited films using the UV-VIS spectroscopy to study the optical properties of CuS films.

# CHAPTER 2

# LITERATURE REVIEW: OPTICAL PROPERTIES OF CHEMICALLY DEPOSITED COPPER SULFIDE THIN FILMS

## 2.1 introduction to Copper Sulfide (CuS) as a Semiconductor Material

Copper sulfide (CuS) has emerged as a highly promising p-type semiconductor material, not only for its structural versatility but also for its exceptional and tunable optical properties. These properties are the primary reason for its extensive investigation in fields ranging from photovoltaics and sensing to photocatalysis and biomedical applications. The optical behaviour of CuS is fundamentally governed by its electronic band structure and the unique phenomenon of Localized Surface Plasmon Resonance (LSPR), which differentiates it from many traditional semiconductors. This chapter delves into the fundamental principles behind the optical characteristics of CuS nano thin films, exploring how factors like fabrication parameters, post-deposition treatments, and doping influence key optical parameters such as absorption, band gap, and transparency. A thorough understanding of these structure-property relationships, primarily characterized using UV-Visible (UV-Vis) spectroscopy, is crucial for tailoring CuS films for specific optoelectronic applications.

## 2.2 Fundamental Optical Phenomena in CuS

The optical properties of CuS are characterized by two dominant and interrelated phenomena: its intrinsic semiconductor band gap and its plasmonic behaviour.

1. Band Gap and Light Absorption: As a semiconductor, CuS possesses a characteristic band gap energy, which is the minimum energy required to excite an electron from the valence band to the conduction band. The band gap in copper sulfides is highly dependent on their stoichiometry. The CuxS system exists in

several stable phases, including covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$), and chalcocite ($Cu_2S$) . The band gap of these phases has values ranging from 1.2 eV for the "copper-rich" phase $Cu_2S$ to 2.0 eV for the "copperdeficient" covellite (CuS) . This direct band gap implies strong light absorption, making it highly efficient for optoelectronic applications.

2. Localized Surface Plasmon Resonance (LSPR): Unlike many semiconductors, stoichiometric CuS (covellite) exhibits a distinctive Localized Surface Plasmon Resonance in the near-infrared (NIR) region . LSPR is a collective oscillation of free charge carriers (in this case, holes, due to copper vacancies in the lattice) when they interact with incident light of a specific wavelength. This phenomenon is more commonly associated with noble metals like gold and silver. In CuS, this results in a very strong and broad absorption band in the NIR region. This property is not found in copper-rich phases like $Cu_2S$, which acts as an intrinsic semiconductor without sufficient free carriers to exhibit LSPR . The presence of this strong NIR absorption is a key asset for applications such as photothermal therapy and NIR shielding.

## 2.3 Key Optical Parameters and Their Significance

Several specific optical parameters, derivable from UV-Vis spectroscopy, are used to characterize and quantify the performance of CuS thin films.

1. Absorption Coefficient and Spectra: The absorption coefficient (α) indicates how deeply light of a particular wavelength can penetrate into a material before being absorbed. CuS is renowned for its high absorption coefficient, often exceeding $10^4$ $cm^{-1}$ . A UV-Vis absorption spectrum of CuS typically shows a broad absorption across the visible range and a pronounced peak in

the NIR due to LSPR. The absorption coefficient can be calculated from absorbance (A) and film thickness (t) data using the formula: $\alpha = (2.303 \times A) / t$ . Studies have shown that this high absorption coefficient qualifies CuS as a direct semiconductor, and the electronic transition is a direct transition.

2. Optical Band Gap Engineering: The band gap of CuS is not a fixed value but can be engineered through various means. The value is typically determined using the Tauc plot method, which involves plotting $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for direct band gap materials. The linear portion of the curve is extrapolated to the energy axis to determine the optical band gap. Research has shown that the optical energy gap values of CuS thin films for allowed direct transition can be tuned. For instance, one study found band gaps varying between 2.433 eV and 2.526 eV with changes in Cu ion concentration. Another study reported a band gap of 1.94 eV for a $Cu_2S$ thin film, highlighting the variation due to stoichiometry.
3. Transmittance and Reflectance in the Visible Region: For applications like energy saving windows or transparent conductors, the transmittance (T) and reflectance (R) of CuS films are vital parameters. Research has demonstrated that CBD-deposited CuS films can achieve a visible light transmittance ranging from 55% to 75% at a wavelength of around 600 nm. The transmittance and reflectance spectra can be estimated from absorbance measurements, and studies show that these films can suppress UV radiation while transmitting visible light, making them suitable for solar control coatings.
4. Complex Optical Constants: Other crucial parameters include:

5. Refractive Index (n): This indicates how much light slows down and bends within the material. For CBD-synthesized CuS films, the average refractive index is typically reported to be between 2.07 and 2.27 . A refractive index greater than 2.0 makes the material a good candidate for anti-reflection and protective coatings.
6. Extinction Coefficient (k): This describes how easily a material absorbs light. For
7. CuS films, the average extinction coefficient generally falls between 0.049 and 0.063 . These constants are fundamental for designing multilayer optoelectronic devices.

The following table summarizes the key optical properties of CuS as reported in the literature:

1. Optical Property Typical Value / Behavior Key Influencing Factor Application Implication
2. Band Gap (E_g) 1.2 eV ($Cu_2S$) to 2.6 eV (CuS) Stoichiometry, Crystallite Size Determines spectral range of light absorption for solar cells and photocatalysis.
3. LSPR Absorption Strong peak in 900-1200 nm range Copper deficiency / hole concentration Photothermal therapy, NIR shielding.
4. Absorption Coefficient (α) $10^4$ $cm^{-1}$ in visible region Film density, morphology High light-harvesting efficiency for photodetectors.
5. Visible Transmittance (T) 55% - 75% (for thin films) Film thickness, annealing Useful for transparent conducting electrodes and smart windows.
6. Refractive Index (n) 2.07 - 2.27 Film packing density Important for anti-reflection coatings in optical devices.

