Method Article

Rapid chemical bath deposition and optical property of CuS films using sodium ethylenediamine tetraacetate as chelating agent

Abstract: CuS films were fabricated by a chemical bath deposition process in an aqueous solution of cupric acetate, thiourea, and different contents of sodium ethylenediamine tetraacetate (EDTA-2Na) ~~with different contents~~ at 50 ℃. The films were characterized by X-ray diffraction, atomic force microscopy, ultraviolet-visible spectrophotometry and photoluminescence spectrophotometry. The effects of EDTA-2Na content and deposition time on the deposition rate, thickness, transmittance, band gap energy, and photoluminescence of the films were investigated. The films were fast deposited with this method. Molar ratio of EDTA-2Na/Cu^{2+}=1.0 led to fastest deposition. The band gap energy of the films is in the range~~d from~~ of 2.59−2.92 eV, decreasing with increasing deposition time. The films showed broad emission centered at ~443 nm.

Keywords: CuS; film; chemical deposition; temperature; chelating agent; optical properties

1. Introduction

Copper sulfides (Cu_xS, x = 1–2) are significant binary compounds that attract much attention due to their wide range of applications in optical and electrical devices, such as photo thermal conversion, microwave shielding coatings, solar control coatings, dye-sensitized solar cells, potential nanometer-scale switch, cathode materials in lithium rechargeable batteries and some chemical sensors [1-4]. Additionally, it has recently been reported that CuS can transform into a superconductor below the 1.6 K because of its metallic conduction behavior ~~property~~ [5].

Even though physical techniques are very suitable for synthesizing uniform and high quality films, they are very expensive and consume large amounts of energy. On the other hand, chemical methods are economical and suitable for maintaining desired structures. Thus, to prepare CuS thin films with desired components and structures, many different chemical methods have been developed, such as liquid–liquid interface reaction [6], chemical vapor deposition (CVD) [7], chemical vapor reaction (CVR) [8], electrochemical method [9], successive ionic layer adsorption and reaction (SILAR) [10], atomic layer deposition (ALD) [11], spray-ion layer gas reaction (ILGAR) [12], chemical bath deposition (CBD) [13–15], etc. Among them, CBD tends to be a better method to deposit CuS films with desired component, particular orientation, and thickness because of the advantages of having a variety of substrates (insulators, semiconductors and metals) for deposition, ~~a~~ suiting large surface area deposition, simplicity, and lower cost. However, bath solution generally contains Cu salt, triethanolamine, thiourea, and large amount of sodium hydroxide and/or ammonia for most cases. With such solution the deposition usually required a significant long time to achieve the enough film thickness. To enhance the deposition rate, microwave [16] and thermal [17−19] assistances has been introduced to the CBD. In addition, small amount of other chemical bath solution composition, such as, aqueous solutions of copper sulphide and thioacetamide mixed together with chelate agent of acetic acid [15], aqueous solution of copper ni~~k~~trate, concentrated ethylene glycole ($C_2H_6O_2$), thioacetamide with different pH [19], etc., have been used and verified to be suitable for CBD growth of the CuS film.

In this paper, we present (i) fast fabrication of uniform CuS films with a simple CBD; (ii) the effects of chemical bath solution composition and deposition time on the thickness and the optical properties of the deposited films.

2. Experiment method

2.1. Deposition of the film

The starting materials used were all analytic grade chemicals without any further processing. The bath solution was composed of 0.01 mole cupric acetate ($Cu(CH_3COO)_2.H_2O$), 0.015 mole thiourea ($SC(NH_2)_2$), 80 ml deionized water and different amounts of disodium ethylenediamine tetraacetate (EDTA-2Na, $C_{10}H_{14}N_2Na_2O_3$) (0.005, 0.01, and 0.015 mole). The solutions were~~as~~ homogenized by magnetic stirring for 10 min in ~~a~~beakers at room temperature. Commercial glass slides were used as ~~a~~ substrates and were ultrasonically cleaned in acetone and methanol respectively for 0.5 h. At room temperature (~20 ℃), the film deposited for 7.5 h was grey white, indicating it can not be CuS crystal phase. However, at 50℃ the deposited films are dark brown, which may indicates the formation of CuS crystal phase. Therefore the deposition temperature of 50 ℃ was selected. After the solutions were put into a furnace, the furnace was heated from room temperature to 50 ℃ and maintained for 10 min to make actually solution temperature reach to 50 ℃. Three glass substrates were then put vertically into each of the three solutions. After 0.5 h, 1.0 h, and 1.5 h of deposition, the films were successively taken out from the solutions, and rinsed with deionized water to remove the residual bath solution and loosely adhered CuS particles on the films and then naturally dried in air.

