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TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF COPPER ZINC SULPHIDE THIN FILMS

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Abstract

In this study, ternary copper zinc sulphide (CZS) thin films were produced using the chemical bath deposition (CBD) technique at 30 0° C. The aim was to investigate the influence of deposition concentrations($x = 0.2, 0.4, 0.6, and\ 0.8$), *and durations (10, 12, 14, and 16 hours) on the transmission electron microscopy (TEM) characteristics of the prepared CZS thin films. The process involved using an ammonia solution to adjust the pH and triethanolamine (TEA) as a complexing agent. The CBD technique is recognized as a cost-effective and straightforward method, as reported by numerous researchers. The deposited films exhibited crystalline grains that were ellipsoidal in nature and randomly distributed across the substrate, with sizes varying (from 0.2 to 0.6) according to the deposition parameters. The influence of deposition time on the morphological characteristics has also been explored. These findings confirm that the CBD-deposited films can be modified from amorphous to polycrystalline for various device applications.*

Keywords: *concentrations, CZS, thin film, morphology, chemical bath deposition.*

Introduction

The physical form and structure of a material, known as its morphology, can significantly impact its characteristics and behavior. From a materials science standpoint, a material morphology can influence its mechanical, thermal, electrical, and optical properties, among other attributes [1–4]. For instance, the absorption and emission properties of nano-films can be optimized for optoelectronic applications by controlling their sizes and shapes [1]. A lot of work has been done over the years to create high-quality materials for real-world uses. Many research groups are now studying copper zinc sulphide (CZS) as a semiconducting material since it is easy to modify its band gap and morphological properties for device applications [5–9]. Accordingly, CZS is a promising ternary semiconductor material for the production of solar cells, light-emitting diodes (LEDs), plasma display devices, lasers, and sensors [6,8]. The material is widely accessible due to the presence of copper, zinc, and sulphur in the earth's crust [9]. Copper zinc sulphide thin films can be synthesized using a variety of well-defined techniques, including chemical spray pyrolysis (CSP), chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), Metal-organic chemical vapor deposition (MOCVD), solution growth technique (SGT), and electron beam evaporation (EBE) [5–10]. When metallic sulphide are prepared using the physical methods, the films' plasma-induced defect—which results from the energetic ions bombarding the film's surface—is a case of disturbance [11].

Mane and Lokhande [12], documented the advantages of chemical bath deposition (CBD) as a large area semiconductor growth technology for usage in electrical devices such as solar cells, LEDs, etc. Consequently, at low processing temperatures, the CBD can produce single-layer, multilayer, composite, nanostructure, and functionality-graded thin films with carefully controlled dimensions and unique

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topologies. CBD has rapidly expanded and is currently one of the main processing methods for the deposition of coatings and thin films for a range of applications because of its versatility [13,14]. Additionally, the CBD method has been used to fabricate binary, ternary, and quaternary thin films in recent times [3,4,15]. The deposition process allows for tailoring the material properties, making CBD thin films a subject of academic interest [16]. Likewise, the efficacy of CBD chalcogenides, their relatively simple chemistry, and the absence of environmental concerns associated with their use have piqued the curiosity of researchers globally [13,16].

Previous researches have focused on fabricating and characterizing CZS thin films using various deposition techniques. However, studies examining the morphological properties of these films using transmission electron microscopy (TEM) remain limited. The potential to engineer the morphological parameters through the deposition process has spurred interest in CZS thin films for device applications. Furthermore, CZS thin films are garnering increased attention due to their favorable performance with relatively simple chemistry and the lack of environmental concerns associated with their use. Thus, this work presents the synthesis of CZS thin films via the CBD technique and an investigation into the effects of the deposition parameters (concentration and time) on the morphological properties using TEM and the associated selected area electron diffraction (SAED).

Materials and Methods

Chemicals

To synthesis copper zinc sulphide thin films, chemicals of analytical grade were utilized, and they were used exactly as they were obtained. They include; ammonia solution (NH_4OH), copper (II) sulphate ($CuSO_4$), zinc acetate [$Zn(CH_3CO_2)_2$], thioacetamide (C_2H_5NS), triethanolamine ($C_6H_{15}NO_3$) and distilled water.

