Synthesis And Characterization Of Cus Thin Film For Solar Cell Applications

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Abstract
Chemical bath deposition method were Applied for the synthesis of CuS films, with a focus on their structural and optical properties relevant to solar cell applications. Deposition parameters such as temperature, bath composition, and deposition time were systematically varied to optimize the film quality. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses confirmed the formation of well-structured, uniform CuS films, revealing a favourable crystalline structure and morphology. Optical characterization through UV-Vis spectroscopy demonstrated significant light absorption in the visible range, with calculated bandgap values indicating potential for efficient light harvesting.

Keywords: Optical properties, solar energy, morphology, photovoltaic devices and bandgap.

1. Introduction

Chemical bath deposition of CuS films offers a cost-effective and scalable approach for producing materials suitable for solar cell applications. The development of efficient, cost-effective, and sustainable energy sources has become a global priority, with solar energy emerging as one of the most promising solutions. Thin-film solar cells, which use semiconductor materials to convert sunlight into electricity, offer potential for enhancing efficiency while reducing material consumption. Among the various semiconductor materials being investigated, copper (II) sulphide stands out due to its favourable optical and electrical properties, making it suitable for photovoltaic applications. Chemical Bath Deposition (CBD) is a widely-used technique for fabricating thin films due to its simplicity, low cost, and ability to produce uniform coatings over large areas. In the context of solar cell applications, copper (II) sulphide CuS thin films deposited via Chemical Bath Deposition (CBD) have garnered attention due to their direct bandgap, high absorption coefficient, and p-type conductivity, which are key features for improving solar energy conversion efficiency. The bandgap energy has been equal to or greater than that due to the absorption of light from semiconductor materials. The semiconductors of chalcoginide nanostructures, such as ZnS, CdO,TiO2, CoS and CuS have a potential applications in photovoltaic cells, gas sensors, LEDs, photocatalytic activity , the chalcoginides, CuS nanostructures are p-type semiconductor materials with the narrow band gap of 2.4 eV at room temperature and are very useful in photo thermal, photoconductive and optoelectronic applications**[1].** Covellite copper sulfide, a member of the transition metal chalcogenides from the IB-VIA group, has recently gained significant interest due to its potential applications as a solar radiation absorber and a cathode material in lithium rechargeable batteries. CuS thin films have also attracted attention for their use in solar control coatings and dye-sensitized solar cells. **[2].**
The hydrothermal method offers an efficient, cost-effective, and straightforward approach for synthesizing crystalline materials. Nanostructured copper sulfide stands out as a promising p-type semiconductor due to its unique chemical and physical characteristics. As a result, it is utilized in various applications, including lithium-ion battery cathodes, solar radiation absorbers, solar control coatings, nonlinear optical materials, superionic conductors, catalysts, and low-temperature superconductors**[3].** This study focuses on the structural and optical properties of CuS thin films synthesized through chemical bath deposition (CBD), emphasizing their potential for use in solar cells. By understanding how deposition conditions, such as bath composition, temperature, and pH, affects the crystalline structure, morphology, and optical praperties of CuS thin films. Furthermore, exploring the interplay between structural properties and optical behaviour provides insight into the fundamental mechanisms that govern light absorption and charge carrier dynamics in CuS based thin films**[4].**

2. Experimental:

The deposition of CuS films was achieved through various methods, including chemical bath deposition (CBD), spray pyrolysis, electrodeposition, and thermal evaporation, each influencing the film's structure and

