

**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 °C. 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<sup>2+</sup>=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<sub>x</sub>S, 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,

23 dye-sensitized solar cells, potential nanometer-scale switch, cathode materials in  
24 lithium rechargeable batteries and some chemical sensors [1-4]. Additionally, it has  
25 recently been reported that CuS can transform into a superconductor below the 1.6 K  
26 because of its metallic conduction behavior property [5].

27 Even though physical techniques are very suitable for synthesizing uniform and high  
28 quality films, they are very expensive and consume large amounts of energy. On the  
29 other hand, chemical methods are economical and suitable for maintaining desired  
30 structures. Thus, to prepare CuS thin films with desired components and structures,  
31 many different chemical methods have been developed, such as liquid–liquid  
32 interface reaction [6], chemical vapor deposition (CVD) [7], chemical vapor reaction  
33 (CVR) [8], electrochemical method [9], successive ionic layer adsorption and reaction  
34 (SILAR) [10], atomic layer deposition (ALD) [11], spray-ion layer gas reaction  
35 (ILGAR) [12], chemical bath deposition (CBD) [13–15], etc. Among them, CBD  
36 tends to be a better method to deposit CuS films with desired component, particular  
37 orientation, and thickness because of the advantages of having a variety of substrates  
38 (insulators, semiconductors and metals) for deposition, ~~a~~-suiting large surface area  
39 deposition, simplicity, and lower cost. However, bath solution generally contains Cu  
40 salt, triethanolamine, thiourea, and large amount of sodium hydroxide and/or  
41 ammonia for most cases. With such solution the deposition usually required a  
42 significant long time to achieve the enough film thickness. To enhance the deposition  
43 rate, microwave [16] and thermal [17–19] assistances has been introduced to the CBD.  
44 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 nitrate, 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 ( $Cu(CH_3COO)_2 \cdot H_2O$ ), 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 homogenized by magnetic stirring for 10 min in beakers at room temperature. Commercial glass slides were used as substrates and were ultrasonically cleaned in acetone and methanol respectively for 0.5 h. At room temperature ( $\sim 20^\circ C$ ), the film deposited for 7.5 h was grey white, indicating it can not be CuS crystal phase. However, at  $50^\circ C$  the deposited films are dark brown, which may indicate the formation of CuS crystal phase. Therefore the deposition temperature of  $50^\circ C$  was selected. After the solutions were put into a furnace, the furnace was heated from room temperature to  $50^\circ C$  and

maintained for 10 min to make actually solution temperature reach to 50 °C. 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.

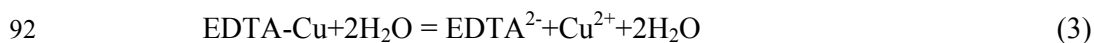
## 2.2. Characterization of the films

The phase and structure of the deposited CuS thin films were identified at room temperature using an X-Ray diffractometer (XRD,  $\text{CuK}_{\alpha 1}$ ,  $\lambda=0.15406\text{nm}$ , 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  $2\theta \sim 18^\circ$  was identified as-to be related with yarrowite  $\text{Cu}_2\text{S}$  (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.

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



94 CuS has a very small solubility constant ( $K_{\text{sp}} = 1.27 \times 10^{-36}$ ) and so is easily formed  
95 from the  $\text{Cu}^{2+}$  and  $\text{S}^{2-}$  ions in the aqueous solution and very stability in aqueous  
96 environment. However, Since the  $\text{Cu}^{2+}$  can be chelated with EDTA, so the release rate  
97 of  $\text{Cu}^{2+}$  from the chelate compound EDTA-Cu could control the formation rate of the  
98 CuS. Higher temperature can speeds up this release rate and so the film deposition.

99 Figure 2 shows AFM micrographs of the CuS films deposited with EDTA-2Na/ $\text{Cu}^{2+}$   
100 =1.0. In these micrographs, bright parts could be images of the particles while dark  
101 parts should be images of boundary and gaps between the particles. The each films  
102 were was composed of uniform particles (bright parts). With increasing deposition  
103 time, the average particle size increased and particle morphology tended to be more  
104 rodlike. The thickness of the films determined from AFM analysis are shown in Fig. 3.  
105 The thickness increased as increase in deposition time, which can be ascribed to the  
106 formation and deposition of the particles in succession with deposition time.  
107 Moreover, the deposition rate also shows a maximum at the moderate molar ratio of  
108 EDTA-2Na/ $\text{Cu}^{2+}$ =1.0. At lower molar ratio of EDTA-2Na/ $\text{Cu}^{2+}$ =0.5, excessive  $\text{Cu}^{2+}$   
109 anion-cation in the solution led to the formation of CuS particle too fast and  
110 undesirably large particles formed. Particles with such size have difficulty of tightly