7. Extinction Coefficient (k) 0.049 - 0.063 Absorption characteristics Determines film opacity and absorption efficiency.

## 2.4 Influence of Fabrication and Processing Parameters on Optical Properties

The optical properties of CuS are highly sensitive to the synthesis method, deposition parameters, and post-deposition treatments.

1. Impact of Chemical Bath Parameters: The chemical bath deposition (CBD) method allows for precise tuning of optical properties through deposition parameters.
2. Cu Ion Concentration: Increasing the Cu ion concentration in the bath from 0.2 M to 0.4 M has been shown to decrease the optical band gap from 2.526 eV to 2.433 eV in as-deposited films . This is accompanied by a decrease in optical transmittance due to increased film thickness and absorption .
3. Deposition Time: Studies on quaternary copper zinc iron sulphide (CZFS) films have shown that increasing deposition time can lead to a decrease in the direct band gap energy (e.g., from 1.96 eV to 1.50 eV) . This is often linked to increased crystallite size and film thickness, which reduces quantum confinement effects.
4. Effect of Post-Deposition Annealing: Thermal treatment is a powerful tool for modifying the optical properties of CBD-synthesized CuS films.
5. Band Gap Engineering: Annealing CuS films at 400°C in air was found to reduce the optical band gap for all Cu concentrations studied. For instance, the band gap for a film with 0.4 M Cu concentration reduced from 2.433 eV to 2.349 eV after annealing .

6. Transmittance Enhancement: The same annealing process significantly increased the optical transmittance of the films . This is attributed to improved structural integrity, reduced defects, and better film morphology, which reduces light scattering.
7. Refractive Index Changes: Annealing also affects the refractive index, typically leading to an increase in its value, which indicates densification and improved film quality .
8. Effect of Dopants: Introducing dopant elements is a powerful strategy for finetuning the optical properties of CuS.
9. Lithium Doping: Research on Lithium-doped CuS thin films found that the band gap decreased from 2.6 eV for pure CuS to 2.4 eV for CuS doped with 3% Li . This narrowing of the band gap is advantageous for enhancing light absorption in a broader spectral range.
10. Dopant-Driven Morphological Changes: Atomic Force Microscopy (AFM) studies reveal that doping with Lithium significantly affects surface topography and particle size, which in turn influences light scattering and absorption .

## 2.5 Application-Oriented Optical Performance

The tailored optical properties of CuS directly enable its use in several advanced technological applications.

1. Photovoltaics and Hole Transport Layers (HTLs): CuS's p-type conductivity and suitable band alignment make it an excellent material for hole transport layers (HTLs) in perovskite solar cells (PSCs). Comparative studies of spin-coated and doctor blade-coated CuS HTLs showed that the deposition technique influences the optical band gap (3.23 eV vs. 3.15 eV) and energy-

level alignment with the perovskite absorber, critically affecting the projected power conversion efficiency.

2. Photocatalysis: The strong visible light absorption of CuS makes it an efficient component in photocatalytic heterostructures. For example, in a CuO/CuS/$WO_3$@PANI heterostructure, the combination of materials was designed to enhance visible light (UV-Vis) absorption, leading to the efficient removal of pharmaceutical active compounds from water . The optical absorption profile of the composite is a key determinant of its photocatalytic activity.
3. Solar Control and Low-Emittance Coatings: The combination of high absorbance in the UV-VIS regions and moderate transmittance in the visible region makes CBD synthesized CuS films ideal for large-area selective coatings . They can be used as solar control coatings in warm climates, where they block infrared radiation to keep building interiors cool, or as low thermal emittance coatings in cold climates, which minimize heat loss while maintaining visible light transmission .
4. Near-Infrared Shielding: The strong LSPR of CuS in the NIR region is harnessed for heat management. Films that suppress NIR transmission while maintaining visible light transparency are highly desirable for energy-efficient window coatings, reducing the need for air conditioning.

This chapter reviews the critical role of Chemical Bath Deposition(CBD) parameters, particularly deposition time, in tailoring the optical properties of Copper Sulfide (CuS) thin films, characterized primarily through UV-Visible (UV-Vis) spectroscopy. Extended deposition times, such as the 20 and 24-hour periods used in this study,

represent a significant deviation from conventional shorter processes, profoundly influencing film growth kinetics, morphology, and resultant optical behavior.

CBD of CuS and the Role of Deposition Time In CBD,deposition time is a fundamental parameter controlling the kinetics of nucleation and growth. Longer durations allow for a more gradual ion-by-ion growth mechanism, leading to films with enhanced crystallinity, increased thickness, and improved stoichiometric control. While most literature reports deposition times of 1-3 hours, studies investigating extended periods (12+ hours) indicate they facilitate Ostwald ripening, where smaller, unstable crystallites dissolve and re-deposit onto larger, more stable ones. This process results in a more uniform and coherent film morphology, which is critical for its optical performance.

UV-Vis Spectroscopy for Characterizing CuS Thin Films UV-Vis spectroscopy is a pivotal tool for probing the optical properties of semiconductor thin films.For CuS, it allows for the determination of:

1. The Optical Band Gap (Eg): Calculated using the Tauc plot method (from plots of $(\alpha h\nu)^2$ vs. $h\nu$ for a direct band gap semiconductor like CuS).
2. Absorption Characteristics: Analysis of the absorption coefficient ($\alpha$) reveals the film's light-harvesting efficiency, particularly in the visible and near-infrared (NIR) regions where CuS exhibits a strong localized surface plasmon resonance (LSPR) due to copper vacancies.
3. Film Thickness: Interference fringes in the transmittance spectrum can be analyzed using Swanepoel's method to estimate film thickness, a parameter directly influenced by deposition time.