Preparation of CZS thin films

Copper zinc sulphide thin films were deposited at room temperature on glass substrates using the CBD technique. The chemical solution was prepared by dissolving each powder (copper (II) sulphate, zinc acetate, and thioacetamide) in distilled water separately. 12 ml of 0.1 M copper (II) sulphate and zinc acetate were transferred into a separate 50 ml beaker, and 5 ml of triethanolamine was introduced. Subsequently, 15 ml of thioacetamide was slowly added to the mixture. The total volume of 50 ml was achieved by adding distilled water to the solution, which was then stirred continuously to ensure the homogeneity of the solution. A pH of 7.0 was attained with the help of the ammonia solution. The final solution was stirred at room temperature for approximately 30 minutes. A clean glass substrates were vertically dipped into the bath solution for a period of 10 hours, and four ($Cu_xZn_{1-x}S$) film samples with different concentrations (x=0.2,0.4,0.6, and 0.8), were formed and categorized as a, b, c, and d. Additionaly, sample c or ($Cu_{0.6}Zn_{0.4}S$) was further subjected to four deposition periods of 10h, 12h, 14h, and 16h respectively. Finally, the glass substrates underwent washing and drying at room temperature.

Characterization of CZS thin films

Morphological characterization was performed using a TECNAI F20 high-resolution transmission electron microscope (TEM). This versatile ultra-high-resolution-transmission electron microscope is widely utilized in materials science and engineering research. Additionally, selected area electron diffraction (SAED) analysis was employed to determine the crystallinity of the deposited materials.

Results and Discussions

Literature reviews indicate that a diverse array of instruments have been employed to characterize the properties of thin films. These include techniques such as transmission electron microscopy [17], Differential thermal analysis [18], Atomic force microscopy [19], X-ray diffraction [20], Raman spectroscopy [21], Photoluminescence spectroscopy [22], Fourier transform infrared spectroscopy [9, 17], Electrical resistivity measurements [23], UV-visible spectrophotometer [24, 25], and Scanning electron microscopy [7].

Transmission electron microscopy (TEM) is an excellent tool for examining a film's nanostructure. It relies on the interaction between energetically accelerated electron beams at high voltages and the materials under investigation [26]. As the beams pass through the transmission electron microscopy column, a picture is displayed on the screen. Since electrons have a shorter wavelength than light, TEM images exhibit higher resolution and magnification compared to other microscopy techniques. As a result, this method can be used to determine the structure, crystalline and elemental composition of a given film [26]. Table 1 highlights the advantages and limitations of TEM measurements [26,27].

Table 1. Advantages and limitations of transmission electron microscopy (TEM)

Advantages of TEM	
1.	Among nano-structural tools, transmission electron microscopes boast the most powerful magnification capabilities, potentially reaching magnifications exceeding one million times.
2.	It has a wide range of applications and can be utilized in various scientific, educational, and industrial fields.
3.	It provides information on the elemental and compound structure of the material.
4.	The images are detailed and of excellent quality.
5.	It enables the observation of surface features, shape, size, and structure.
6.	It is easy to operate.
Limitations of TEM	
1.	Large and very expensive to maintain
2.	Conducting operations and analyses necessitates specialized training
3.	Samples are limited to those that are electron transparent, able to withstand the vacuum, and fit within the chamber.

The TEM images and the associated SAED patterns of the synthesized CZS thin films at different concentrations are shown in Figure 1. The TEM images reveal a mixture of nanoparticles with varying sizes within the samples. The TEM examination of Sample ‘a’ or ($Cu_{0.2}Zn_{0.8}S$) (Figure 1(a)) reveals that the grains are dispersed with fine particles of varying sizes. The grain sizes range from several micrometers to around 0.2 micrometers, depending on their location. The film also contains smaller grains that are partially bonded into clusters. It is known that the formation on a substrate occurs when the ionic product of the metallic and sulphur ions exceeds the solubility product. Consequently, the addition of copper concentration in the reaction solution leads to the alteration of the particle growth, shapes, and sizes exhibited by the deposited material [28].