111 adhering on the film, which resulted in slower deposition rate of the film. However, at  
112 higher molar ratio of EDTA-2Na/Cu<sup>2+</sup> = 1.5 the release of Cu<sup>2+</sup> anion cation from the  
113 EDTA-Cu was slower, and so the deposition rate was als lower. As a comparison, a  
114 room temperature CBD deposited CuS films with a thickness of ~470 nm taken ~8 h  
115 [16].

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

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

130 
$$(\alpha h\nu)^2 = C(h\nu - E_g)$$

131 where  $h\nu$  is photon energy and  $C$  is a constant. ~~¶~~The absorption coefficient ( $\alpha$ ) can be  
132 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  $(ah\nu)^2$  vs. photon energy ( $h\nu$ ) for the CuS thin films. The linear dependence of  $(ah\nu)^2$  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  $\text{Cu}_x\text{S}$  film. Sartale and Lokhande [22] reported optical band gap energy of 2.36 eV of SILAR deposited  $\text{Cu}_x\text{S}$  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/ $\text{Cu}^{2+}$ =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

155 nanorods (420, 450 and 462 nm [23], and 515 nm [24]) and nanoplates (339 nm [25]).  
156 The emission peaks of ~443 nm corresponded to photon energy of ~2.79 eV that is  
157 closed to the band gap energy estimated from the transmittance spectra. This indicated  
158 that the emission could come from a near band gap emission. The decrease in the  
159 emission intensity ~~of the emission~~ with the deposition time can be also observed in  
160 Fig. 7. Roy et al [24] ascribed the decrease in the luminescence intensity of their  
161 powders to the increase of particle size due to the decrease in the content of surface  
162 oxygen vacancy and defect with increasing the size of materials. In fact, their result  
163 indicated that the decrease in the emission intensity was also accompanied by  
164 morphology change from nanoparticles to nanorods. Therefore, the decrease in the  
165 emission intensity of the CuS films could be associated with the change in the  
166 morphology and the crystal orientation (Fig. 1) and the increase in the particle size of  
167 the films.

168

#### 169 **4. Conclusion**

170 CuS semiconductor films were fabricated on a glass substrate in a simple chemical  
171 bath solution containing EDTA-2Na as the chelating agent. Thermal assistance was  
172 used to accelerate deposition. The effect of EDTA-2Na proportion on the deposition  
173 rate and optical properties of the films were investigated, and it was found that the  
174 molar ratio of EDTA-2Na/Cu<sup>2+</sup>=1.0 was most effective. At this proportion, the film  
175 thickness reaches ~541 nm in a relative short deposition time of 1.5 h. Such  
176 deposition rate is larger than that produced by usual chemical bath deposition. The



177 optical band gap energies of the films are in range of 2.59–2.92 eV. The films showed  
178 the emission peaks centered at ~443 nm. The optical properties have some  
179 dependences of microstructure including morphology, particle size and crystal  
180 orientation. We believe this simple chemical bath deposition technique can be further  
181 extended to the fabrication of other semiconductor films.

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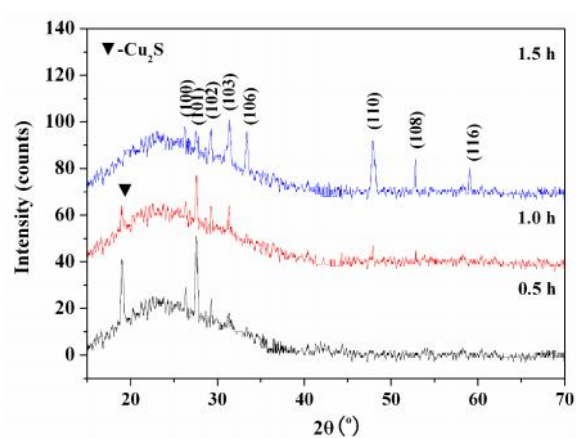
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295 **Figures:**

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298 Figure 1. XRD patterns of the CuS films fabricated at the molar ratio of

