

# Electrochemical synthesis of nanoplatelets-like $\text{CuS}_{0.2}\text{Se}_{0.8}$ thin film for photoluminescence applications

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Copper sulfide-selenide ( $\text{CuS}_{0.2}\text{Se}_{0.8}$ ) thin films were deposited on FTO coated glass substrate (fluorine doped tin oxide) and stainless steel substrates using electrodeposition technique. Deposited thin films were characterized using different characterization techniques viz. X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectroscopy, photoluminescence spectroscopy and surface wettability. XRD study showed polycrystalline nature with cubic phase of the films. Scanning electron microscopy showed that the surface area of the substrate was covered by the nanoplatelets structure of a thickness of 140 to 150 nm and optical study showed that the direct band gap was  $\sim 1.90$  eV. Surface wettability showed hydrophobic nature of the  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin films.

Keywords:  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin film; nanoplatelets; electrodeposition; photoluminescence (PL)

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## 1. Introduction

$\text{CuS}_{0.2}\text{Se}_{0.8}$ -based thin films are attracting considerable interests as the light-absorbing materials for thin film solar cells on account of their inherent advantages, such as high absorption coefficient, adjustable bandgap and high stability under high energy irradiation. IB – VIA is a very important group because CuS and CuSe thin films are useful in various fields, including nanoelectronics, nanophotonics, biotechnologies, also for energy storage and conversion [1]. Cadmium sulfide (CdS) and cadmium selenide (CdSe) belong to IIB-VIA group which is also very important because its band gap is in between the visible solar spectrum (1 to 3 eV) [2].

Copper sulphate and copper selenide are p-type semiconductors. CuS and CuSe are binary materials used in various applications, such as photovoltaics, optoelectronics etc., also they are used as a solar cell absorber layer. CuS thin film is used as a counter electrode in quantum dot dye solar cells [3, 4]. This film is also used as

a cathode in lithium battery [5] and gas sensing applications at low temperature [6]. Copper sulfide selenide ( $\text{Cu}_{2-x}(\text{S}_y\text{Se}_{1-y})$ ) is a ternary thin film and its energy gap is dependent on chalcogenide ratio and crystallographic structure [7].

Copper sulfide has been deposited by various methods, such as electrodeposition [8], chemical bath deposition [9], spray pyrolysis [10], successive ionic layer adsorption and reaction method [11]. Copper selenide has been deposited by different methods, such as electrodeposition [12], solution growth technique [13], chemical bath deposition [14, 15], water evaporation induced assembly [16], modified hydrothermal method [17], whereas copper sulfide selenide has been deposited by cation exchange and electrochemical lithiation [18].

In present paper, we report the electrochemical synthesis of copper sulfide-selenide thin films obtained by a simple, cheap, standard three electrode electrodeposition method in a potentiostatic mode. The electrodeposited films are characterized in terms of structural, morphological, optical, absorption and wettability properties.

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## 2. Experiment

The chemicals used in the experiment were of analytical grade.  $\text{CuSO}_4$ ,  $\text{SeO}_2$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (95.5 % purity) were purchased from S.D. Fine Chemical, Mumbai India. Stainless steel and FTO coated glass substrates were used as the working electrode. Stainless steel substrates of a surface area  $1 \times 5 \text{ cm}^2$  were polished with a smooth paper (zero fine grades), washed with labogent and ultrasonically cleaned in an ultrasonicator for 30 min. FTO substrate was cleaned with labogent and ultrasonically treated for 15 min prior to electrodeposition. The cleaned substrate was used for deposition of  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin films. For electrolytic bath 0.01M  $\text{CuSO}_4$  (20 mL), 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  (4 mL) and 0.01 M  $\text{SeO}_2$  (16 mL) solutions were taken and stirred for 10 min, while its pH was maintained in the range of 2 to 3, using 10 % sulfuric acid. The experiment was performed using a standard three electrode system, where graphite was used as a counter electrode, stainless steel or FTO coated glass substrate as a working electrode and saturated calomel electrode (SCE) as a reference electrode. The experiment was performed in potentiostatic mode.

Cu layer was deposited on the substrate at a reduction potential of  $-0.65 \text{ V}$  and the film was deposited at the same reduction potential [8]. We fixed the deposition potential as  $-0.65 \text{ V}$  versus SCE. The films were deposited for 30 min at room temperature. The deposited films were washed with double distilled water and dried in air atmosphere. The prepared films were annealed at 373 K for one hour and used for characterization.

