# Physical, optical and electrical properties of copper selenide (CuSe) thin films deposited by solution growth technique at room temperature

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## Abstract

Copper selenide (CuSe) thin films are grown onto amorphous glass substrate from an aqueous alkaline medium using solution growth technique (SGT) at room temperature. The preparative parameters were optimized to obtain good quality of thin films. The as-deposited films were characterized for physical, optical and electrical properties. X-ray diffraction (XRD) pattern reveals that the films are polycrystalline in nature. Energy dispersive analysis by X-ray (EDAX) shows formation of stoichiometric CuSe compound. Uniform deposition of CuSe thin films on glass substrate was observed from scanning electron microscopy (SEM) and atomic force microscopy (AFM) micrographs. Average grain size was determined to $144.53 \pm 10$ nm using atomic force microscopy. The band gap was found to be 2.03 eV with direct band-to-band transition. Semi-conducting behaviour was observed from resistivity measurements. Ohmic behaviour was seen from $I–V$ curve with good electrical conductivity.
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## 1. Introduction

Thin chalcogenide films are of particular interest for the fabrication of large area photodiode arrays, solar selective coatings, solar cells, photoconductors, sensors, etc. [1]. Copper chalcogenide thin films have number of applications in various devices such as solar cells, superionic conductors, photodetectors, photothermal conversion, electro-conductive electrodes, microwave shielding coating, etc. [2–5]. Copper selenide (CuSe) is a semiconducting material, which has electrical and optical properties suitable for photovoltaic application. It has many phases and structural forms: stoichiometric $\alpha$-$Cu_2Se$, $Cu_3Se_2$, CuSe, and $CuSe_2$, as well as non-stoichiometric, $Cu_{2-x}Se$. CuSe is reported as hexagonal at room temperature and undergoes transition to orthorhombic at 48 °C and back to hexagonal at 120 °C [6]. Copper selenide has p-type conductivity, property useful in the solar cell production. $Cu_{2-x}Se$ is reported to possess a direct band

gap of 2.2 eV and an indirect band gap of 1.4 eV for $x = 0.2$ [7]. However, Vohl et al. [8], Okimura et al. [4], and Tadashi et al. [9] has obtained only wide direct band gap of 2.0 eV. While Sharma et al. [10,19] and Padam [11] has obtained a direct band gap of around 1.2 eV. The cuprous selenide single crystal however, gives absorption edge at 1.2 eV [12]. The wide variation in band gaps are thought to be due to sharp cut off of the wavelength with spectral transmittance instead of slow increase [10], wide range of stiochiometric deviation, the presence of large number of dislocations, changes in barrier height due to variation in grain size in polycrystalline films and quantum size effect [13]. The direct band gap is always preferred over indirect one, due to reasons of momentum conservation and fast response. The use of copper selenide films to form a junction with n-type semiconductors either as absorber in heterojunction with CdS or as window material in heterojunction with n-Si has been demonstrated [4,7,14,15], showing conversion efficiencies of up to 8.8%. This is the main motivation to study copper selenide thin films. A number of reports on growth and characterization of thin films of this compound have been presented by several workers using various deposition techniques like Vacuum evaporation

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[7], melting of Cu and Se [16], electro deposition [17,18], solution growth [19] and chemical bath deposition [20,21] to name a few. Though the literature ensures a lot of work is done on this compound; but still researchers are in constant search to explore the vast number of applications provided by this compound due to its excellent properties.

In the present investigation, semi-conducting copper selenide thin films have been deposited at room temperature onto glass substrates using solution growth technique (SGT). The paper deals with preparation, characterization, growth mechanism and some of its properties. The results are discussed and compared with the reported data wherever necessary.