The TEM images of the films made at x=0.4, 0.6 and 0.8 respectively are displayed in Figures 1(b), (c), and (d). With increasing concentrations, it was observed that the grains grew in sizes and were tightly packed with films that were not evenly distributed across the substrate and lacked a consistent pattern. This characteristic nano-crystalline structure as well as the absence of cracks within the grains show that the properties of the produced thin films were determined by the copper concentrations used for deposition. Prior research has documented comparable findings [17]. Nonetheless, such films are essential for optoelectronic device applications [18].

Figures 1(e-h) show the appropriate SAED patterns, which validate the films' crystalline nature. Thus, the SAED patterns identify several film types, including amorphous, single-crystalline, and polycrystalline ones, and provide crystallographic information about the deposited material [29]. The deposited films exhibit a thick, diffuse ring pattern in Figure 1(e), likely owing to the amorphous nature of the materials. However, Figures 1(f), (g) and (h) reveal the emergence of bright-spot-rings as the copper concentration increases, suggesting the formed films are polycrystalline with grain clusters. Similar findings for chalcogenide thin films have been reported [30]. However, this observation reinforced the XRD crystallographic analysis of CZS thin films done by Olofinjana et al. [18], which showed that manipulating the deposition parameters could potentially enhance the crystallinity of CZS thin films.

