

## Temperature influence study on copper selenide films

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Copper selenide was prepared by film is successfully deposited on a Fluorine-doped Tin Oxide (FTO) substrate by a brush plating technique. The film was uniform, had good adherence to the substrate and was annealed at 300 °C and 500 °C. As the annealing temperature increased, the orientation of the crystallites is more randomized than in the as-prepared film. The structural and optical properties of the film were investigated by XRD, SEM, EDAX, UV-Visible and PL. The XRD pattern indicated that this film was crystalline in the structure.

**Keywords:** Brush plating, copper selenide, optical properties.

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### 1. Introduction

Copper selenide (Cu<sub>2</sub>Se) thin films have attracted considerable interest over the last year owing their wide range of applications in optoelectronic devices and solar cells. Copper selenide is an interesting metal chalcogenide semiconductor material. A copper selenide thin film has a direct band gap and is transparent over a wide range of the visible spectrum. It is seen that the photoelectronic and other properties of II–VI class of compound thin films are highly optically-sensitive, which in turn, can severely influence device performance [1]. More progress has been achieved in the fabrication of light emitting diodes, dielectric mirrors and other optically sensitive devices.

Selenium-based alloys are not stable under standard operational conditions because their glass transitions are typically close to room temperature. In order to stabilize these glasses it is common to use an additive which acts as a cross-linking agent and increase the dimensionality of structure and stability of the material [2]. The purpose of present study is to explore and report in detail the structural properties and optical properties of copper selenide thin film prepared by brush plating technique.

### 2. Experimental procedure

The precursor solution was prepared by stirring 1 g of copper(II) sulfate (CuSO<sub>4</sub>) and 0.05 gm of selenium dioxide (SeO<sub>2</sub>) in 5 ml of distilled water until the powder is totally mixed to provide a saturated solution. The Copper Selenide thin films were prepared by Brush Plating technique. The films were grown on Fluorine doped Tin Oxide (FTO) substrate under optimized conditions. These grown films were uniform, blue in color and showed good adherence to the substrate surface. All chemicals were of AR grade.

The as-deposited films were annealed at 300 °C and 500 °C for about 1 hr. The annealed film was utilized for optical- and structural properties studies.

### 3. Results and discussion

#### 3.1. XRD Analysis

Figures 1(a) and (b) show the X-ray diffraction pattern of the brush plated copper selenide thin film. The XRD pattern obtained correlated well with the standard JCPDS (06-680) data.

Crystallite size ( $D$ ) was calculated using Debye-Scherrer's formula [3]:

$$D = 0.94\lambda / \beta \cos \theta,$$

where  $D$  is the crystallite size,  $\lambda$  is the wavelength of the  $k_{\alpha}$  line,  $\beta$  is the full width at half maxima (FWHM) in radians and  $\theta$  is the Bragg's angle. The crystallite grain size increased from 2 – 53 nm as the annealing temperature increased [4]. The observed 'd' values 4.5, 2.2, 2.0, 1.5 Å are in good agreement with the standard 'd' values. Peaks corresponding to (1 1 0), (2 2 0), (3 1 0), (4 0 1) were observed [5].



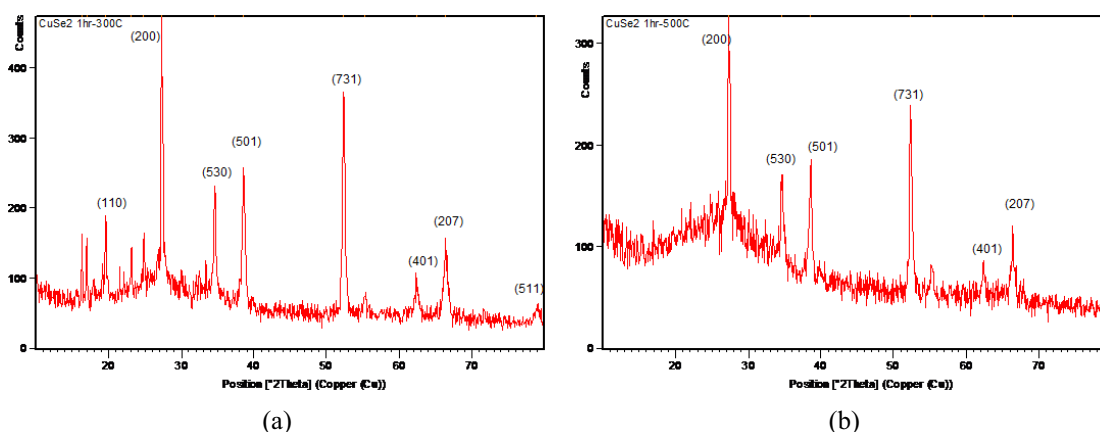


FIG. 1. XRD pattern of Cu<sub>2</sub>Se thin film annealed at 300 °C (a) and 500 °C (b)