## 2. Experimental details

### 2.1. Thin film preparation

Thin films of copper selenide have been grown by solution growth technique using selenium powder, sodium sulphite, cupric chloride and ammonia (AR grade). A solution of sodium selenosulphate was prepared by refluxing 100 ml of 0.4 M sodium sulphite with selenium powder for about 5–6 h. This solution will contain excess of sodium sulphite which prevents the oxidation of selenide to selenium [15]. Reaction bath contains 10 ml 0.1 M $CuCl_2 \cdot 2H_2O$, 0.8 ml of 30% $NH_3$ aqueous, 10 ml of freshly prepared solution of $Na_2SeSO_3$ in 100 ml beaker and the rest distilled water to make the volume to 50 ml. On controlling the pH value at 10.0, uniform films of copper selenide have been obtained on glass substrates. Well-cleaned glass substrates were then immersed vertically into the deposition bath against the wall of the beaker containing the reaction mixture. The deposition was allowed to proceed at room temperature for different time durations. After deposition, the glass microslides were taken out from the bath, washed with de-ionized water and was dried in air. By several trails, we optimized the preparative parameters, concentration of the reactant solutions ($CuCl_2$ and $Na_2SeSO_3$), 0.1 M, pH 10, deposition temperature 300 K and deposition time 6 h. The as-deposited films of copper selenide were further studied for various properties.

### 2.2. Characterization techniques

The thin films of CuSe were characterized for structural, optical and electrical properties. The CuSe film thickness was measured by Fizeau fringe technique. X-ray diffraction (XRD) patterns of the film were recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 10–60° (2$\theta$) using Cu K$\alpha$ radiations with wavelength 1.5405 Å. The surface morphology and composition was studied by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) using JOEL-JSM-5600. An atomic force microscopy (AFM) study was done using Nanoscope IIIa provided by Vecco digital instruments. To study the optical characteristics of the film, absorbance spectra were recorded in the range 350–850 nm by means of Systronic UV–vis spectrophotometer 117. The resistivity measurements were done using DC four point probe method in the temperature range 300–500 K. The *I–V* characteristics were studied using lab equipment unit (model no. 2004), over the range from ±1 V.

## 3. Results and discussions

### 3.1. Growth mechanism

The CuSe films are obtained from an aqueous alkaline bath containing $Cu^{2+}$ and $Se^{2-}$. The deposition process based on the release of $Cu^{2+}$ and $Se^{2-}$ ions in the solution, which then condense ion-by-ion basis on the substrate that are suitably mounted in a reaction solution. For the deposition of the film, the availability of the nucleation centers over the substrate is necessary. Such
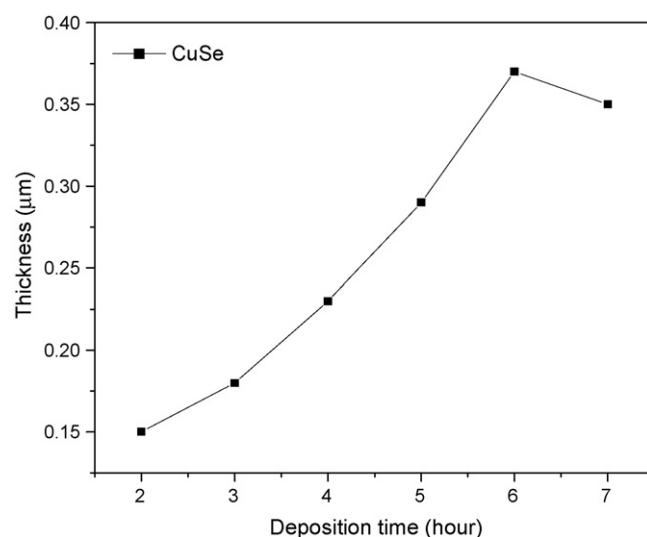


Fig. 1. Plot of variation of thickness with deposition time for CuSe thin films.