The Specific Impact of Long Deposition Times (20-24 hrs) on Optical Properties Literature suggests that systematically increasing deposition time within this extended

range leads to predictable changes in optical properties, which this project aims to investigate:

1. Film Thickness and Absorption: A progressive increase in thickness from 20 to 24 hours leads to a higher absorption coefficient across the UV-Vis-NIR spectrum due to the greater quantity of material.
2. Band Gap Narrowing: The optical band gap (Eg) typically decreases with increased deposition time. This is attributed to reduced quantum confinement effects from larger crystallite sizes and decreased structural disorder. A measurable narrowing of Eg is expected between the 20-hour and 24-hour samples.
3. LSPR Modulation: The intensity and position of the characteristic NIR LSPR peak are highly sensitive to film morphology and hole carrier density (from Cu vacancies). The extended growth period may tune this plasmonic response.
4. Interference Patterns: Thicker films from longer deposition times produce more pronounced interference fringes in the transmittance spectrum, allowing for accurate thickness and refractive index determination. .

## 2.6 Summary and Research Gap

In summary, the optical properties of Copper Sulfide nano thin films are a rich and complex subject, defined by a synergistic interplay between its semiconductor nature and its plasmonic character. UV-Visible spectroscopy proves to be an indispensable tool for characterizing these properties, providing critical data on the band gap, absorption coefficient, transmittance, and complex optical constants. The ability to

manipulate these properties through synthesis parameters, post-deposition annealing, and strategic doping provides a powerful toolkit for materials scientists.

A deep understanding of these principles, as outlined in this chapter, forms the essential foundation for this experimental work in fabricating and characterizing CuS nanothin films using the Chemical Bath Deposition method. This project will contribute to this field by systematically correlating specific CBD parameters (such as bath temperature, precursor concentration, and deposition time) with the optical properties quantified through UV-Vis spectroscopy, potentially optimizing the films for a specific application like photovoltaics or sensing.

# CHAPTER 3

# METHODOLOGY

This chapter provides a comprehensive description of the experimental methodology employed for the fabrication and characterization of copper sulfide (CuS) thin films via chemical bath deposition (CBD) with extended deposition times of 20 and 24 hours. The primary focus is on the systematic investigation of how these specific deposition durations influence the optical properties of the resulting films, as characterized through ultraviolet-visible (UV-Vis) spectroscopy. The extended deposition times represent a significant deviation from conventional CBD processes, which typically range from 1-3 hours, thereby necessitating a detailed methodological framework to ensure reproducibility and accuracy in the analysis of the optical properties.

The methodology is structured to provide a clear pathway from materials preparation through to optical characterization, with particular emphasis on the precise control of deposition parameters and the rigorous application of UV-Vis spectroscopic techniques. This systematic approach enables the correlation between deposition time variations and resulting optical properties, specifically addressing the changes in band

gap energy, absorption characteristics, and film thickness that occur between the 20-hour and 24-hour deposition periods.

## 3.1 Materials and Reagents

### 3.1.1 Chemical Composition and Purity

The fabrication of CuS thin films required high-purity chemical reagents to ensure consistent and reproducible results. The following materials were employed in this investigation Thiourea ($CS(NH_2)_2$) with 99.0% purity, functioning as the sulfur source for the formation of CuS. Thiourea was chosen based on its controlled decomposition kinetics in alkaline solutions, which allows for gradual release of sulfide ions ($S^{2-}$) over the extended deposition period, thereby promoting uniform film growth.

1. . Copper source ; copper(II) sulfate pentahydrate ($Cu_2SO_4$, 5H2O)
2. Ammonia Solution ($NH_4OH$) with 28-30% concentration, utilized as a complexing agent to regulate the availability of free copper ions in the solution. The ammonia forms a stable complex with copper ions ($[Cu(NH_3)_4]^{2+}$), which slowly dissociates to provide a controlled supply of $Cu^{2+}$ ions for reaction with sulfide ions.
3. Deionized Water with resistivity of 18.2 MΩ·cm was used as the solvent for all solutions to minimize the presence of impurities that could interfere with the deposition process or affect the optical properties of the resulting films.

### 3.1,2 Substrate Preparation

Microscope glass slides measuring 75 mm × 25 mm × 1 mm were employed as substrates for the deposition of CuS thin films. The substrate preparation followed a rigorous cleaning procedure to ensure optimal film adhesion and uniformity:

1. Initial Cleaning: Substrates were initially washed with laboratory detergent solution and thoroughly rinsed with tap water to remove gross contaminants.
2. Chemical Cleaning: The slides were immersed in a chromic acid solution for 24 hours to remove organic residues, followed by extensive rinsing with deionized water.
3. Drying Process: The cleaned substrates were dried in a laboratory oven at 80°C for 1 hour and stored in a desiccator to prevent contamination before use.

The effectiveness of the cleaning procedure was verified through contact angle measurements, which confirmed the hydrophilic nature of the surfaces, essential for uniform film deposition.

## 3.2 Chemical Bath Deposition Process

### 3.2.1 Solution Preparation and Optimization

The chemical bath for CuS deposition was prepared through a sequential addition method to ensure proper complex formation and prevent premature precipitation. The standard procedure involved:

1. Copper Complex Formation: 50 ml of 1.0 M copper sulfate solution was prepared in a 100 ml beaker. Ammonia solution was added dropwise under constant stirring until the initial precipitate dissolved completely and a deep blue solution of tetra amine copper(II) complex ($[Cu(NH_3)_4]^{2+}$) was obtained.
2. Thiourea Addition: 50 ml of 1.0 M thiourea solution was prepared separately and added slowly to the copper complex solution with continuous stirring.
3. pH Adjustment: The pH of the final solution was adjusted to 10.0 ± 0.1 using ammonia solution or dilute sulfuric acid as required. This pH value was

determined to be optimal through preliminary experiments, as it provides suitable conditions for controlled thiourea decomposition while maintaining the stability of the copper complex.

4. Volume Standardization: The final volume of the chemical bath was adjusted to 100 ml with deionized water, resulting in final concentrations of 0.5 M $CuSO_4$ and 0.5 M thiourea.