The films were characterized for their structural properties using a Philips X-ray diffractometer PW-3710 ( $\lambda = 1.54 \text{ \AA}$ ) for copper ( $\text{CuK}\alpha$ ) in 10 to  $100^\circ$  range. The surface morphology of the film was studied by scanning electron microscopy (SEM) using JEOL JSM-6360. Optical absorption study of the films deposited on FTO coated glass substrate was carried out in the wavelength range of 350 to 950 nm using a systronic model-119 spectrophotometer, and photoluminescence (PL) spectra were recorded using a PC based spectrofluorophotometer (JASCO Model FP-750, Japan). To

study the interaction between liquid and thin film surface, contact angle measurement was carried out using Rame-hart USA equipment with CCD camera.

## 3. Results and discussion

### 3.1. X-ray diffraction (XRD) studies

Fig. 1 (A, B, C), shows the representative X-ray diffraction patterns of CuS, CuSe,  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin films on a stainless steel substrate. From these XRD patterns it is seen that all these films are polycrystalline in nature with a cubic structure, with strong preferential orientation of the crystallites along [511] direction for all the films. X-ray diffraction patterns (Fig. 1 (A, B)) show that the location of the patterns is in good agreement with the CuS [19] and CuSe [20], JCPDS card reference, which confirms their formation. Fig. 1 (C) shows that in addition to both phases, one peak at  $2\theta = 29.38^\circ$ , which may come from ternary  $\text{CuS}_{0.2}\text{Se}_{0.8}$ , was also formed. Wang et al. [7] reported similar result for  $\text{Cu}_{2-x}(\text{S}_y\text{Se}_{1-y})$  thin film using a facile one-pot method. The grain or crystallite size was determined using Scherrer equation:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is the wavelength of the X-ray ( $1.5406 \text{ \AA}$ ),  $\theta$  is the Bragg's angle and  $\beta$  is the full-width at half-maximum (FWHM). The strain ( $\epsilon$ ) was calculated from the slope of  $\beta \cos\theta$  versus  $\sin\theta$  plot using the relation 2:

$$\beta = \frac{\lambda}{D \cos \theta} - \epsilon \tan \theta \quad (2)$$

The dislocation density ( $\delta$ ), defined as the length of dislocation lines per unit volume of the crystal, was evaluated from the relation 3:

$$\delta = \frac{1}{D^2} \quad (3)$$

The comparison of observed interplaner spacing  $d$ -values and standard  $d$ -values for different compositions of CuS, CuSe,  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin films is given in Table 1. The observed values of  $d$  are

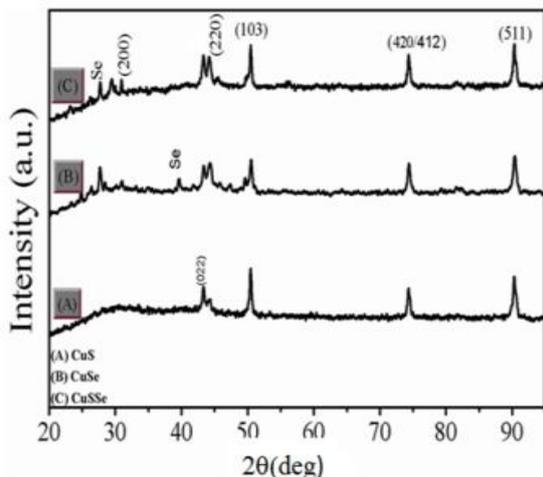


Fig. 1. X-ray diffraction patterns of  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin film.

in good agreement with the standard values. The values of the grain size ( $D$ ), strain ( $\epsilon$ ), dislocation density ( $\delta$ ) for all the samples of CuS, CuSe,  $\text{CuS}_{0.2}\text{Se}_{0.8}$  along [511] direction of cubic phase, calculated using equations 1 and 2, are given in Table 2. It is clear from Table 2 that for the CuS and CuSe thin films, the values of FWHM, strain and dislocation density are minimum.

Table 1. d-values for different compositions of thin films.