centers are normally formed through the adsorption of metal hydroxo species over the surface. The hydroxo group would be substituted by sulfide and selenide ions, which would thereby form an initial layer of the metal chalcogenide [21]. The information regarding growth mechanism can be obtained by studying the variation of the film thickness with deposition time at constant bath temperature (300 K). The deposition time was varied between 2 and 7 h. After 3 h, clear solution was changed into faint red colour, indicating initiation of the reaction. Fig. 1 shows the variation of CuSe film thickness with deposition time. Initially, CuSe film thickness was increased linearly up to 6 h and slightly decreased for further deposition time. The maximum thickness of the CuSe film was found to be 0.37 μm; and further film was powdery and film thickness decreased due to dissolution of film in the solution [22]. In addition, at longer deposition time, the reaction in the bath is completed and hence there is absence of $Cu^{2+}$ and $Se^{2-}$ ions. So, the optimized deposition time is 6 h.
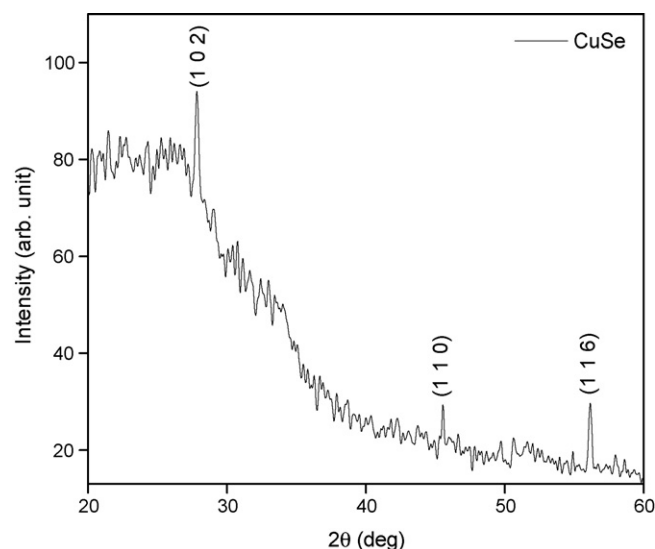


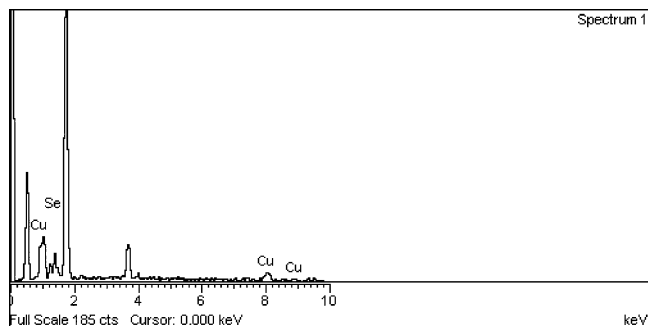Fig. 2. XRD patterns of as-deposited CuSe thin films at room temperature.

Fig. 3. EDAX spectrum of as-deposited CuSe thin films at room temperature.

## 3.2. Structural and compositional analysis

Fig. 2 shows X-ray diffraction patterns of CuSe thin films of 0.37 μm thickness. X-ray diffraction pattern reveals that the films of CuSe deposited by solution growth technique are polycrystalline in nature. It was observed that the highest intensity reflection peaks at $2\theta = 27.83°$ (1 0 2) plane, $2\theta = 45.55°$ (1 1 0) plane, and $2\theta = 56.16°$ (1 1 6) plane for CuSe thin film. A comparison of observed and the standard (h k l) planes ensures that the deposited films are of CuSe (mineral Klockmannite) with hexagonal structure [23]. The broad hump observed in the Fig. 1 is due to the amorphous glass substrate. After refinement, the cell constants were calculated to be $a = b = 3.978$ Å and $c = 17.156$ Å; which are consistent with the reported data [23]. Although, there are more than eight stoichiometries of copper selenide, and some stoichiometries have different phases each of them has their own characteristic X-ray diffraction pattern [24]. Therefore, the X-ray diffraction patterns give the most positive evidence of the formation of CuSe phase, which was desired. The compositional analysis of the films was carried out using energy dispersive X-ray analysis technique to study the Stoichiometry of the films. Fig. 3 shows the energy dispersive analysis by X-ray spectrum for CuSe thin films by solution growth technique. The elemental analysis was carried out only for Cu and Se; the average atomic percentage of Cu:Se was 51.15:48.85. It is close to 1:1
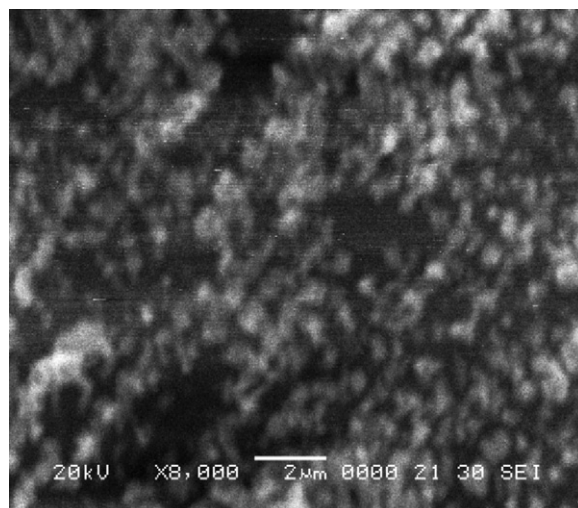


Fig. 4. SEM micrograph of as-deposited CuSe thin films at room temperature.

stoichiometry. Similar results for CuSe were reported by Li et al. [25] using energy dispersive analysis by X-ray data.

