COMPARATIVE STUDY OF THE PROPERTIES OF CuS THIN FILMS DEPOSITED USING DIFFERENT BATH PROCESSES

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In this work, we present the influence of the reaction time of a complex substance (trisodium citrate) with a copper source ($Cu_2SO_4 \cdot 5H_2O$) on the structural, morphological and optical properties of CuS thin films deposited at 55-70 min. using chemical bath deposition onto glass substrate. In the first process, trisodium citrate and $Cu_2SO_4 \cdot 5H_2O$ were mixed for 1 min, while the substances were mixed for 1 h. in the second process. The hexagonal structure of the deposited polycrystalline thin films with a preferred orientation along (130) was determined by the XRD technique except for the thin films deposited at 70 min. The surface roughnesses of the thin films were different from each other. The direct optical band gaps of CuS thin films obtained from the first process were found to be 2.39-2.45, whereas those of the second process were found to be 2.34-2.48 eV.

1. Introduction

Copper is stable in media and resists high temperatures. These inherent material properties make copper one of the most important materials for industrial applications. Nowadays, copper-based thin films make up a group of highly demanded materials [1]. One of these is copper sulfur (CuS) thin films. CuS thin films have chemical stability, a high absorbent coefficient, high refractive index, and transparence in the visible IR range [2]. It is well known that these properties are strongly dependent on the method used to obtain the thin films. To obtain the thin films, several methods are used by researchers. Unfortunately, these methods require rigorous experimental conditions such as high temperature, high cost, sophisticated equipment and expensive substrates [3-4]. Chemical bath deposition (CBD) offers a good alternative for fabricating thin films due to its simplicity, low processing temperature, inexpensive equipment, non-hazardous nature, reproducibility and suitability to deposit large area thin films [5-6]. The basis of this technique is to coat a substrate with a precursor solution containing the metal components in the required proportion. Several important parameters (the ratio of the precursor, the kind of substrate, the temperature and time of deposition, and bath process) can be changed in the CBD method, but in each case, careful optimization of the deposition process should be made to obtain high quality thin films. To the best of our knowledge, no one study has been conducted to compare the reaction time between the metal source and the complex substance. Therefore, the goal of this work was to determine what effect the reaction time has on the properties of the thin films.

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2. Experimental procedures

The CuS thin films were fabricated on commercial glass substrate by utilizing the CBD method. Before the deposition process, the substrates were cleaned in detergent, chromic acid and ethyl alcohol. They were then rinsed with deionized water and dried in an oven for 40 min at 100 °C. Chemical baths were prepared by two different processes. In the first process, 0.4 M, 20 ml trisodium citrate (TSC) as the complex substance and 0.5 M, 10 ml $Cu_2SO_4.5H_2O$ as the Cu source were mixed for 1 min, whereas 0.4 M, 20 ml TSC and 0.5 M, 10 ml $Cu_2SO_4.5H_2O$ were mixed for 1 h in the second process. Then, for both of these process the steps following were performed chronologically during the actual course of deposition:

• 0.5 M, 10 ml thiourea $SC(NH_2)_2$ as the sulfur source was added to the solution,

•10 ml NaOH/NaCl pH=10.4 was added to the solution,

•Finally, 50 ml deionized water was added to the solution.

It was considered that the mechanism below is effective in the formation of the thin film on a substrate

$$[Cu(TSC)]^{2+}+SC(NH_2)_2+2OH^- \rightarrow CuS+TSC+CN_2H_4O+H_2O$$

The substrates (2.5×7.5 cm^2) were immersed vertically in this solution and placed in an oven at 60 °C. The deposition time was varied from 55 to 70 min, at 5 min steps. Then the thin films obtained were washed with deionized water to get rid of loosely adhered material and air dried at room temperature. One edge of the substrate was cleaned with cotton moistened with HCl for further characterization. The X-ray diffraction (XRD) technique using a Bruker D8 advance X-ray diffractometer with CuK_α radiations (λ=0.154056 nm) was used to determine the crystalline phase and crystal orientation of the films. The diffraction patterns were recorded automatically with a scanning speed of 2∘/min. The surface morphologies of the thin films were examined by atomic force microscopy (AFM) using a Veeco Multimode 8. The thicknesses of the films were also measured by means of AFM. Normal incidence transmittance (T) spectra were recorded at room temperature in the range from 300 to 1100 nm using a double-beam spectrophotometer, model Perkin Elmer UV/vis Lambda 2S spectrophotometer.