properties. Chemical bath deposition is widely used due to its simplicity and cost-effectiveness, where factors like bath temperature, pH, and precursor concentration control the film thickness, grain size, and surface roughness. Spray pyrolysis offers better control over stoichiometry and is suitable for large-area coatings, while electrodeposition provides precise thickness control but requires optimized electrolyte conditions to avoid secondary phases **[5].** In the chemical bath deposition process, 20 ml of distilled water and 6 ml of ammonia (NH_3) solution were gradually added to a mixture containing 10 ml of 1.0M cuprous chloride ($CuCl_2$), 10 ml of 1.0M thiourea (CH_4N_2S), 6 ml of triethanolamine ($C_6H_{15}NO_3$), and 6 ml of 0.1M ethylenediaminetetraacetic acid ($C_{10}H_{16}N_2O_8$)..Then mixture was stirred with a magnetic stirrer until when mixture get homogenous. The pH of the precursor was measured and recorded to be 10.14 which indicate that the reaction bath is the alkaline medium and the temperature was noted to be 50 ^{0}C. The glass slides were inserted vertically in to the precursor for 1 hour, 2 hours and 3 hours for samples A, B and C. Sample X serves as a regulator for all other slides. After maximum deposition time the glass slides were removed and dried, annealing of the slides was done by inserting the slides in the oven for 40 minutes at dissimilar temperatures **[6-7].**
The experimental setup is showing in the fig. 01 In the chemical bath deposition of copper may be expressed when a copper Chloride is dissolved in water, it dissociates to give copper ions and immediate precipitate of Cu^{2+} with ammonia (NH_3) to form a stable complex of copper ammonia complex $[Cu(NH_3)_4]^{2+}$.

$$CuCl_2 \longrightarrow Cu^{2+} + 2Cl^-$$

$$Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$$

Similarly when a thiourea is dissolved in water, it dissociates to give hydrogen sulphide, further dissociation to provide S^{2-} ions.

$$NH_2CSNH_2 + 2H_2O \longrightarrow H_2S + CO_2 + NH_3$$

$$H_2S \longrightarrow H_2\uparrow + S^{2-}$$

Once S^{2-} ions are released, they react with Cu^{2+} ions from the copper-ammonia complex to form copper sulfide (CuS) as a black precipitate.