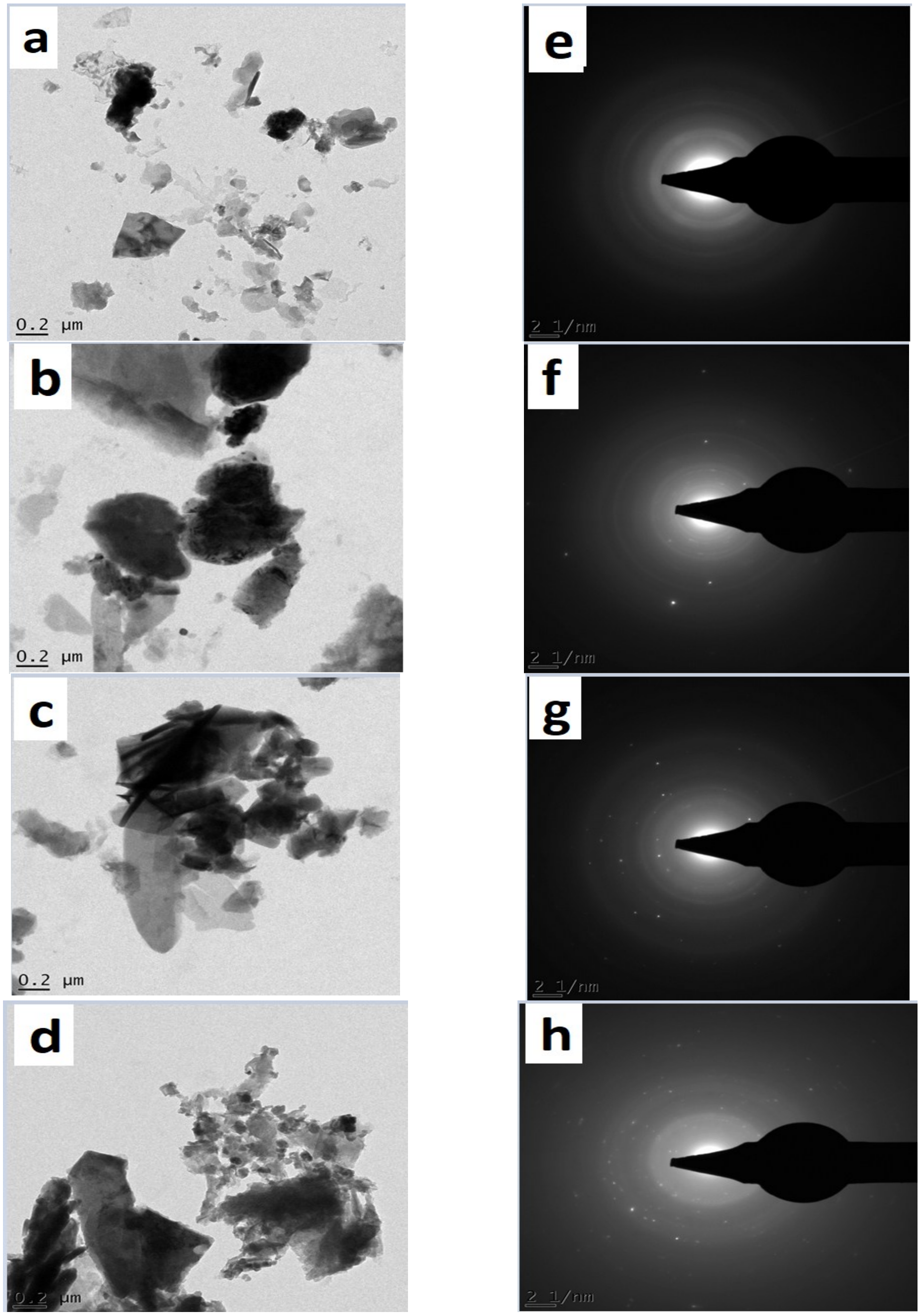

Figure 1. TEM images and SAED patterns of CZS thin films at various concentrations