Thin films	$2\theta$ (deg.)	d-calculated	d-standard
CuS	90.33	1.08	1.10
CuSe	90.40	1.08	1.10
CuSSe	90.34	1.08	1.10

### 3.2. Morphological studies

The two dimensional surface morphology of  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin film at different magnifications is shown in Fig. 2 (A, B, C). It can be seen that the fluorine doped tin oxide (FTO) substrate is well covered by  $\text{CuS}_{0.2}\text{Se}_{0.8}$  composite thin film. The grains are irregular in size and shape, with nanoplatelets-like structure [21]. The thickness of the nanoplatelets, as seen from SEM image, is in the range of 140 to 150 nm. The nanoplatelets in

the film are randomly spread and they collide with each other. This may be due to the slow growth of the nanoplatelets. Average thickness of electrodeposited  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin film is 975 nm.

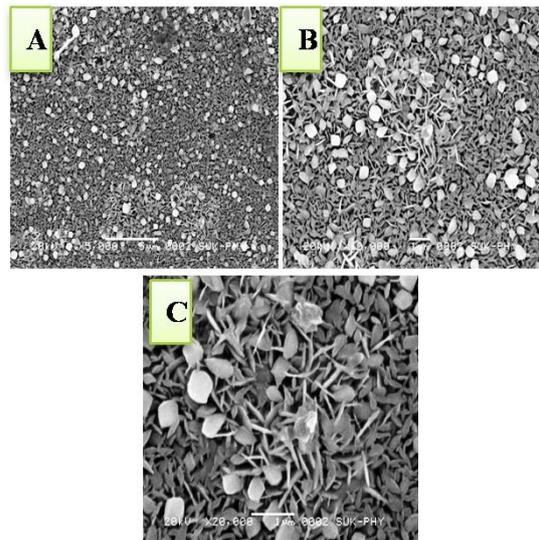


Fig. 2. SEM images of  $\text{CuS}_{0.2}\text{Se}_{0.8}$  film at three different magnifications (5000 $\times$ , 10000 $\times$  and 20000 $\times$ ).

### 3.3. Optical absorption study

Fig. 3A shows the optical absorption spectra of an electrodeposited  $\text{CuS}_{0.2}\text{Se}_{0.8}$  film recorded in the range between 300 and 1100 nm using UV-Vis spectrophotometer (UV1800, Shimadzu, Japan). Absorption coefficient of the film is calculated using relation 4:

$$\alpha = \frac{A(h\nu - E_g)}{h\nu} \quad (4)$$

where  $\alpha$  is the absorption coefficient,  $h$  is Planck constant,  $h\nu$  is photon energy. Energy band gap was obtained by extrapolating the line of the plot  $(\alpha h\nu)^2$  against  $(h\nu)$ . The intersection of the extrapolated line on the energy axis gives the energy band gap as 1.90 eV, which is shown in Fig. 3A. This band gap value is appropriate for thin films used as absorbing layer in solar cells. The value reported in present investigation is nearly the same as reported in the literature [7].

Table 2. Dislocation density for all the samples.

Thin film	2 $\theta$	FWHM)	Grain size (nm)	Strain (lines <sup>-2</sup> m <sup>-4</sup> )	Dislocation density ( $\delta \times 10^{13}$ ) (lines/m <sup>2</sup> )
CuS	90.33	0.49	22.99	0.0860	0.001892
CuSe	90.40	0.52	21.68	0.0911	0.002127
CuS <sub>0.8</sub> Se <sub>0.2</sub>	90.34	0.54	20.86	0.0948	0.002298

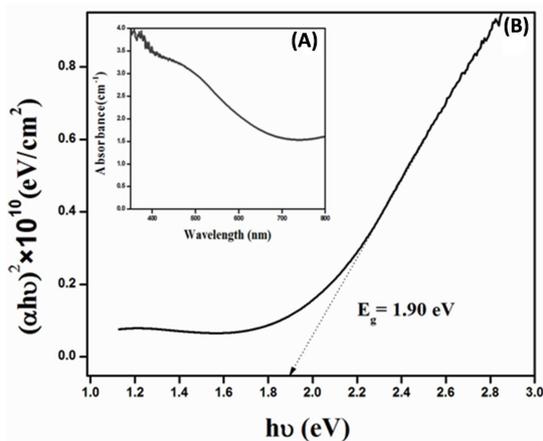


Fig. 3. (A) Optical absorption spectra of electrodeposited CuS<sub>0.2</sub>Se<sub>0.8</sub> film; (B) plots of band gaps of CuS<sub>0.2</sub>Se<sub>0.8</sub> film.