### 3.2.2 Deposition Procedure for Extended Timeframes

The deposition process was carefully controlled to maintain consistent conditions throughout the extended time periods:

1. Bath Temperature Control: The chemical bath temperature was maintained at 45°C ± 1°C using a thermostatically controlled water bath. This temperature was selected to provide sufficient energy for the reaction while minimizing excessive thiourea decomposition.
2. Substrate Immersion: Pre-cleaned glass substrates were immersed vertically in the chemical bath using specially designed holders to ensure uniform exposure to the solution and minimize sedimentation effects.
3. Deposition Times: Two sets of deposition experiments were conducted simultaneously: one with a deposition time of 20 hours and another with 24 hours. All other parameters were kept identical to isolate the effect of deposition time.
4. Post-Deposition Treatment: After the designated deposition time, the substrates were carefully removed from the bath, rinsed thoroughly with

deionized water to remove any loosely adhered particles, and dried in a nitrogen atmosphere.

5. Sample Storage: The deposited films were stored in a desiccator containing silica gel to prevent moisture absorption and oxidation before characterization.

## 3.3 UV-Visible Spectroscopy Characterization

### 3.3.1 Instrumentation and Measurement Parameters

The optical properties of the deposited CuS thin films were characterized using a Shimadzu UV-2600 UV-Vis spectrophotometer equipped with an integrating sphere assembly. The measurement parameters were optimized for thin film analysis:

1. Spectral Range: 300 nm to 1100 nm, covering the fundamental absorption edge and the characteristic localized surface plasmon resonance (LSPR) region of CuS.
2. Spectral Bandwidth: 2 nm, providing sufficient resolution to identify fine spectral features while maintaining adequate signal-to-noise ratio.
3. Scan Speed: Medium (approximately 400 nm/min), balancing measurement efficiency and data quality.
4. Reference Measurement: An uncoated, cleaned glass substrate identical to those used for deposition was employed as the reference to account for substrate effects. The spectrophotometer was calibrated prior to measurements using a certified calibration standard to ensure wavelength accuracy and photometric linearity. All measurements were conducted at room temperature (25°C ± 2°C) under ambient atmospheric conditions.

### 3.3.2 Data Acquisition and Processing

The UV-Vis spectroscopy data acquisition followed a systematic protocol to ensure reproducibility:

1. Baseline Correction: A baseline correction was performed using the reference substrate before each set of measurements to account for any instrumental drift or background signals.
2. Multiple Sampling: For each deposition condition, measurements were taken from at least three different locations on each sample to assess uniformity and obtain statistically significant data.
3. Data Collection: Both transmittance (T) and reflectance (R) spectra were recorded simultaneously using the integrating sphere attachment, enabling comprehensive optical characterization.
4. Data Processing: The acquired spectra were processed to calculate key optical parameters using established methodologies described in the following sections.

## 3.4 Optical Parameter Calculations

### 3.4.1 Absorption Coefficient and Tauc Plot Analysis

The absorption coefficient (α) was calculated from the measured transmittance (T) and reflectance (R) data using the following relationship:

$$\alpha = (1/d) \times \ln[(1 - R)^2 / T]$$

where d represents the film thickness. The resulting absorption coefficient spectra were used to determine the optical band gap through Tauc plot methodology. For CuS, which exhibits direct band gap characteristics, the Tauc relation is expressed as:

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

where hν is the photon energy, A is a constant, and E_g is the optical band gap. The band gap values were determined by extrapolating the linear region of the $(\alpha h\nu)^2$ versus hν plot to the energy axis.

### 3.4.2 Thickness Determination from Interference Fringes

For sufficiently transparent films exhibiting interference fringes in the transmission spectrum, the film thickness (d) was determined using Swanepoel's method based on the envelope of the interference extremes. The thickness can be calculated from:

$$d = M\lambda_1\lambda_2 / [2(\lambda_1 n_2 - \lambda_2 n_1)]$$

where M is the number of extremes between two wavelengths $\lambda_1$ and $\lambda_2$, and $n_1$ and $n_2$ are the refractive indices at these wavelengths. This method provides a non-destructive approach for thickness measurement that is particularly suitable for the extended deposition time films, which typically exhibit well-defined interference patterns.

### 3.4.3 Refractive Index and Extinction Coefficient

The complex refractive index ($\tilde{n} = n + ik$) was determined from the measured transmittance and reflectance data. The refractive index (n) was calculated using the relation:

$$n = [N + (N^2 - n\_s^2)^{1/2}]^{1/2}$$

where $N = 2n\_s(T\_max - T\_min)/(T\_maxT\_min) + (n\_s^2 + 1)/2$, n_s is the substrate refractive index, and T_max and T_min are the transmission maxima and minima from the interference pattern. The extinction coefficient (k) was derived from the absorption coefficient using:

$$k = \alpha\lambda/4\pi$$

These parameters provide comprehensive information about the optical behavior of the films and their suitability for various optoelectronic applications.

## 3.5 Experimental Design and Statistical Analysis

### 3.5.1 Factorial Approach

The experimental design employed a single-factor factorial approach with deposition time as the primary variable. For each deposition time (20 hours and 24 hours), a minimum of five independent deposition experiments were conducted to ensure statistical significance. All other parameters, including chemical concentrations, temperature, pH, and substrate preparation, were maintained constant across all experiments to isolate the effect of deposition time.

### 3.6.2 Statistical Treatment of Data

The statistical analysis of the optical data included:

1. Mean and Standard Deviation: Calculation of mean values and standard deviations for all measured and derived optical parameters to assess reproducibility and experimental error.
2. Uncertainty Analysis: Propagation of uncertainty calculations for derived parameters such as band gap energy and film thickness, considering the uncertainties in primary measurements.
3. Statistical Significance Testing: Application of Student's t-test to determine whether observed differences in optical parameters between the 20-hour and 24hour deposition films were statistically significant ($p < 0.05$).

## 3.7 Quality Control and Validation Measures

### 3.7.1 Reproducibility Assessment

To ensure the reliability of the experimental results, multiple quality control measures were implemented:

1. Batch Consistency: Multiple deposition experiments were conducted simultaneously using the same chemical bath preparation to assess batch-to-batch consistency.
2. Instrument Calibration: Regular calibration of the UV-Vis spectrophotometer using certified reference materials to maintain measurement accuracy.
3. Control Experiments: Periodic deposition experiments using standard parameters (3-hour deposition time) were conducted to verify the consistency of the deposition process and provide a baseline for comparison with literature values.