### 3.2. Morphological studies and compositional analysis

Scanning electron microscopy is a convenient tool to study the surface morphology of micro- and nanoscale materials as well as thin films. Fig. 2(a,b) shows the SEM images of CuSe thin films annealed at 300 °C and 500 °C recorded at 20 kV with the magnification 10000 using the instrument JSM-6390. The particle size increased as the annealing temperature increased [6].

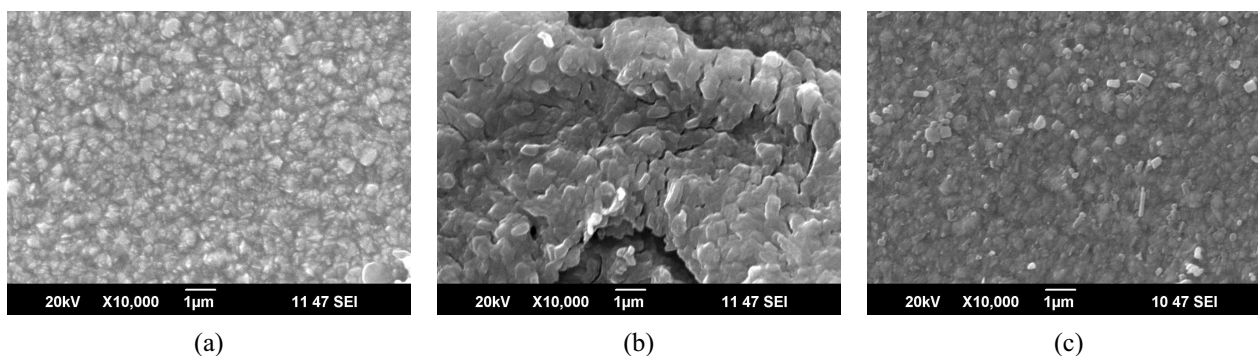


FIG. 2. SEM image of Cu<sub>2</sub>Se as deposited (a); annealed at 300 °C (b) and 500 °C (c)

The EDAX analysis from Fig. 3(a-c) revealed that the presence of copper, selenium, oxygen and other elements like silicon, tin on the FTO substrate. The EDAX spectrum recorded in the binding energy region of 0 – 10 keV showed the presence of copper and selenium in thin films. EDAX analysis of the mass % and atom % of copper selenide films are tabulated in Table 1. EDAX spectrum confirms the presence of copper and selenium in the thin films [7].

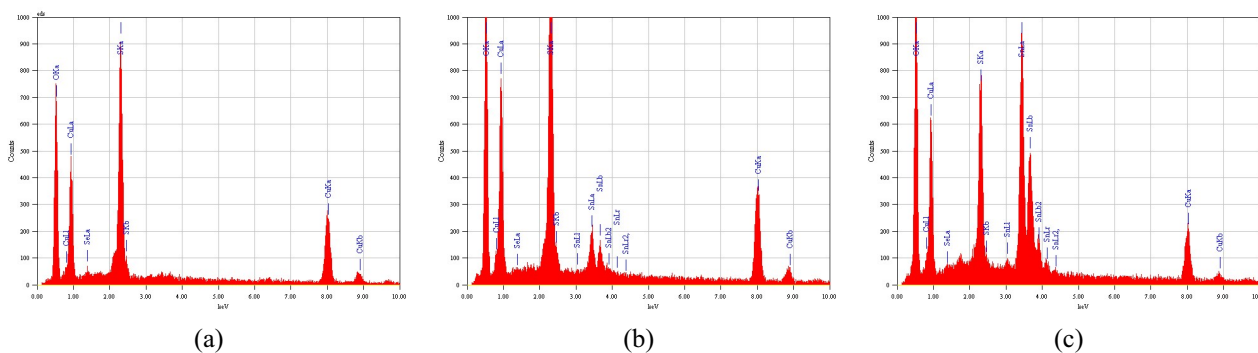


FIG. 3. EDAX analysis of Cu<sub>2</sub>Se as deposited (a); annealed at 300 °C (b) and 500 °C (c)