3. Results and discussion

Fig. 1a-b presents the XRD patterns of the CuS thin films obtained from the first and second processes, respectively. When the XRD patterns are examined, the diffraction peak is seen at 2θ≈ 31.757 in the XRD patterns of the thin films deposited using both of the processes at 55-60-65 min. and can be indexed to the (103) planes of CuS, which is in good agreement with the hexagonal structure of CuS [7]. In addition, there are small peaks in Fig. 1b 60-65 min, these small peaks are at 2θ≈ 45.545 and correspond well to the (008) planes in the standard literature data [7]. Fig. 1a-70 min. and 1b-70 min. have an amorphous structure. This may be the result of breaking away from the surface. According to Fig. 1, if the Cu source and complex substance react for a long time, a new oriented peak can be observed in the XRD pattern. The grain size of the CuS thin films was calculated by using the Scherrer equation for the (130) peak (Table 1). This implied that the grain size in the process, mixed TSC[Cu]$^{2+}$ at 1 h, enlarged with increased time in contrast to the other process. Their high values suggest higher structural quality compared to the other process.
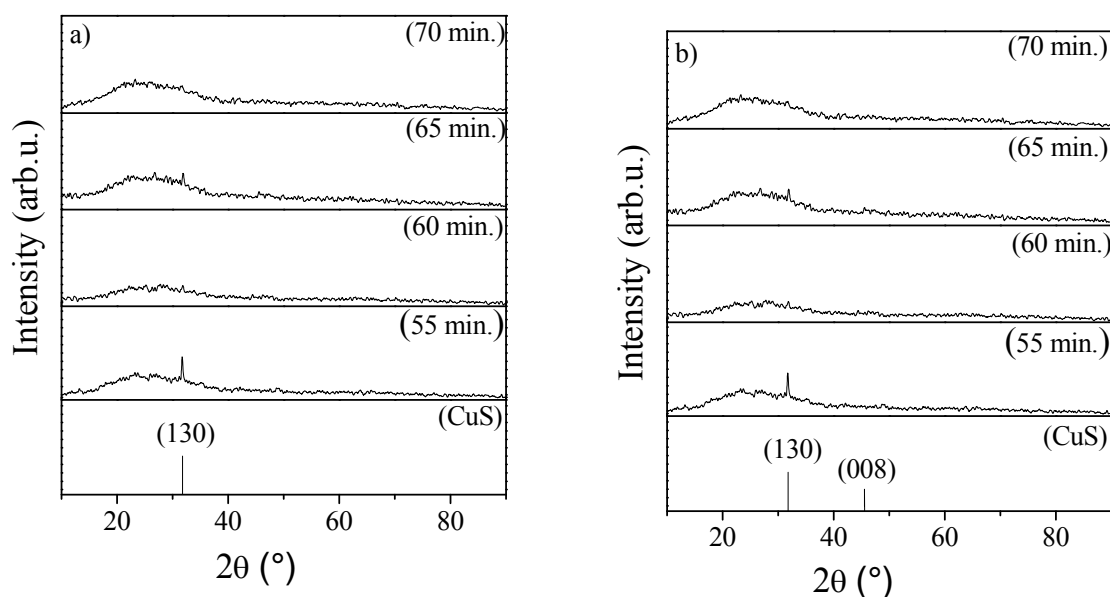
Fig. 1 XRD patterns of CuS thin films a) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 min b) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 h.

Table 1 The deposition conditions, film thickness, grain size and surface roughness of the CuS thin films.

The name of thin films	The first process	The second process	Deposition time (min.)	The film thickness (nm)	Grain size (nm)	Surface roughness (nm)
FFF26	✓		55	358.377	70	105.62
FFF32		✓	55	304.907	42	94.315
FFF27	✓		60	323.470	11	83.803
FFF33		✓	60	190.917	14	73.953
FFF28	✓		65	254.887	12	77.007
FFF34		✓	65	165.070	35	65.532
FFF29	✓		70	119.424	-	61.203
FFF35		✓	70	117.656	-	32.657