2.2. Characterization of the films

The phase and structure of the deposited CuS thin films were identified at room temperature using an X-Ray diffractometer (XRD, $CuK_{\alpha1}$, λ=0.15406nm, Model No: D/Max-2200PC, Rigaku, Japan). The morphology and texture of the films were analyzed using atomic force microscopy (AFM, Model No: SPI3800N, NSK, Japan). The transmittance spectra of the films was determined with an ultraviolet-visible spectrophotometer (Model No: 752N, Feilo, China). The photoluminescence spectrum of the films was measured on a photoluminescence spectrophotometer (Model no: F-4600, Hitachi, Japan).

3. Results and discussion

Figure 1 shows the XRD patterns of the CuS films. The main phase of the films was hexagonal covellite CuS (JCPDS: 05-0464). The peak at 2θ~18° was identified ~~as~~ to be related with yarrowite Cu_2S (JCPDS: 36-0379) which decreased with the increase in deposition time and disappeared when the deposition time was 1.5 h. This could be due to CuS is formed at initial stage of the film deposition and covered by CuS with films further deposition.

The chemical process for the CuS film formation can be given by:

$$\text{EDTA-2Na}+\text{Cu}^{2+}=\text{EDTA-Cu}+2\text{Na}^{+} \tag{1}$$

$$\text{SC(NH}_2)_2+2\text{H}_2\text{O}\xrightarrow{50\ ℃}2\text{NH}_4^{+}+\text{CO}_2+\text{S}^{2-} \tag{2}$$

$$\text{EDTA-Cu}+2\text{H}_2\text{O} = \text{EDTA}^{2-}+\text{Cu}^{2+}+2\text{H}_2\text{O} \tag{3}$$

$$\text{Cu}^{2+}+\text{S}^{2-}=\text{CuS} \tag{4}$$

CuS has a very small solubility constant ($K_{sp}=1.27\times10^{-36}$) and so is easily formed from the Cu^{2+} and S^{2-} ions in the aqueous solution and very stability in aqueous environment. However, Since the Cu^{2+} can be chelated with EDTA, ~~so~~ the release rate of Cu^{2+} from the chelate compound EDTA-Cu could control the formation rate of the CuS. Higher temperature can speeds up this release rate and so the film deposition.

Figure 2 shows AFM micrographs of the CuS films deposited with EDTA-2Na/Cu^{2+} =1.0. The each films ~~were~~ was composed of uniform particles. With increasing deposition time, the average particle size increased and particle morphology tended to be more rodlike. The thickness of the films determined from AFM analysis are shown in Fig. 3. The thickness increased as increase in deposition time, which can be ascribed to the formation and deposition of the particles in succession with deposition time. Moreover, the deposition rate also shows a maximum at the moderate molar ratio of EDTA-2Na/Cu^{2+}=1.0. At lower molar ratio of EDTA-2Na/Cu^{2+}=0.5, excessive Cu^{2+} ~~antion~~ cation in the solution led to the formation of CuS particle too fast and undesirably large particles formed. Particles with such size have difficulty of tightly adhering on the film, which resulted in slower deposition rate of the film. However, at higher molar ratio of EDTA-2Na/Cu^{2+} =1.5 the release of Cu^{2+} ~~antion~~ cation from the

EDTA-Cu was slower, and so the deposition rate was als lower. As a comparison, a room temperature CBD deposited CuS films with a thickness of ~470 nm taken ~8 h [16].

Figure 4 shows the transmittance spectra of the CuS films fabricated with different EDTA-2Na proportions. The transmittance of the films decreases with increasing the deposition time for each EDTA-2Na proportion. The films fabricated with EDTA-2Na/Cu^{2+}=1.0 had the greatest decrease in transmittance with deposition time, while the films deposited with EDTA-2Na/Cu^{2+}=0.5 and 1.5 show relative small transmittance decreases with deposition time. This is consistent with the increases of the film thicknesses as shown in Fig. 3. ~~However, the decrease in transmission with the deposition time does not seems to be out of scale with the film thickness. This could be mainly attributed to higher transmittance of Cu_2S than CuS [20].~~ In addition, the transmittance is also associated with average particle size, crystallinity, crystal orientation to some extent.