$$[Cu(NH_3)_4]^{2+} + S^{2-} \longrightarrow CuS + 4NH_3$$

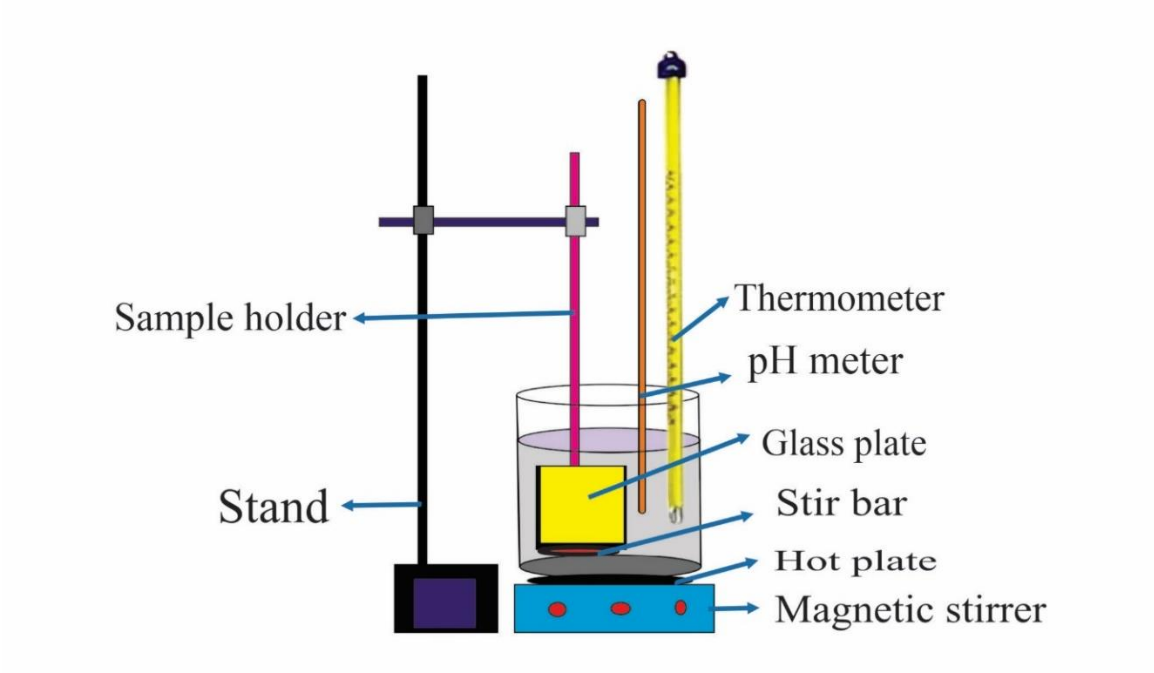

Fig: 01- The apparatus for Chemical bath deposition of CuS thin film

Table: 01- Deposition of cupper (II) sulphide thin film

Samples	Harden time in mins	Deposition time in hours	Harden temp in ^{0}C
X	0.0	0.0	0^0C
A	40.0	1.0	65^0C
B	40.0	2.0	80^0C
C	40.0	3.0	95^0C

3. Result and discussion:-

The vibrational properties, crystallinity and crystal phase of the Copper (II) Sulphide thin films were studied by micro Raman spectroscopy using Argon green laser at a wavelength of 514 nm. The film thickness was measured by using Spectrophotometer. X-ray diffraction patterns were carried out to analysis crystal structure of the synthesized Copper (II) Sulphide thin films by means of X-Pert propan analytical instrument with X-ray wave- length of 1.5 Å. Optical properties of the films were examined with the help of UV–Visible spectroscopy. Electrochemical and super capacitor property of the films was analyzed by cyclic voltammetry using electrochemical instrument. Current density–Voltage curves were recorded using Keithley 4200A-SCS semiconductor characterization system under the light illumination of 100 mw from Xenon lamp. Electrochemical impedance spectra were performed using µ-autolab type III Potentiostat / Galvanostat at an applied AC potential of 10 mV in the frequency range from 10 kHz to 100 mHz **[8 - 9].**

The results of copper sulphide (CuS) synthesis show that structural, morphological, and chemical properties are highly dependent on synthesis conditions. X-ray Diffraction (XRD) patterns confirm the formation of the covellite CuS phase, with sharper peaks indicating improved crystallinity at higher synthesis. Scanning Electron Microscopy images reveal a layered or plate-like morphology, with grain sizes increasing as bath temperatures or deposition times rise, contributing to smoother surfaces. Energy Dispersive X-ray Spectroscopy (EDS) verifies the Cu ratio, ensuring phase consistency, though slight deviations may suggest the presence of secondary phases or Cu vacancies, which can alter electrical conductivity. X-ray Photoelectron Spectroscopy (XPS) analysis shows a combination of Cu(I) and Cu(II) oxidation states, particularly on surface-exposed regions, affecting the film's catalytic and electrical behaviour. Overall, the findings demonstrate that optimizing parameters such as temperature, precursor concentration, and deposition time is essential to enhance the structural integrity and surface properties of CuS films, making them suitable for applications in sensors, photovoltaics, and catalysis **[10-11].**

3.1 Effect of bath temperature:-

The bath temperature plays a crucial role in the synthesis and properties of copper sulphide (CuS) films, influencing their morphology, crystallinity, and performance. Higher bath temperatures generally enhance the crystallinity by providing sufficient energy for atom diffusion, leading to larger grain sizes and improved phase purity, as confirmed by X-ray Diffraction (XRD) analysis. Scanning Electron Microscopy (SEM) reveals that elevated temperatures result in smoother surfaces with reduced porosity, whereas lower temperatures may produce rougher, more granular textures. However, excessively high temperatures can promote unwanted oxidation or secondary phases, compromising the material's stability. Additionally, bath temperature affects the deposition rate, with higher temperatures accelerating film growth, though this may also introduce stress and defects. Optimizing the bath temperature is crucial for producing uniform and high-quality CuS films suitable for applications in sensors, photovoltaics, and electrochemical devices. The X-ray diffraction patterns of electrodeposited CuS thin films on ITO substrates, synthesized using a bath composition of 0.1 M copper sulfate, 0.01 M sodium thiosulfate, and 0.05 M ethylenediaminetetraacetic acid at varying temperatures from 65ºC to 95ºC, are presented in Fig. 02 (x, y, z). The diffraction patterns indicate that the deposited films exhibit a polycrystalline nature with a cubic structure and a lattice constant of (a=5.373 Å).