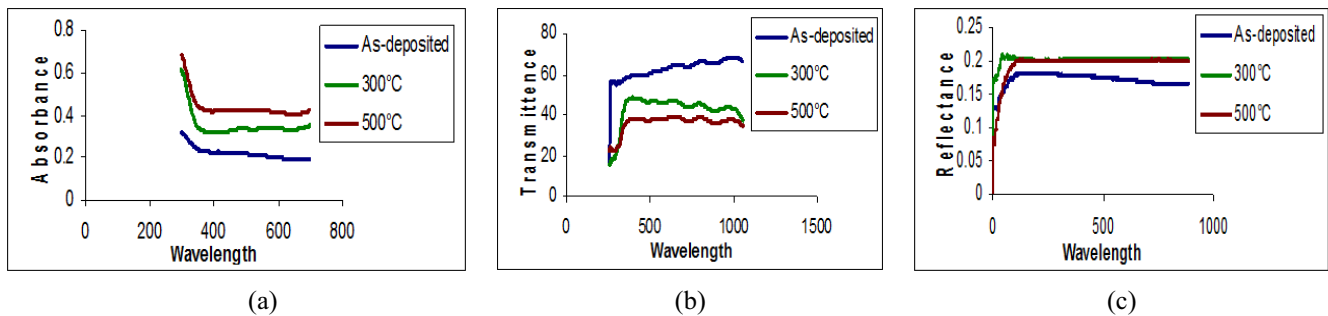


TABLE 1. Mass and Atom percentage of Cu<sub>2</sub>Se annealed at 300 °C and 500 °C

Sample	Mass %		Atom %	
	Copper	Selenium	Copper	Selenium
As-deposited	49.35	1.19	26.23	0.51
Annealed at 300 °C	38.73	0.42	21.78	0.19
Annealed at 500 °C	16.37	0.41	12.89	0.26

### 3.3. Optical absorption, transmittance and reflectance measurement

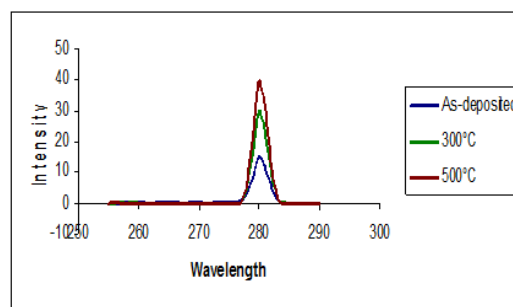
The typical optical absorbance, transmittance  $T(\%)$  spectra and reflectance spectra of the films prepared using brush plating method are presented in Fig. 4(a–c) respectively for the as-deposited and annealed samples (at 300 °C and 500 °C). Annealing the film at 300 °C and 500 °C resulted in some changes in the optical transmittance and absorbance spectra of the films.

FIG. 4. Absorption (a), transmittance (b) and reflectance (c) spectra for Cu<sub>2</sub>Se

The Egdir values for the samples were as follows: as-deposited – 2.95 eV; 300 °C annealing – 2.86 eV and 500 °C annealing – 2.75 eV. The Egind values were as follows: as-deposited – 2.16 eV; 300 °C annealing – 2.54 eV and 500 °C annealing – 2.38 eV. The indirect band gap values were as follows: re as-deposited – 2.16 eV; 300 °C annealing – 2.54 eV and 500 °C annealing – 2.38 eV. All these optical band gap values are close to those previously obtained for the material used for solar cells, which means that these materials have good utility for this purpose [8].

### 3.4. Photoluminescence spectrum

The photoluminescence spectra of Cu<sub>2</sub>Se thin films are shown in Fig. 5. From the spectra, the photons are excited at a wavelength of 280 nm. As the annealing temperature increases, the intensity of the peak increases. From the spectra, the peaks observed in emission of Cu<sub>2</sub>Se thin films are at a wavelength 561 nm [9]. The spectra of the as-deposited Cu<sub>2</sub>Se films and the annealed films showed increasing intensity as the annealing temperature increased.

FIG. 5. Excitation Spectra of Cu<sub>2</sub>Se



#### 4. Conclusion

Copper Selenide thin films were successfully deposited on FTO substrates by a brush plating technique. The films were uniform and had good adherence to the substrate. The XRD of Copper Selenide films formed a cubic structure. The crystalline size of the films were determined by Scherrer's formula and it increased from 2 – 53 nm as the annealing temperature increased [10]. The energy gap values of the films were determined and compared with the reported one. The emitted and excited wavelength were determined from the photoluminescence spectra. The structural properties, surface morphological studies and chemical composition analysis were investigated and reported.

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