299 EDTA-2Na: Cu<sup>2+</sup> = 1.0

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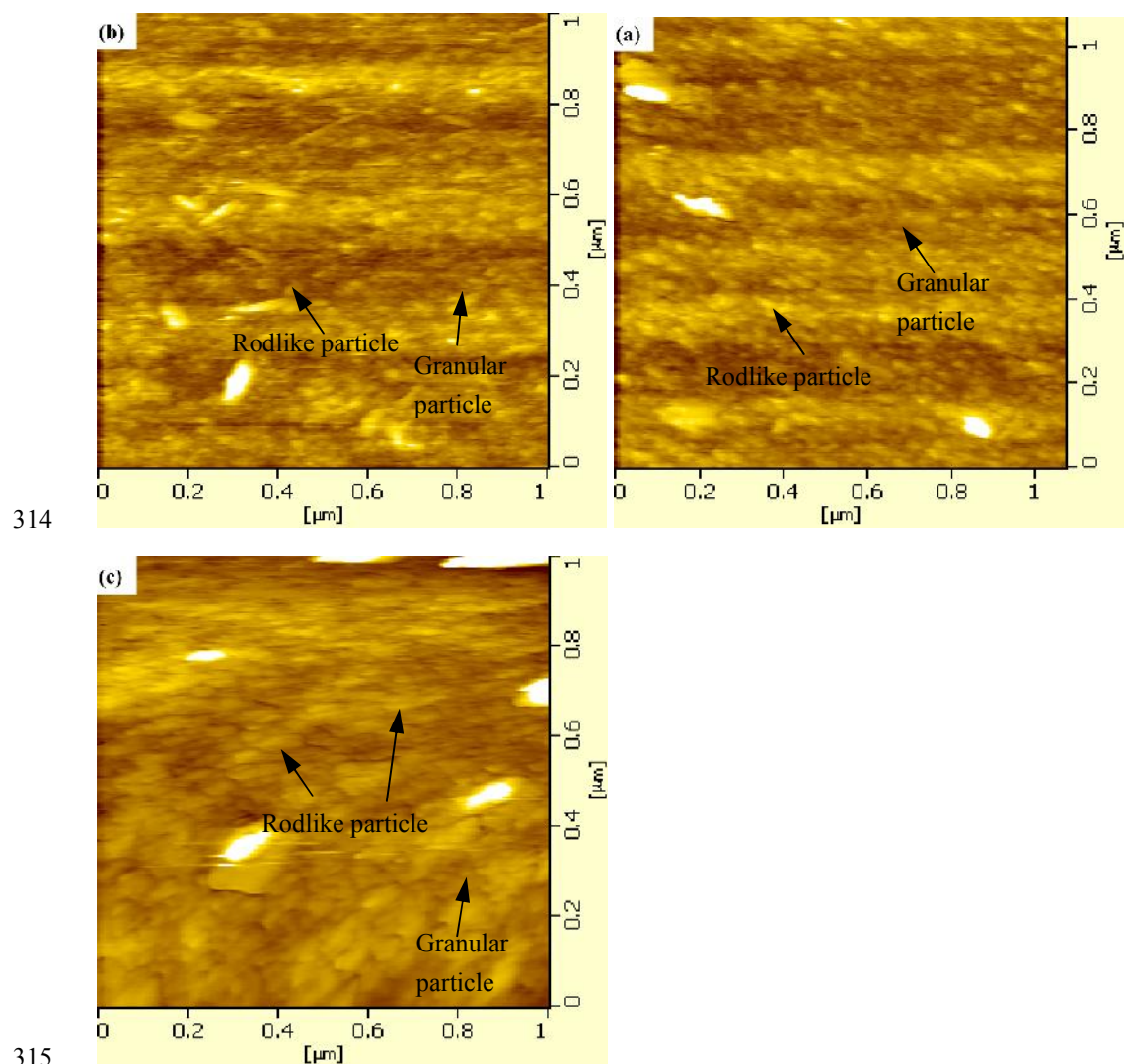
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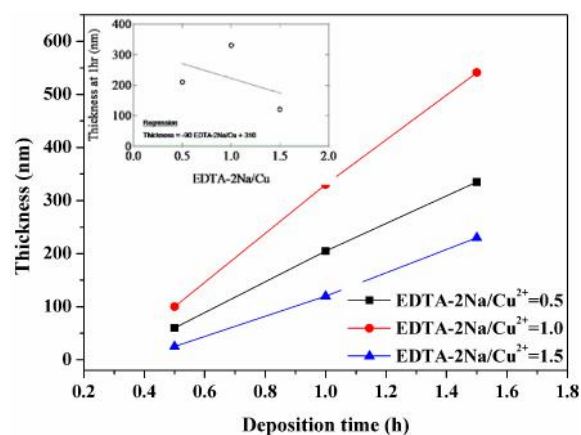
316 Figure 2. AFM micrographs of the CuS films deposited at molar ratio of