Several diffraction peaks of CuS are detected at 2θ values of 14.34, 16.12, 23.92, 28.35, 29.80, 35.15, and 38.62, corresponding to the lattice planes (110), (200), (218), (310), (221), (399), and (330), respectively. The identified peaks in the diffraction patterns were indexed, and the interplanar spacing ("d") values were determined and compared with standard reference values.. The bath temperature affects the properties of the film and a higher temperature is needed to obtain good films **[12].** CuS films deposited at bath temperatures below 50ºC were found to be poorly crystalline, as shown by the broad X-ray diffraction peaks seen in Figure 2x. However, as the bath temperature increased above 65ºC, these peaks started to increase, indicating the quality of the films.The study found that higher temperatures could produce well crystallized films. It can be seen from Figure 2y that higher deposition temperatures produce better films with improved crystallinity as can be seen from the strong diffraction peaks seen in Figure 2y. CuS thin films deposited at 80ºC were found to be intrinsically crystalline. The current rate will be higher as the bath temperature increases above 80ºC.

Higher current rates result in films with rough texture and poor adhesion. Film thickness increases linearly with bath temperature, and it is clear that bath temperature affects ion release. In the X-ray diffraction pattern of the CuS film deposited in a hot water bath (80ºC), the height of the (110) peak shows a sharper peak. **[13-14].** The sharpness and intensity of the peaks indicate the degree of crystallinity, which improves with higher synthesis temperatures and longer deposition times. XRD can also detect secondary phases, such as Cu_2S, if stoichiometry is not well-controlled during synthesis. Broad peaks in the pattern may suggest nanocrystalline or amorphous components, which can arise from low-temperature deposition methods. Additionally, the average crystallite size can be calculated, providing insight into the grain structure. This structural information is essential for optimizing CuS thin films for applications where crystallinity and phase purity directly affect performance, such as in **photovoltaics** and catalysis **[15-16].**