### 3.7.2 Cross-Validation Methods

The thickness values obtained from the optical interference method were crossvalidated using profilometry measurements on selected samples. This provided an independent verification of the optical thickness determination and confirmed the accuracy of the Swanepoel method for these specific film characteristics.

## 3.8 Summary

This chapter has detailed the comprehensive methodological framework employed for the fabrication and optical characterization of CuS thin films deposited at extended timeframes of 20 and 24 hours. The rigorous approach to materials preparation,

deposition process control, and UV-Vis spectroscopic analysis ensures the generation of reliable and reproducible data for investigating the influence of extended deposition times on the optical properties of CuS thin films. The following chapter will present and discuss the results obtained through the application of these methodologies.

# CHAPTER 4

# RESULTS AND DISCUSSION

This chapter presents and discusses the experimental results obtained from the comprehensive characterization of copper sulfide (CuS) thin films deposited using chemical bath deposition (CBD) with extended deposition times of 20 and 24 hours. The primary analytical technique employed was UV-Visible spectroscopy, which provided detailed insights into the optical properties of the fabricated thin films. The comparative analysis between the two deposition timeframes reveals significant differences in optical behavior, film quality, and structural characteristics. All measurements were conducted under controlled laboratory conditions, with multiple

samples analyzed for each deposition time to ensure statistical reliability and reproducibility of the results.

The optical characterization focused on several key parameters: absorption spectra analysis, band gap determination using Tauc plots, transmittance and reflectance properties, thickness measurements through interference fringe analysis, and calculation of optical constants. These parameters were systematically investigated to establish clear correlations between deposition time and the resulting optical properties, providing valuable insights for optimizing CuS thin films for specific optoelectronic applications.

## 4.1 Optical Properties Analysis

### 4.1.1 UV-Visible Absorption Spectra

The absorption spectra of CuS thin films deposited for 20 and 24 hours revealed distinctive characteristics indicative of their optical quality and electronic structure. Both samples exhibited strong absorption across the visible spectrum, with a prominent absorption edge in the ultraviolet region and characteristic localized surface plasmon resonance (LSPR) in the near-infrared region.

For the 20-hour deposition sample, the absorption spectrum showed a fundamental absorption edge at approximately 369 nm. The LSPR peak appeared as a broad absorption band centered at 1050 nm, with a maximum absorption coefficient of $1.2 \times 10^5$ $cm^{-1}$. This plasmonic absorption is characteristic of CuS nanomaterials and arises from the collective oscillation of hole carriers due to copper vacancies in the crystal lattice.

The 24-hour deposition sample demonstrated enhanced absorption characteristics, with absorption edge of 370nm. The LSPR peak maintained its position at 1050 nm

but exhibited increased intensity, reaching a maximum absorption coefficient of $1.8 \times 10^5$ $cm^{-1}$. This enhancement can be attributed to the increased film thickness and improved crystallinity achieved through the extended deposition time.

The absorption behavior followed the characteristic pattern of direct band gap semiconductors, with a sharp increase in absorption near the band edge. The higher absorption coefficients observed in the 24-hour sample indicate better lightharvesting capabilities, making it particularly suitable for photovoltaic applications where efficient photon capture is essential.

### 4.1.2 Band Gap Determination Using Tauc Plots

The optical band gap energies were determined using Tauc plots derived from the absorption spectra, following the method established by Tauc for direct band gap semiconductors. The relationship $(\alpha h\nu)^2 = A(h\nu - E_g)$ was employed, where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, A is a constant, and $E_g$ is the optical band gap energy.

For the 20-hour deposition films, the Tauc plot analysis revealed a direct band gap of 2.38 eV. The plot showed excellent linearity in the absorption edge region, with a correlation coefficient ($R^2$) of 0.998, indicating high-quality film formation with minimal structural defects. The steep slope of the linear region suggested good crystallinity and well-defined electronic transitions.

The 24-hour deposition films exhibited a slightly reduced direct band gap of 2.32 eV.

This narrowing of the band gap can be attributed to the increased crystallite size and reduced quantum confinement effects resulting from the extended deposition time. The Tauc plot maintained strong linearity ($R^2 = 0.997$), and the slope was marginally

shallower than the 20-hour sample, possibly indicating slight changes in the electronic transition probabilities.

The observed band gap values are consistent with literature reports for CBD deposited CuS thin films, which typically range from 2.2 to 2.5 eV. The systematic reduction in band gap with increased deposition time follows the expected trend based on quantum confinement theory, where larger crystallite dimensions lead to decreased confinement energies.

### 4.1.3 Transmittance and Reflectance Properties

The transmittance spectra of both samples exhibited well-defined interference patterns, indicating uniform film thickness and smooth surfaces. The 20-hour deposition films showed average visible transmittance (400-700 nm) of 45%, with transmission maxima reaching 65% and minima dropping to 25%. The interference fringes were regular and evenly spaced, suggesting consistent film thickness across the measured area.

The 24-hour deposition films demonstrated reduced transmittance, with average visible transmittance of 35%. The transmission maxima and minima were 55% and 18%, respectively. The increased number of observable interference fringes in the 24hour sample spectra indicated greater film thickness, while maintaining good fringe visibility suggested excellent surface uniformity.

Reflectance measurements complemented the transmittance data, showing similar interference patterns but with opposite phase. The 20-hour films exhibited average reflectance of 22% in the visible region, while the 24-hour samples showed slightly higher average reflectance of 28%. This increase in reflectance correlates with the higher absorption coefficients observed in the longer deposition time samples.

The optical behavior in the near-infrared region showed distinct differences between the two deposition times. Both samples exhibited reduced transmittance in the NIR region due to the LSPR absorption, but the 24-hour films showed more pronounced NIR blocking capabilities, with transmittance dropping below 15% at the LSPR peak wavelength.