317 EDTA-2Na:Cu<sup>2+</sup>=1.0 for deposition time of (a) 0.5 h, (b) 1.0 h, and (c)

318 1.5 h

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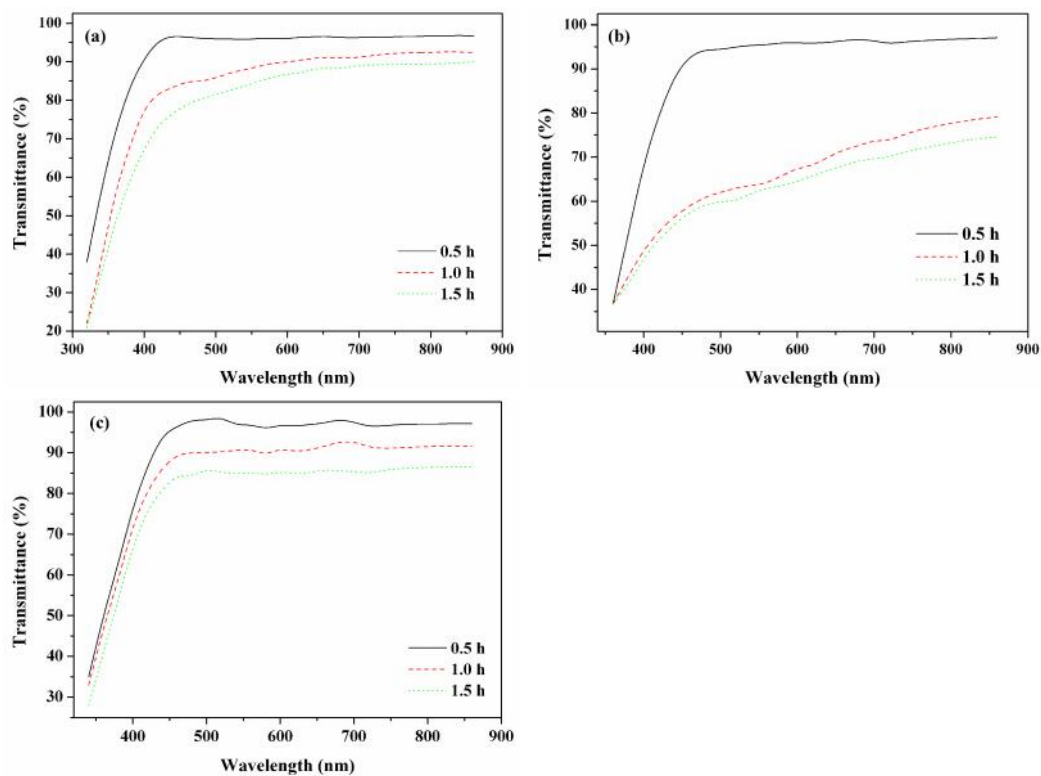
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323 Figure 3 . Film thickness vs. deposition time. Insert is the film thickness after

324 deposition of 1 h vs. EDTA-2Na/Cu ratio

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330 Figure 4. Transmittance spectra of the CuS films deposited at molar ratio of



EDTA-2Na: Cu<sup>2+</sup>= (a) 0.5, (b) 1.0, and (c) 1.5.