CuS is considered as a direct band gap semiconductor, so the relationship between the absorption coefficient (α) near the absorption edge and the optical band gap energy (E_g) ~~for direct band transitions~~ obeys the following formula [20]:

$$(\alpha h\nu)^2 = C\left(h\nu - E_g\right)$$

where $h\nu$ is photon energy and C is a constant. ~~t~~The absorption coefficient (α) can be calculated by equation

$$\alpha = \frac{1}{d}\ln\frac{1}{T}$$

where T is the transmittance and d is the film thickness. Fig. 5 shows the graphs of

$(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for the CuS thin films. The linear dependence of $(\alpha h\nu)^2$ on $h\nu$ at higher photon energies indicates that the CuS films are essentially direct-transition-type semiconductors. The straight-line portion of the curve, as extrapolated to zero, gives the optical band gap energy E_g~~. The estimated E_g was~~ in range of 2.59−2.92 eV ~~and~~ decreased with increasing deposition time (Fig. 6). This could be ascribed to quantum size effect due to increase of average particle size with deposition time. As a comparison, Gadave and Lokhande [21] reported optical band gap energies of 2.2 eV and 2.5 eV for CBD and dip coating deposited Cu_xS film. Sartale and Lokhande [22] reported optical band gap energy of 2.36 eV of SILAR deposited Cu_xS from nonaqueous medium. Puspitasari et al [15] reported optical band gap energy of 2.8 eV for the CuS film prepared by a simple chemical method. The variation of the band gap energy with deposition time has been reported by some researcher [16]. They reported that the band gap energy of the CuS film decreased and then increased with microwave-assisted deposition time. The detailed reason for this variation is unclear at present. We believe that the different phases, Cu/S ratio, average particle size, film thickness, crystal orientation, and crystallinities are responsible for this variation.

Figure 7 shows the photoluminescence spectra of the CuS films deposited at the EDTA-2Na/Cu^{2+}=1.0. They were measured at excitation wavelength of 350 nm. The emission peaks were centered at ~443 nm. This value is different from that of CuS nanorods (420, 450 and 462 nm [23], and 515 nm [24]) and nanoplates (339 nm [25]).. The emission peaks of ~443 nm corresponded to photon energy of ~2.79 eV that is closed to the band gap energy estimated from the transmittance spectra. This indicated that the emission could come from a near band gap emission. The decrease in the emission intensity ~~of the emission~~ with the deposition time can be also observed in Fig. 7. Roy et al [24] ascribed the decrease in the luminescence intensity of their powders to the increase of particle size due to the decrease in the content of surface oxygen vacancy and defect with increasing the size of materials. In fact, their result indicated that the decrease in the emission intensity was also accompanied by morphology change from nanoparticles to nanorods. Therefore, the decrease in the emission intensity of the CuS films could be associated with the change in the morphology and the crystal orientation (Fig. 1) and the increase in the particle size of the films.

4. Conclusion

CuS semiconductor films were fabricated on a glass substrate in a simple chemical bath solution containing EDTA-2Na as the chelating agent. Thermal assistance was used to accelerate deposition. The effect of EDTA-2Na proportion on the deposition rate and optical properties of the films were investigated, and it was found that the molar ratio of EDTA-2Na/Cu^{2+}=1.0 was most effective. At this proportion, the film thickness reaches ~541 nm in a relative short deposition time of 1.5 h. Such deposition rate is larger than that produced by usual chemical bath deposition. The optical band gap energies of the films are in range of 2.59−2.92 eV. The films showed the emission peaks centered at ~443 nm. The optical properties have some dependences of microstructure including morphology, particle size and crystal orientation. We believe this simple chemical bath deposition technique can be further extended to the fabrication of other semiconductor films.

References

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Coating Techniques, Formation of Cu$_x$S films through a chemical bath deposition process, Thin Solid Films 550 (2014) 291–297.