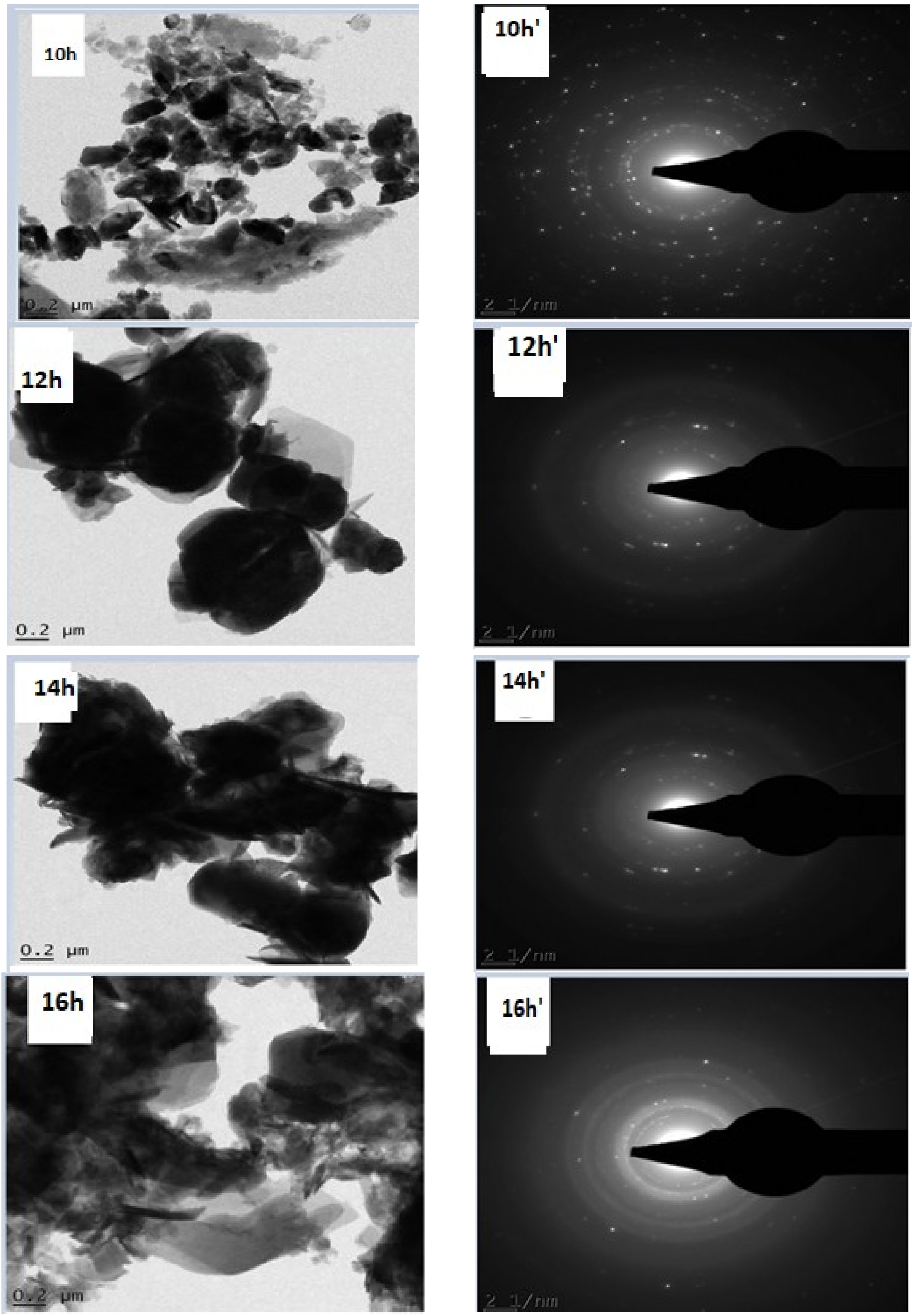

Figure 2. The TEM and SAED patterns of CZS thin films at various deposition periods

The TEM images in Figure 2 depict the deposited films at various deposition durations. The film deposited at 10 hours (Figure 2(10h) exhibits a randomly dispersed pattern of ellipsoidal nanostructures. The size of the nanocrystals constituting the layer varies from several micrometers to approximately 0.4 micrometers, contingent on the crystal's position. Moreover, the film encompasses smaller grains that are essentially aggregated into clusters. As the deposition period increases to 12 hours, the film exhibits larger grains that are randomly distributed across the substrate. The grain sizes range from 2.5 to approximately 6.0 micrometers, with an average of around 4.0 micrometers. For films deposited at 14 and 16 hours, it was observed that the smaller grains coalesce to form morphologically homogeneous clusters with particle sizes larger than 4.0 micrometers. Additionally, as the deposition time increased, the nanoparticles within the films coalesced to form a columnar growth dispersed across the substrates. Similar morphological formations have been reported in literature for CZS thin films using scanning electron microscope (SEM). The study found that weak surface forces and strong chemical bonds facilitate the agglomeration of smaller grains, leading to the formation of larger secondary grains as the deposition process progresses [2]. Hence, Figure 2(16h) shows partially dense, compact grains covering the substrates, which may be the result of an increase in nucleation rate with deposition time.

Moreover, the crystallinity of the deposited films was verified by the SAED pattern (Figure 2 (10h'-16h'). The visible Debye-Scherer ring in the images indicates that the deposited CZS thin films have grain clusters and are polycrystalline in nature [30,31] Due to these characteristics, CZS thin-films are well-suited for thin-film solar cell manufacturing [2]. Similar observation was also reported by Noriyuki et al [30].

Conclusions

The deposition of nanostructural CZS films can be produced using the CBD technique with thioacetamide as the sulphur source, providing an alternative method for depositing the material with the advantage of large-area deposition. This simple and cost-effective approach is well-suited for the large-scale production of CZS thin films.

The TEM characterization reveals that the CZS films consist of larger, randomly distributed, ellipsoidal grains with morphological structures of approximately 0.4 μm in size. The nature of the grains distribution can be employed for solar cell energy conversion applications.

The corresponding SAED patterns indicated that the deposited films exhibited a combination of polycrystalline and amorphous characteristics, which is well-suited for optoelectronic applications.

Future work should focus on the following:

Exploring alternative thin film deposition methods like sputtering and evaporation, and comparing the TEM characteristics of the resulting films.

Employing Hall Effect measurements to ascertain the carrier concentrations, Hall coefficients, and mobility characteristics within the CZS thin films.

Utilizing electroluminescence and photoluminescence analyses to uncover the luminescent characteristics of the deposited thin films.

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