### 3.4. Photoluminescence spectroscopy

Fig. 4 shows the photoluminescence spectra of the CuS<sub>0.2</sub>Se<sub>0.8</sub> thin film prepared by electrodeposition method. It shows an excitation and an emission peak (due to the recombination of the electron and hole) at  $\lambda$  of 442 nm 450 nm, respectively. Emission wavelength  $\lambda$  of CuS thin film is reported as 355 nm [22]. The variation in the excitation peak of CuS<sub>0.2</sub>Se<sub>0.8</sub> thin film may be due to the variation in the composition and morphology of the material.

### 3.5. Wettability studies

The interaction between liquid and solid is studied using the contact angle measurement [23]. The relation between surface water contact angle and wettability is given by the Young's relation [24]. If a contact angle of a film is higher, wettability of the film is less. Fig. 5 shows the contact angle of

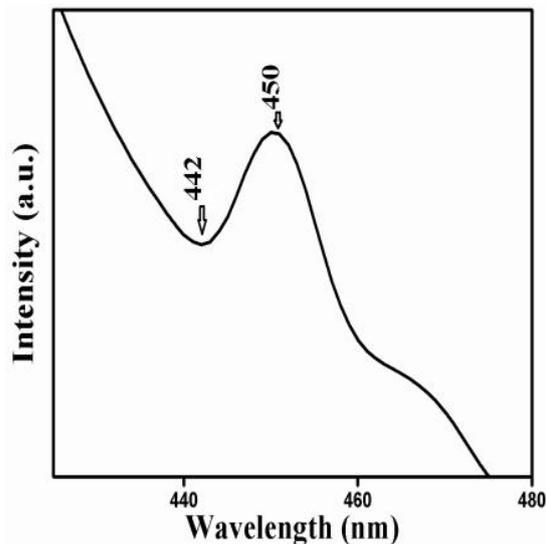


Fig. 4. Photoluminescence (PL) spectra of CuS<sub>0.2</sub>Se<sub>0.8</sub> thin film.

CuS<sub>0.2</sub>Se<sub>0.8</sub> film deposited on a stainless steel substrate. The contact angle of 96° indicates that the film is hydrophobic, which may be due to the weak cohesive force between the film and the water droplet. The water droplet showed the same shape on the thin film whenever we tilted the film at some angle.

The contact angle measurement is used to estimate surface free energy. The surface free energy of a solid is calculated from its surface and interfacial behavior in processes, such as wetting and adhesion. The surface free energy of the CuS<sub>0.2</sub>Se<sub>0.8</sub> surfaces is calculated using the following expression [25]:

$$\gamma_{sv} = \frac{\gamma_w(1 + \cos \theta)}{4} \quad (5)$$

Surface adhesion is an important parameter for the wetting of solid surfaces. The strength of adhesion

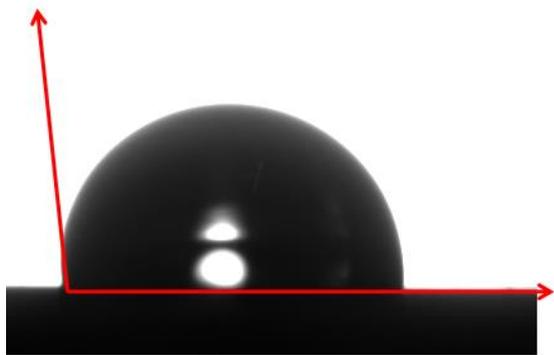


Fig. 5. Contact angle measurement of  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin film.

to a solid surface can be measured directly using the following equation:

$$W_{sl} = \gamma_w(1 + \cos \theta) \quad (6)$$

where  $\gamma_w$  is the surface tension of water, i.e. 71.99 mN/m,  $W_{sl}$  is the work of adhesion between the solid and liquid surfaces and  $\gamma_{sv}$  is surface free energy of the solid.