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Figures:

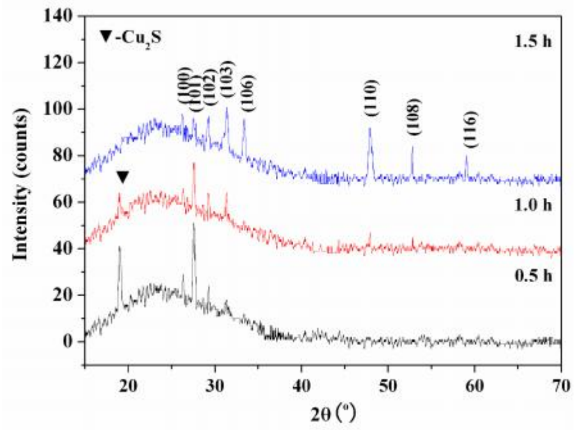

Figure 1. XRD patterns of the CuS films fabricated at the molar ratio of EDTA-2Na: Cu^{2+} = 1.0

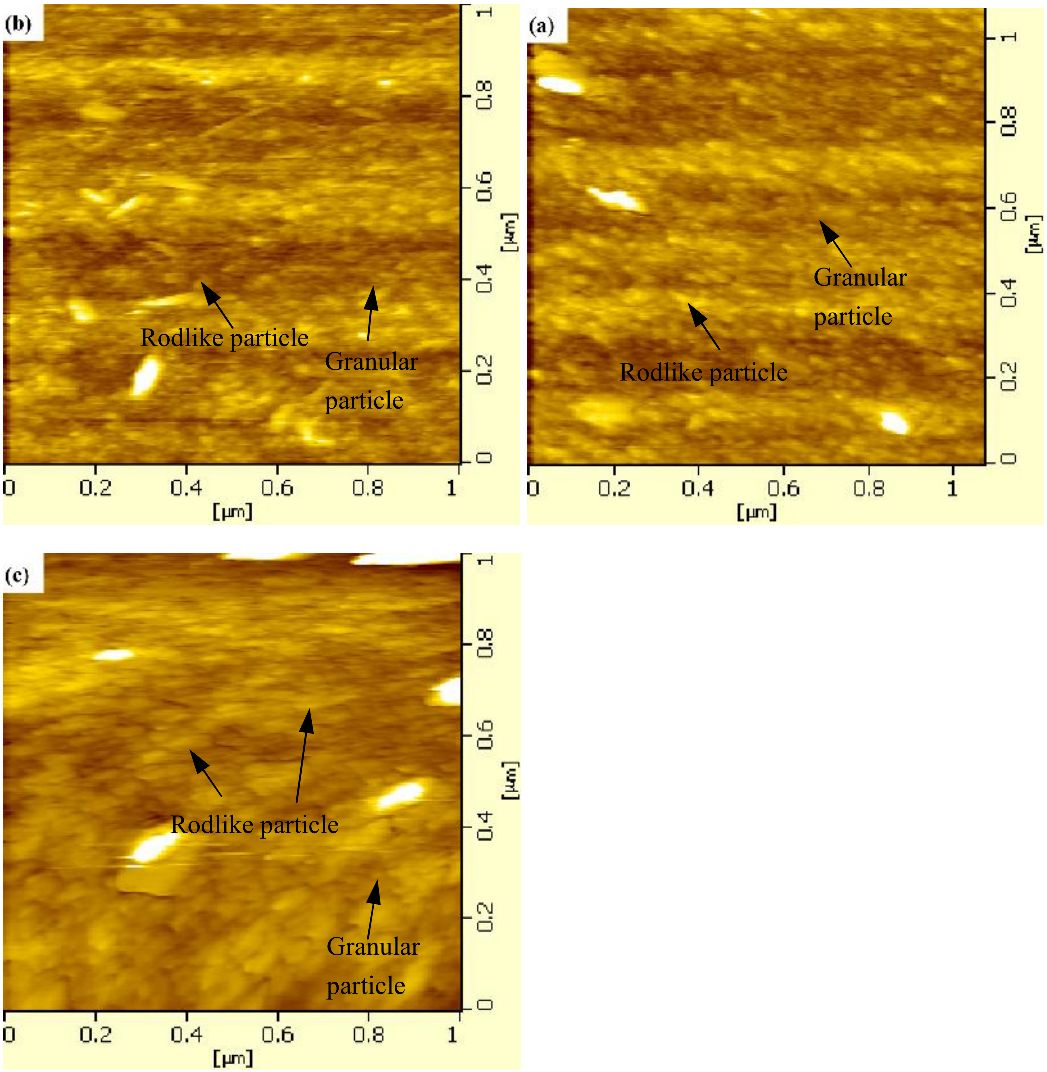

Figure 2. AFM micrographs of the CuS films deposited at molar ratio of EDTA-2Na:Cu^{2+}=1.0 for deposition time of (a) 0.5 h, (b) 1.0 h, and (c) 1.5 h