Fig. 2a and b shows the AFM images of the CuS thin film deposited from the first and second processes, respectively. The surface roughness of the CuS thin films deposited using both processes are shown in Table 1. The surface roughness of the thin films deposited using the second process are somewhat lower than that of the thin films deposited from the first process despite the same deposition time, this we attribute to the difference in the bath process used for thin film deposition. Additionally, as the thickness decreased, both grain size values and the surface roughness decreased. All these results are coherent with the literature and Fig. 1 [8].
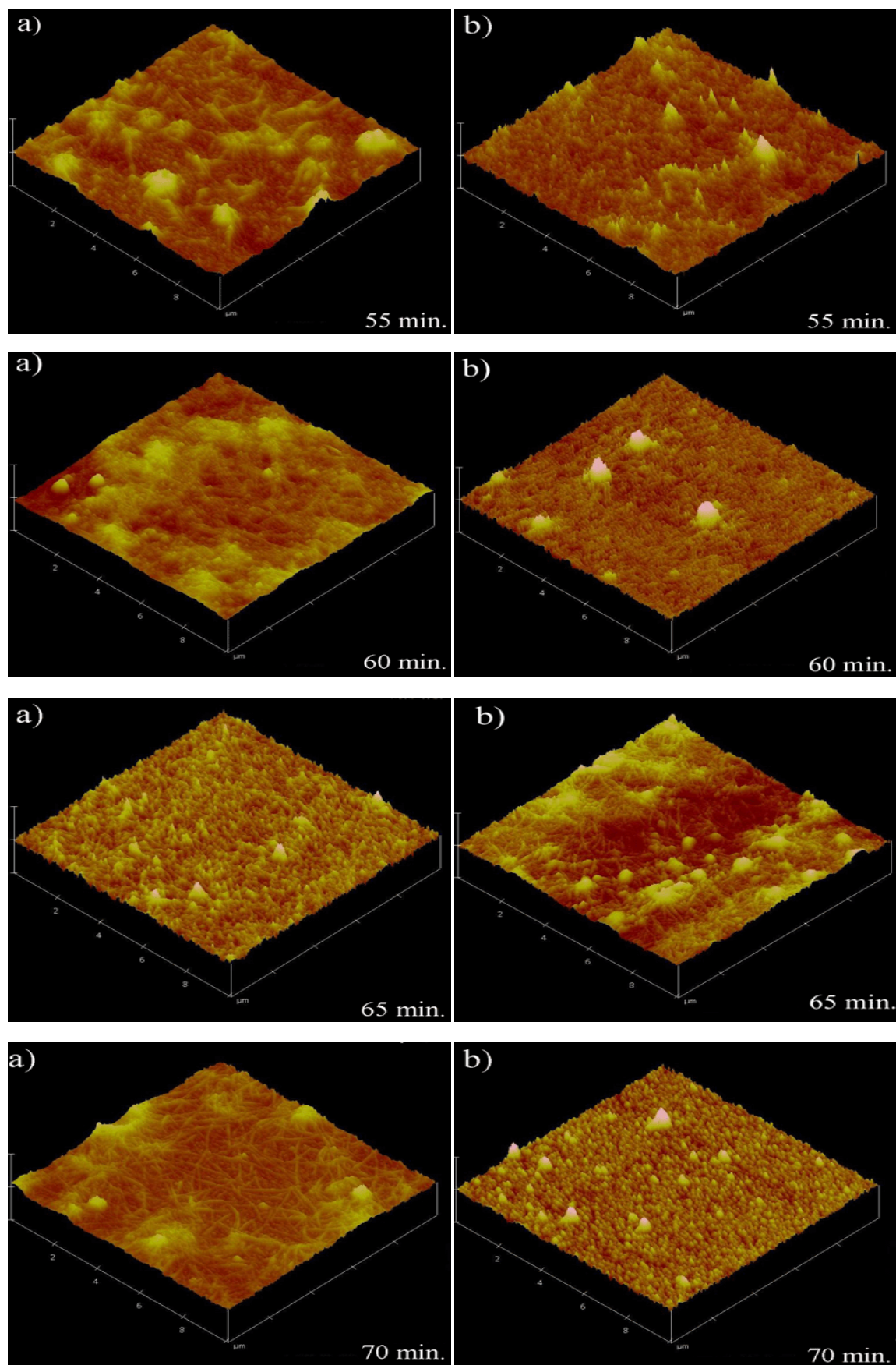
Fig. 2 AFM pictures of CuS thin films a) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 min. b) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 h.

The transmission spectra of the thin films deposited with increasing thickness samples are shown in Fig. 3a-b. Generally, the transmittance increases with decreasing thickness. The average UV transmission ratios of the thin film fabricated from the second process were smaller than those of the first process. The difference in transmission ratios in the visible was nearly 3%. The characteristic UV–vis absorption band also centered at 611 and 637 nm for the thin films deposited using the first and second process, respectively.
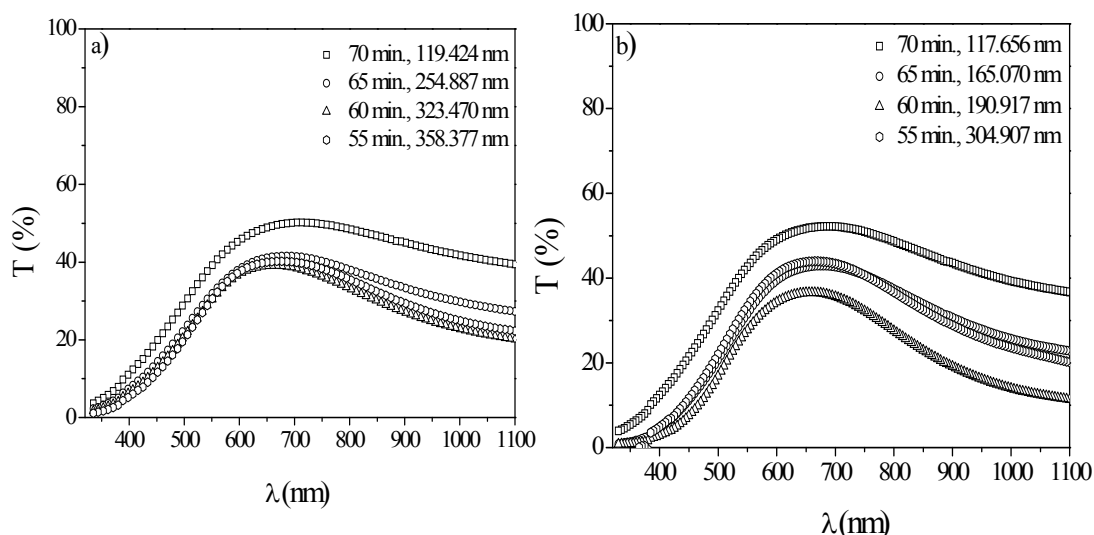