#### 4. Conclusion

In present work, we have reported the electrochemical synthesis of copper sulfide selenide thin films of nanoplatelets-like morphology. Their XRD patterns show that the films are polycrystalline in nature with a cubic crystal structure. The surface morphology shows that the whole surface of the substrate is covered by nanoplatelets. The  $\text{CuS}_{0.2}\text{Se}_{0.8}$  thin films have an energy band gap of 1.90 eV. Optical and structural study revealed that the copper sulfide selenide thin films may be suitable to be used as absorber layers in solar cell applications. Contact angle study showed that the films are hydrophobic in nature.

#### References

- [1] WU Y., WADIA C., MA W., SADTLER B., ALIVISATOS A.P., *Nano Lett.*, 8 (2008), 2551.
- [2] SHINDE S.K., THOMBARE J.V., DUBAL D.P., FULARI V.J., *Appl. Surf. Sci.*, 282 (2013), 561.
- [3] JIANG Y., ZHANG X., GE Q.Q., YU B.B., ZOU Y.G., JIANG W.J., SONG W.G., WAN L.J., HU J.S., *Nano Lett.*, 14 (2014), 365.
- [4] KALANUR S.S., CHAE S.Y., JOO O.S., *Electrochim. Acta*, 103 (2013), 91.
- [5] CHEN Y., DAVOISNE C., TARASCON J.M., GUERY C., *J. Mater. Chem.*, 22 (2012), 5295.
- [6] SAGADE A.A., SHARMA R., *Sensor. Actuat. B-Chem.*, 133 (2008) 135.
- [7] WANG J.J., XUE D.J., GUO Y.G., HU J.S., WAN L.J., *J. Am. Chem. Soc.*, 133 (2011), 18558.
- [8] DHASADE S.S., PATIL J.S., HAN S.H., RATH M.C., FULARI V.J., *Mater. Lett.*, 90 (2013), 138.
- [9] CHAKI S.H., DESHPANDE M.P., TAILOR J.P., *Thin Solid Films*, 550 (2014), 291.
- [10] ADELIFARD M., ESHGHI H., MOHAGHEGHI M.M.B., *Appl. Surf. Sci.*, 258 (2012), 5733.
- [11] YILDIRIMA M.A., ATEŞ A., ASTAM A., *Physica E*, 41 (2009), 1365.
- [12] DHASADE S.S., PATIL S., RATH M.C., THOMBARE J.V., FULARI V.J., *Mater. Lett.*, 107 (2013), 265.
- [13] MANDAL A., PRAMANIK, *J. Solid State Chem.*, 47 (1983), 81.
- [14] BARI R.H., GANESAN V., POTADAR S., PATIL L.A., *Bull. Mater. Sci.*, 32 (2009), 37.
- [15] PEJOWA B., GROZDANOV I., *J. Solid State Chem.*, 158 (2001), 49.
- [16] XU J., ZHANG W., YANG Z., DING S., ZENG C., CHEN L., WANG Q., YANG S., *Adv. Funct. Mater.*, 19 (2009) 1759.
- [17] MALOTO N., PUGGENS H., GOVINDRAJU S., RAKGALAKANE B., KALENGA M., *Thin Solid Films*, 531 (2013), 446.
- [18] DILENA E., DORFS D., GEORGE C., MISZT K., POVIA M., GENOVESE A., CASU A., PRATO M., MANNA L., *J. Mater. Chem.*, 22 (2012), 13023.
- [19] CuS JCPDS Card No. 01-075-2241.
- [20] CuSe JCPDS Card No. 01-071-0044.
- [21] JUSTIN RAJ C., KIM B.C., CHO W.J., LEE W.G., SEO Y., YU K.H., *J. Alloy. Compd.*, 586 (2014), 191.
- [22] MAGESHWARI K., MALI S.S., HEMALATHA T., SATHYAMOORTHY R., PATIL P.S., *Prog. Solid State Ch.*, 39 (2011), 118.
- [23] DUBAL D.P., DHAWALE D.S., MORE A.M., LOKHANDE C.D., *J. Mater. Sci.*, 46 (2011), 2288.
- [24] LOKHANDE C.D., BARKSCHAT A., TRIBUTSCH H., *Sol. Energ. Mat. Sol. C*, 79 (2003), 293.
- [25] GURAV A.B., LATTHE S.S., VHATKAR R.S., LEE J.G., KIM D.Y., PARK J.J., YOON S.S., *Ceram. Int.*, 40 (2014), 7151.

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