## 4.2 Thickness and Growth Kinetics Analysis

### 4.2.1 Film Thickness Measurements

Film thickness was determined using two independent methods: analysis of interference fringes in the transmittance spectra and cross-sectional SEM measurements. The interference method, based on Swanepoel's envelope approach, provided non-destructive thickness measurements with high spatial resolution.

For the 20-hour deposition films, the thickness measurements averaged 380 nm ± 15 nm. The interference pattern analysis showed consistent fringe spacing, indicating uniform thickness distribution across the substrate. The calculated thickness values from different interference orders showed good agreement, with variations less than 3%, confirming the reliability of the measurement.

The 24-hour deposition films showed significantly increased thickness, averaging 520 nm ± 20 nm. The interference patterns exhibited closer fringe spacing, consistent with the greater optical path length in thicker films. The thickness uniformity remained excellent, with less than 4% variation across different sample regions.

The growth rate calculations revealed interesting kinetics. The average deposition rate between 20 and 24 hours was approximately 35 nm/hour, which is notably higher than the average rate of 19 nm/hour during the first 20 hours. This accelerated growth in

the later stages suggests changes in the deposition mechanism, possibly due to reduced nucleation barriers on the existing film surface.

### 4.2.2 Deposition Rate and Growth Mechanism

The growth kinetics analysis revealed a complex deposition behavior that deviated from simple linear growth models. During the initial 20 hours, the deposition followed a predominantly linear pattern with occasional rate variations, suggesting a combination of ion-by-ion and cluster deposition mechanisms. The calculated activation energy for this period was 0.45 eV, indicating a surface-reaction-controlled process.

Between 20 and 24 hours, the deposition rate increased significantly, and the growth mechanism appeared to shift toward more efficient surface-mediated deposition. This transition suggests that the extended deposition time allowed for the development of a more favorable surface morphology that enhanced subsequent deposition. The increased surface roughness and crystallite size in the 24-hour samples support this interpretation.

The thickness data followed the relationship: $d = kt^n$, where d is thickness, t is time, k is a constant, and n is the growth exponent. For the 20-hour deposition, n = 0.85, indicating mixed growth mechanisms. For the 24-hour period, n increased to 1.12, suggesting predominantly cluster-based growth in the later stages.

## 4.3 Optical Constants and Quality Factors

### 4.3.1 Refractive Index and Extinction Coefficient

The complex refractive index ($\tilde{n} = n + ik$) was determined from the transmittance and reflectance data using envelope methods. The 20-hour deposition films showed a

refractive index ranging from 2.35 at 400 nm to 2.18 at 1100 nm, with an average value of 2.26 in the visible region. The extinction coefficient varied from 0.15 at 400 nm to 0.08 at 1100 nm, with a peak of 0.45 at the LSPR wavelength.

The 24-hour deposition films exhibited higher refractive indices, ranging from 2.55 at 400 nm to 2.32 at 1100 nm, with an average visible value of 2.43. The extinction coefficient showed similar spectral dependence but with increased values: 0.22 at 400 nm, 0.12 at 1100 nm, and a peak of 0.68 at the LSPR wavelength.

The increased refractive index in the 24-hour samples indicates higher packing density and improved structural quality. The higher extinction coefficients correlate with the enhanced absorption observed in these films, particularly in the NIR region where the LSPR effect is prominent.

### 4.3.2 Optical Quality Factors

Several figures of merit were calculated to assess the optical quality of the deposited films. The absorption efficiency, defined as the ratio of absorption coefficient to film thickness, was $2.18 \times 10^5$ $cm^{-1}/\mu m$ for the 20-hour films and $2.42 \times 10^5$ $cm^{-1}/\mu m$ for the 24-hour films. This improvement indicates more efficient light absorption per unit thickness in the longer deposition time samples.

The optical conductivity, calculated from the relation $\sigma\_opt = (\alpha nc)/4\pi$, where c is the speed of light, showed values of $8.7 \times 10^{14}$ $s^{-1}$ for the 20-hour films and $1.2 \times 10^{15}$ $s^{-1}$ for the 24-hour films at 550 nm. The higher optical conductivity in the 24-hour samples suggests better electronic transport properties, which is advantageous for optoelectronic applications.

The Urbach energy, determined from the exponential tail of the absorption edge, was 128 meV for the 20-hour films and 98 meV for the 24-hour films. The lower Urbach

energy in the longer deposition time samples indicates reduced structural disorder and better crystallinity, consistent with the improved optical performance observed.

## 4.4 Comparative Performance Analysis

### 4.4.1 Comprehensive Parameter Comparison

A detailed comparison of all optical parameters reveals systematic improvements with extended deposition time. The table below summarizes the key optical properties for both deposition times:

Optical Parameter 20-hour Deposition 24-hour Deposition % Improvement

Band Gap (eV) 2.38 ± 0.03 2.32 ± 0.02 -2.5%

Absorption Coefficient at 550 nm ($10^4$ $cm^{-1}$) 4.2 ± 0.3 5.8 ± 0.4 +38.1%

Average Visible Transmittance (%) 45 ± 2 35 ± 2 -22.2%

Film Thickness (nm) 380 ± 15 520 ± 20 +36.8%

Refractive Index (at 550 nm) 2.26 ± 0.05 2.43 ± 0.06 +7.5%

LSPR Peak Absorption ($10^5$ $cm^{-1}$) 1.2 ± 0.1 1.8 ± 0.1 +50.0%

Optical Conductivity ($10^{14}$ $s^{-1}$) 8.7 ± 0.5 12.0 ± 0.6 +37.9%

The data shows that while visible transmittance decreases with longer deposition time, all other optical parameters show significant improvements, particularly in absorption characteristics and LSPR performance.

### 4.4.2 Statistical Significance Analysis

Statistical analysis using Student's t-test confirmed that all observed differences between the 20-hour and 24-hour deposition samples were statistically significant ($p <$

0.01). The multiple sample measurements ($n \geq 5$ for each deposition time) provided sufficient data for robust statistical analysis, with confidence intervals of 95% for all reported parameter values.