Fig. 3 Transmission pattterns of CuS thin films a) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 min. b) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 h.

The optical band gaps of these films were determined with the help of absorption spectra using the Tauc relation [9]. The optical band gap for each CuS thin film was estimated by extrapolation of the linear portion of the curve to its intersection with the x-axis. The band gap estimated for the thin films deposited using the first and second processes ranged from 2.39 eV to 2.45 eV and from 2.34 eV to 2.48 eV, respectively (Fig. 4). These ranges are consistent with the values reported in the literature [10-13]. Additionally, the thin film thickness increased as the band gap value decreased. The decrease of the band gap with increasing CuS thin film thickness has also been reported by others [11].
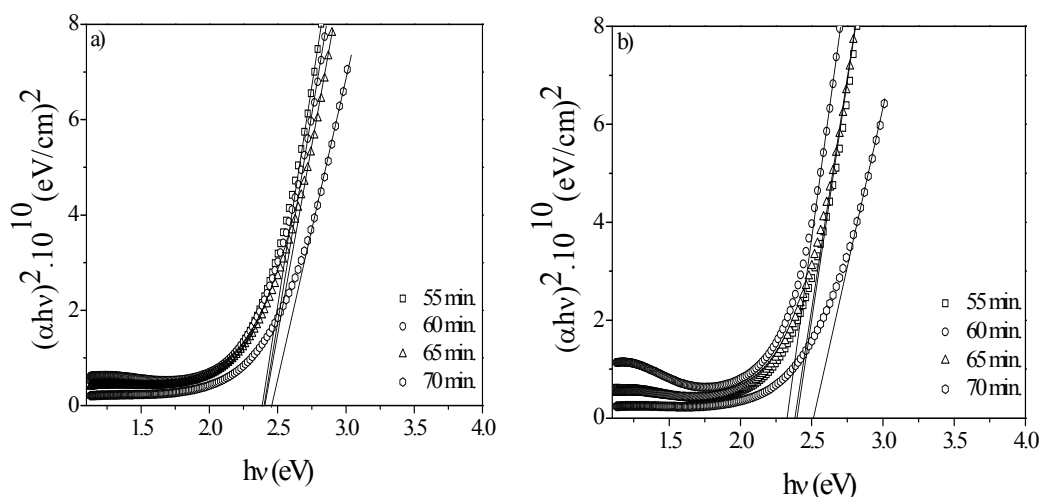

Fig. 4 Plots of $(\alpha h\nu)^2$ vs hν for CuS thin films a) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 min. b) trisodium citrate and $Cu_2SO_4.5H_2O$ mixed for 1 h.

4. Conclusion

A comparative study between the reaction time of a complex substance with a copper source, in which TSC and $Cu_2SO_4.5H_2O$ were mixed for 1 min and 1 h, showed that the bath preparation process strongly affects the structural, morphological and optical properties of CuS thin films deposited using CBD. The XRD pattern suggested that CuS thin films were polycrystalline. The crystallinity of the thin films may be slightly improved by TSC and $Cu_2SO_4.5H_2O$ mixed for 1 h. It was demonstrated that the mixing of the complex substance and metal source for a long time is beneficial for the homogeneous nucleation and growth of the thin films. The surface roughness of the thin films was different despite the same deposited time. Optical absorbance measurements indicated the existence of direct transitions with a corresponding energy gap in the range of 2.39-2.45 eV and 2.34-2.48 eV for substances mixed for 1 min and 1h, respectively. The long mixing time of the complex substance and metal source may cause the absorption edge to shift to a longer wavelength, which is the best way to benefit from sunlight for photovoltaic applications of CuS. All these characterizations distinctly indicate a strong interrelation between the deposition process and structural, morphological and optical properties of the CuS thin films.

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