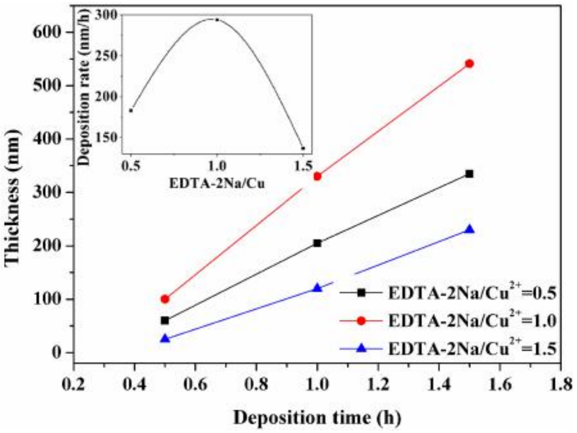

Figure 3 . Film thickness vs. deposition time

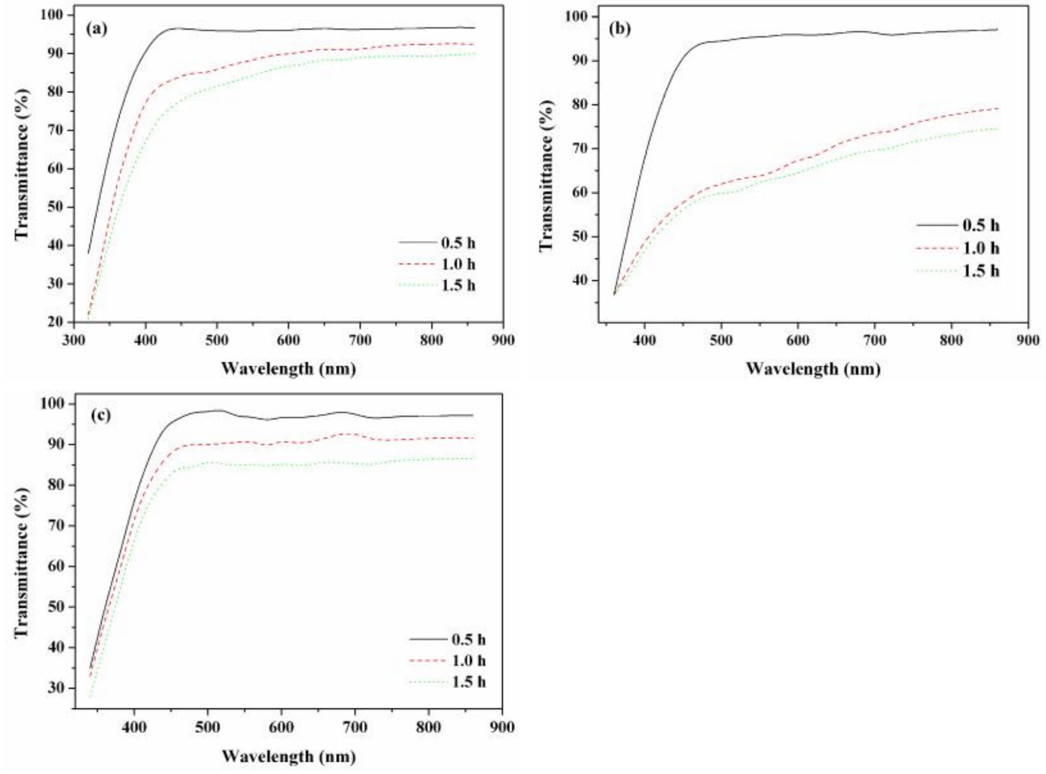

Figure 4. Transmittance spectra of the CuS films deposited at molar ratio of EDTA-2Na: Cu^{2+}=（a）0.5, (b) 1.0, and (c) 1.5.