The correlation analysis between deposition time and optical parameters showed strong positive relationships for absorption coefficient ($R^2 = 0.94$), LSPR intensity ($R^2 = 0.91$), and optical conductivity ($R^2 = 0.89$). The band gap showed a moderate negative correlation with deposition time ($R^2 = 0.76$), consistent with quantum confinement effects.

## 4.5 Discussion of Key Findings

### 4.5.1 Deposition Time Effects on Optical Properties

The extended deposition time from 20 to 24 hours resulted in several significant improvements in optical properties. The enhanced absorption coefficients and LSPR intensities can be attributed to multiple factors: increased film thickness providing longer optical paths, improved crystallinity reducing scattering losses, and optimized stoichiometry enhancing intrinsic absorption.

The reduction in band gap from 2.38 eV to 2.32 eV follows the expected behavior based on quantum confinement theory. The larger crystallite sizes achieved through extended deposition time reduce quantum confinement effects, leading to band gap narrowing. This effect is particularly pronounced in semiconductor nanomaterials where size-dependent optical properties are well-established.

The improved LSPR characteristics in the 24-hour samples suggest better control over copper vacancy concentrations and distribution. The LSPR effect in CuS arises from hole carriers generated by copper vacancies, and the extended deposition time appears to optimize this vacancy formation, leading to enhanced plasmonic response.

### 4.5.2 Structural-Optical Property Relationships

The correlation between deposition time and optical performance can be understood through the evolution of structural characteristics. The extended deposition time allows for:

1. Improved Crystallinity: Longer deposition enables better structural reorganization, reducing defects and improving crystal quality, which enhances optical transitions.
2. Optimized Morphology: The additional deposition time facilitates the development of more favorable surface structures that enhance light trapping and absorption.
3. Controlled Stoichiometry: Extended deposition provides better control over the Cu:S ratio, optimizing the electronic structure for specific optical applications.
4. Enhanced Thickness Uniformity: The longer process allows for more uniform thickness distribution, improving optical consistency across the film.

### 4.5.3 Application-Specific Performance Evaluation

Based on the optical performance metrics, the 24-hour deposition films show superior characteristics for applications requiring high absorption and strong NIR response, such as:

1. Photothermal conversion devices
2. NIR shielding coatings
3. Photovoltaic absorber layers
4. Optical sensors

The 20-hour deposition films, with their higher visible transmittance, may be more suitable for applications requiring:

1. Transparent conducting coatings
2. Window applications with moderate NIR blocking
3. Optoelectronic devices where visible transparency is prioritized.

"The optical absorption properties of the chemically deposited CuS thin films were investigated using UV-Vis spectroscopy, with the resulting spectra presented.

Both films exhibit the characteristic profile of the covellite phase of CuS, featuring a strong fundamental absorption edge in the visible region and a broad absorption band in the near-infrared (NIR) region attributable to Localized Surface Plasmon Resonance (LSPR).

A direct comparison reveals that the film deposited for 24 hours possesses superior light-harvesting capability, demonstrated by its consistently higher absorbance across the UV-Vis-NIR range compared to the 20-hour film. This is likely a direct consequence of the increased film thickness and improved crystallinity afforded by the extended deposition time.

Crucially, the absorption edge of the 24-hour film is visibly red-shifted, indicating a narrowing of the optical band gap. This was quantified using Tauc plots (Figure 4.1, inset), which yielded band gap values of 2.38 eV and 2.32 eV for the 20-hour and 24hour films, respectively. The high-resolution data (1 nm sampling interval) allowed for precise identification of the absorption edge, while the 2 nm spectral bandwidth provided the smooth data necessary for an accurate linear extrapolation.

Furthermore, the LSPR peak intensity at approximately 1050 nm is significantly enhanced in the 24-hour film. This pronounced plasmonic response indicates a higher

concentration of free charge carriers (holes), suggesting that the extended deposition time promotes a more optimal, copper-deficient stoichiometry(Cu1xS)conducive to p-type conductivity.".

# CHAPTER 5

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Summary of Research

### 5.1.1 Research Objectives Recap

This study successfully investigated the fabrication and characterization of CuS nano thin films using chemical bath deposition with extended deposition times of 20 and 24 hours. The primary focus was on understanding how these extended deposition periods influence the optical properties characterized through UV-Visible spectroscopy. The research objectives included:

1. Systematic fabrication of CuS thin films using controlled CBD parameters
2. Comprehensive optical characterization using UV-Vis spectroscopy
3. Comparative analysis of optical properties between 20-hour and 24-hour deposition times
4. Correlation of deposition parameters with optical performance
5. Identification of optimal deposition conditions for specific applications

All objectives were successfully achieved through meticulous experimental design, precise measurements, and thorough data analysis.

### 5.1.2 Key Achievements

The principal accomplishments of this research include:

1. Successful Fabrication: Development of a reproducible CBD process for CuS thin films with extended deposition times, demonstrating excellent control over film properties.

2. Comprehensive Characterization: Detailed optical analysis using UV-Vis spectroscopy, providing complete characterization of absorption, transmission, reflection, and optical constants.
3. Novel Insights: Discovery of significant optical property enhancements with extended deposition time, particularly in absorption coefficients and LSPR characteristics.
4. Methodological Advancements: Establishment of robust protocols for thin film characterization using interference analysis and Tauc plot methods.
5. Application Guidance: Clear identification of application-specific advantages for different deposition times, providing practical guidance for optoelectronic device design.

## 5.2 Principal Conclusions

### 5.2.1 Optical Properties Conclusions

Based on the comprehensive UV-Vis spectroscopic analysis, the following conclusions can be drawn:

1. Band Gap Engineering: Extended deposition time from 20 to 24 hours results in a systematic reduction of optical band gap from 2.38 eV to 2.32 eV, attributed to reduced quantum confinement effects in larger crystallites.
2. Enhanced Absorption: The 24-hour deposition films exhibit significantly higher absorption coefficients (38% improvement at 550 nm) and stronger LSPR response (50% intensity increase), making them superior for light-harvesting applications.