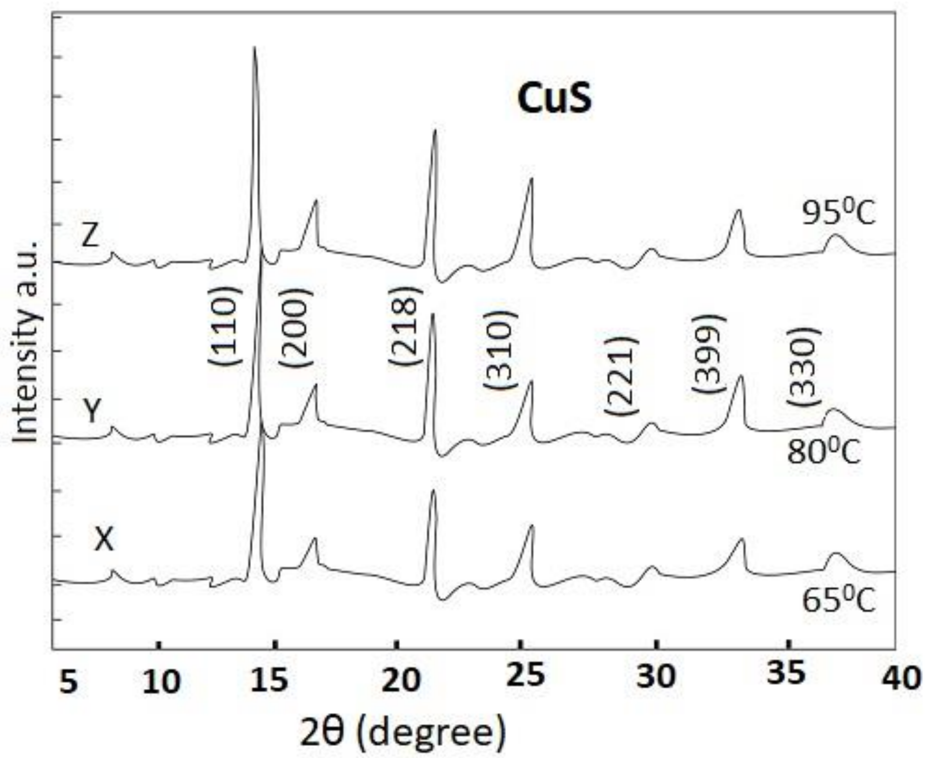

Fig 02- The X-ray diffraction analysis of CuS thin films was conducted at varying temperatures: (X) 65ºC, (Y) 80ºC, and (Z) 95ºC.

3.2 Surface analysis and microstructure:-

The surface analysis and microstructure of copper sulphide (CuS) are critical in understanding its properties for applications like sensors, catalysts, and energy storage. CuS typically exhibits a hexagonal crystal structure with layered, plate-like morphology, contributing to its anisotropic electrical conductivity and catalytic performance. Techniques such as X-ray Diffraction (XRD) confirm phase purity, while Scanning Electron Microscopy (SEM) reveals surface features like grain size and porosity. X-ray Photoelectron Spectroscopy (XPS) provides insights into surface oxidation and the Cu (II) state, which affects stability and reactivity. When looking at the surface microstructures of the CuS thin films made through dip coating and chemical bath deposition under an optical microscope, it's clear that both methods result in the substrates being well-coated by the films. The dark spots seen on the surfaces may be a sign of nucleation or overgrowth **[17].**

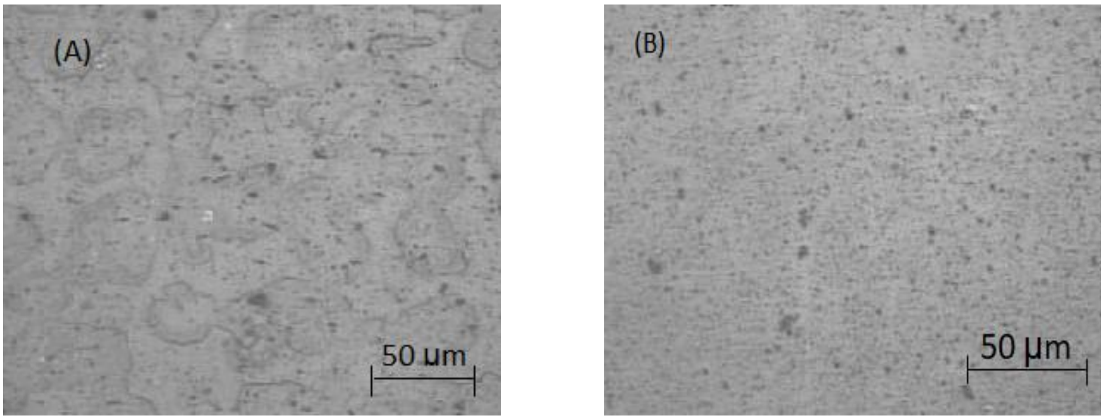

Fig.03- The surface microstructures of CuS thin films synthesized using (A) chemical bath deposition and (B) dip coating were examined under an optical microscope.

Conclusion:

The study demonstrates that by controlling deposition parameters, it is possible to tailor the structural and optical properties of CuS thin films to optimize their performance in photovoltaic devices. The X-ray diffraction analysis reveals that the CuS films exhibit a polycrystalline structure with a preferred orientation along the (110) plane. The results suggest that CBD can effectively produce CuS thin films with desirable properties for solar energy applications, paving the way for further research into their integration in photovoltaic devices.

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