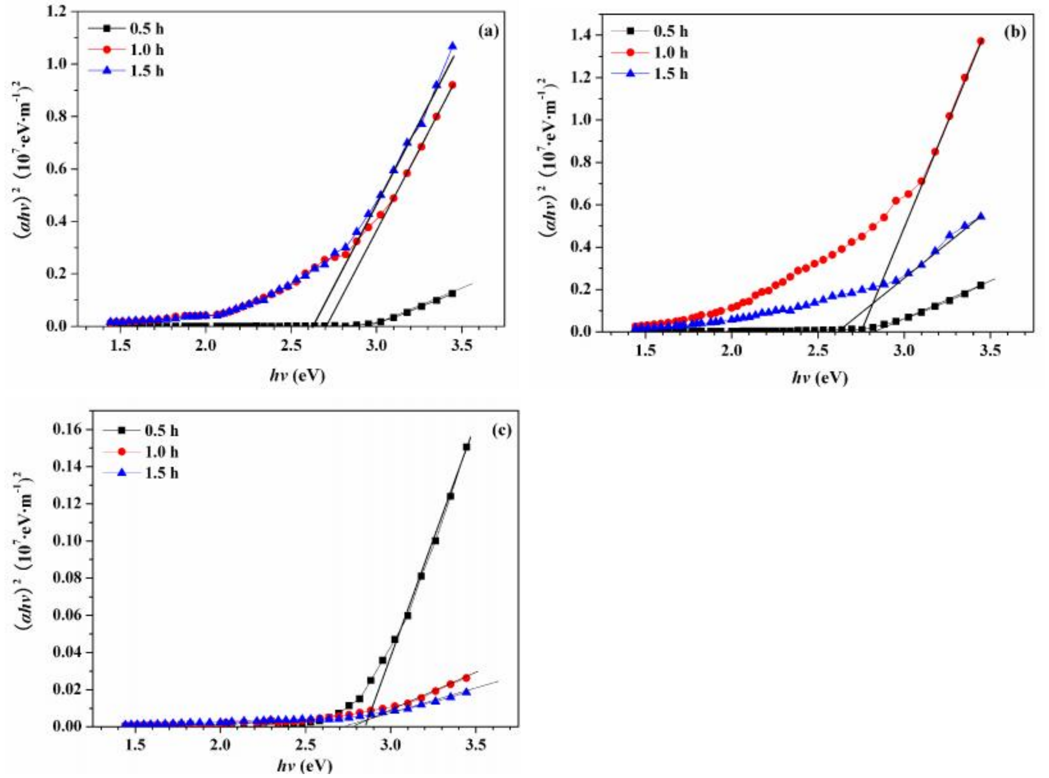

Figure 5. Plots of $(\alpha h\nu\ )^2$ vs. $h\nu$ of the CuS films deposited at molar ratio of EDTA-2Na: Cu^{2+}=(a)0.5, (b)1.0, and (c)1.5

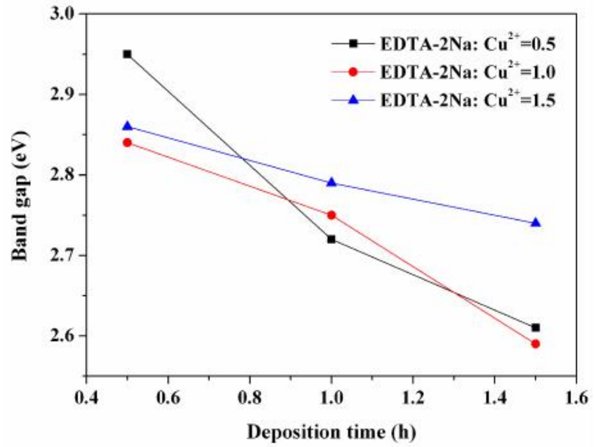

Figure 6 . Optical band gap of the films deposited at at molar ratio of EDTA-2Na: Cu^{2+} as a function of the deposition time

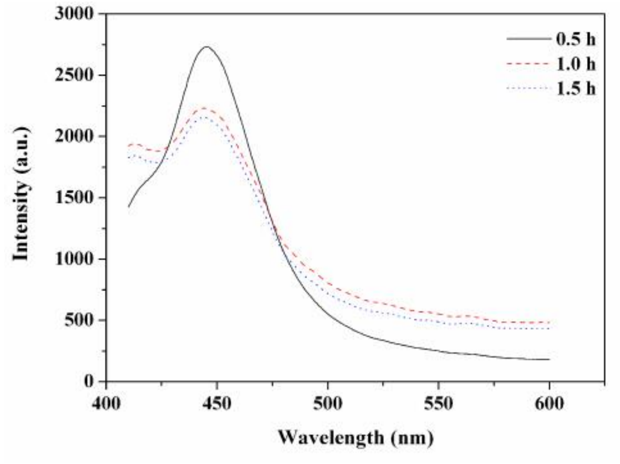

Figure 7. Photoluminescence spectra of the CuS films deposited at EDTA-2Na: Cu^{2+}=1.0 and excited at excitation wavelength of 350 nm.