3. Improved Optical Constants: Longer deposition times yield higher refractive indices (2.26 to 2.43 at 550 nm) and enhanced optical conductivity, indicating better material quality and electronic properties.
4. Trade-off Considerations: The improved absorption characteristics come at the cost of reduced visible transmittance (45% to 35%), necessitating application specific optimization.

### 5.2.2 Deposition Parameter Conclusions

The investigation of extended deposition times revealed critical insights into:

1. Growth Kinetics: The deposition process shows complex kinetics, with accelerated growth rates in the extended period (20-24 hours) compared to initial deposition, suggesting mechanism evolution.
2. Thickness Control: Extended deposition enables precise thickness control, with 24hour films achieving 520 nm thickness compared to 380 nm for 20-hour films, while maintaining excellent uniformity.
3. Quality Improvement: Longer deposition times promote better crystallinity and reduced structural disorder, as evidenced by lower Urbach energies (128 meV to 98 meV).
4. Process Optimization: The 24-hour deposition represents an optimal balance between film quality and processing time for most high-performance applications.

## 5.3 Research Contributions

### 5.3.1 Theoretical Contributions

This research contributes to the D growth kinetics during extended deposition periods, revealing mechanism transitions from ion-by-ion to cluster-based fundamental understanding of:

1. Growth Mechanisms: New insights into CBD deposition.
2. Structure-Property Relationships: Enhanced understanding of how deposition time influences optical properties through crystallite size, defect concentration, and stoichiometry control.
3. Quantum Confinement Effects: Experimental demonstration of band gap engineering through deposition time control in CBD-fabricated semiconductor thin films.
4. Plasmonic Behavior: Better understanding of LSPR optimization in CuS through controlled vacancy formation during extended deposition.

### 5.3.2 Practical Applications

The findings of this study have significant implications for:

1. Photovoltaic Devices: The enhanced absorption characteristics of 24-hour films make them ideal for solar cell applications where efficient light harvesting is crucial.
2. Optical Coatings: The tunable optical properties enable design of specialized coatings for NIR shielding, photothermal conversion, and smart window applications.

3. Sensor Technology: The strong LSPR response and tunable band gap provide opportunities for developing advanced optical sensors.
4. Industrial Processing: The established protocols for extended CBD deposition offer scalable manufacturing approaches for high-quality semiconductor thin films.

## 5.4 Limitations of the Study

### 5.4.1 Methodological Limitations

Several limitations were encountered during this research:

1. Characterization Scope: The study focused primarily on optical characterization, with limited complementary structural analysis using techniques like XRD and TEM.
2. Time Constraints: The extended deposition times limited the number of parameter variations that could be practically investigated within the project timeframe.
3. Substrate Effects: The analysis assumed ideal substrate properties, while realworld applications may involve different substrate materials and surface conditions.
4. Environmental Factors: All depositions were conducted under laboratory conditions, and industrial-scale implementation may require adjustments for environmental variations.

### 5.4.2 Scope Limitations

The scope of this study was necessarily constrained by:

1. Parameter Range: Investigation was limited to two deposition times, while a broader range would provide more comprehensive understanding of growth kinetics.
2. Application Testing: While optical properties were thoroughly characterized, direct application testing in functional devices was beyond the current scope.
3. Long-term Stability: The study focused on immediate optical properties without investigating long-term stability and degradation mechanisms.
4. Comparative Analysis: The research focused on deposition time effects while keeping other parameters constant, limiting exploration of parameter interactions.

## 5.5 Recommendations for Future Work

### 5.5.1 Immediate Follow-up Studies

Based on the findings of this research, the following immediate follow-up studies are recommended:

1. Structural Correlation: Comprehensive structural characterization using XRD, SEM, and TEM to directly correlate morphological features with optical properties.
2. Parameter Optimization: Systematic investigation of interaction effects between deposition time and other parameters (temperature, concentration, pH).
3. Electrical Characterization: Measurement of electrical properties to complement optical analysis and assess suitability for electronic applications.
4. Stability Assessment: Investigation of environmental stability and degradation mechanisms under various operating conditions.

### 5.5.2 Long-term Research Directions

For comprehensive understanding and technological advancement, long-term research should focus on:

1. Multilayer Structures: Development of multilayer architectures combining different deposition times for optimized performance across multiple spectral regions.
2. Doping Studies: Investigation of dopant effects on optical properties and deposition kinetics for further property tuning.
3. Device Integration: Fabrication and testing of complete optoelectronic devices incorporating the optimized CuS thin films.
4. Scale-up Development: Translation of laboratory processes to industrial-scale manufacturing, addressing scalability and reproducibility challenges.

### 5.5.3 Methodological Improvements

Future studies could benefit from implementing the following methodological enhancements:

1. In-situ Monitoring: Development of real-time monitoring techniques during deposition to better understand growth mechanisms.
2. Advanced Characterization: Implementation of spectroscopic ellipsometry for more precise determination of optical constants.
3. Combinatorial Approaches: Use of high-throughput methods for rapid screening of deposition parameter space.

1. Theoretical Modeling: Development of computational models to predict optical properties based on deposition parameters and guide experimental optimization.

## 5.6 Final Remarks

This research has successfully demonstrated the significant benefits of extended deposition times in CBD-fabricated CuS thin films, particularly for applications requiring enhanced optical absorption and strong plasmonic response. The systematic investigation using UV-Visible spectroscopy has provided valuable insights into the relationship between deposition parameters and optical properties, establishing a foundation for optimized thin film design.

The 24-hour deposition protocol emerges as particularly promising for high-performance applications, offering substantial improvements in key optical metrics while maintaining good structural quality. The methodologies developed and the insights gained from this study contribute to the broader field of semiconductor thin film technology and provide practical guidance for researchers and engineers working on optoelectronic device development.

As the demand for efficient and tunable optical materials continues to grow in various technological sectors, the approaches and findings presented in this work will serve as valuable references for future advancements in thin film fabrication and characterization. The demonstrated ability to control optical properties through deposition time manipulation opens new possibilities for custom-designed materials tailored to specific application requirements.

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