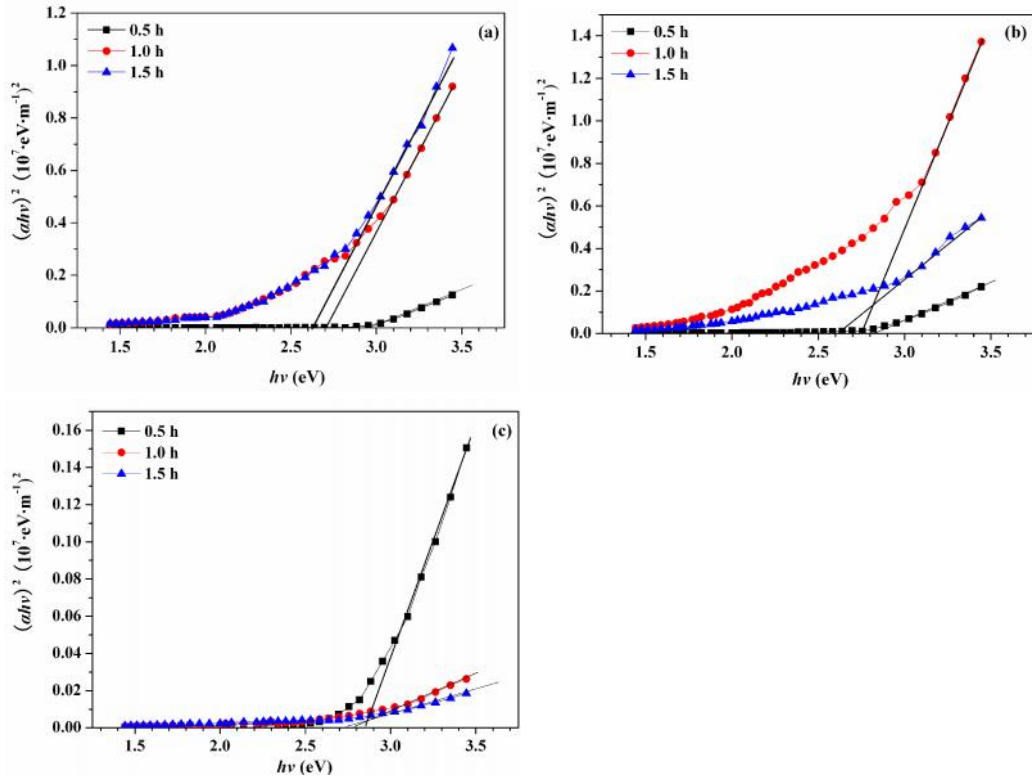


Figure 5. Plots of  $(\alpha h\nu)^2$  vs.  $h\nu$  of the CuS films deposited at molar ratio of

EDTA-2Na: Cu<sup>2+</sup>=(a)0.5, (b)1.0, and (c)1.5

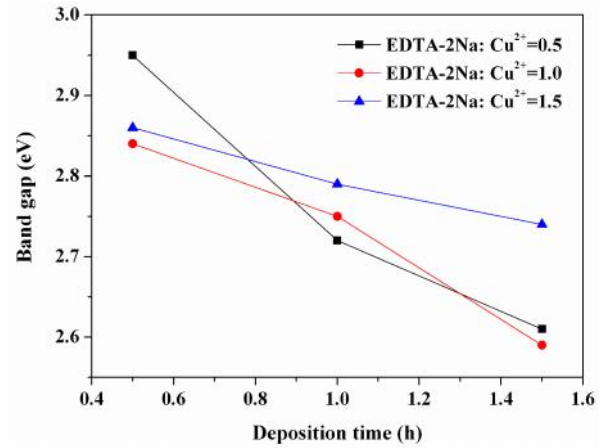


Figure 6 . Optical band gap of the films deposited at at molar ratio of EDTA-2Na: Cu<sup>2+</sup> as a function of the deposition time

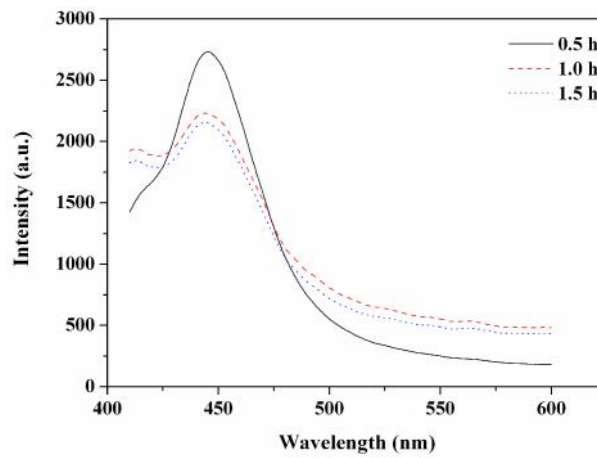


Figure 7. Photoluminescence spectra of the CuS films deposited at EDTA-2Na: Cu<sup>2+</sup>=1.0 and excited at excitation wavelength of 350 nm.