## 3.3. Surface morphological and topographical analysis

Fig. 4 shows the scanning electron microscopy micrograph of as-deposited films with magnification 8000×. It can be observed that the CuSe thin films are uniform and cover the substrate well. From the micrograph it is clear that the films were composed of a compact structure single type of small densely packed microcrystals. The grains are well defined, spherical, of almost similar size, which were uniformly distributed over a smooth homogeneous background that may correspond to the amorphous phase of CuSe film. The presence of fine grain background is an indication of one-step growth by multiple nucleations. Fig. 5 indicates 2D atomic force microscopy image (1.0 × 1.0 μm) of as-deposited CuSe thin film. From the image it is clear that the film is uniform and the substrate surface is well covered by fine spherical or elliptical nature of the grains. The spheri-
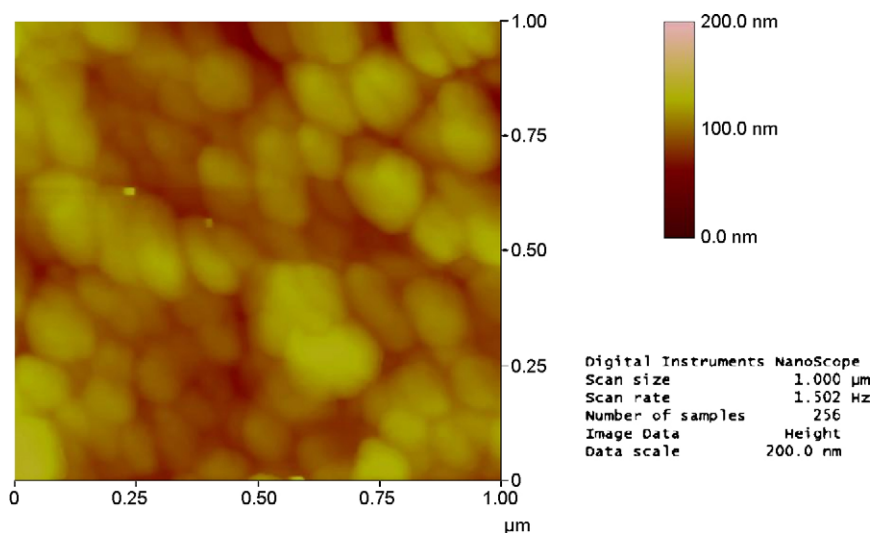


Fig. 5. AFM image of as-deposited CuSe thin films at room temperature.

cal or elliptical grains could be attributed to faster growth due to slightly higher concentration of copper in the composition. There was agglomeration of particles in the most of the cases as evident from the 2D image (Fig. 5). The average grain size was determined to be $144.53 \pm 10$ nm and the surface roughness was 13.1 nm. The surface roughness of the film is unavoidable due to particles are spherical in shape. This observation reveals that the films are crystalline in nature.

### 3.4. Optical analysis

The theory of optical absorption gives the relation between the absorption coefficient and the photon energy, for direct allowed transition as:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad (1)$$

where $A$ is the constant, $E_g$ is the band gap, $h\nu$ is the photon energy.

From Fig. 6 shows the variation of $(\alpha h\nu)^2$ with $h\nu$. By extrapolating straight line portion of $(\alpha h\nu)^2$ against $h\nu$ plot to $\alpha = 0$, the optical band gap energy was found to be 2.03 eV, comparable with the value reported earlier [26] for room temperature deposited CuSe thin film.

### 3.5. Electrical analysis

The dark electrical resistivity of the thin films was measured using a DC four-probe method in the temperature range 300–500 K. A plot of inverse absolute temperature versus log (resistivity) for a cooling cycle is shown in Fig. 7. The dependence is almost linear indicating the presence of only one type of conduction mechanism in the film. A similar behaviour has been reported by earlier workers [27,28] for $Cu_{2-x}Se$ films. Since, our experimental data fit into the relation,

$$\rho = \rho_0 \exp(-E_a/KT) \qquad (2)$$



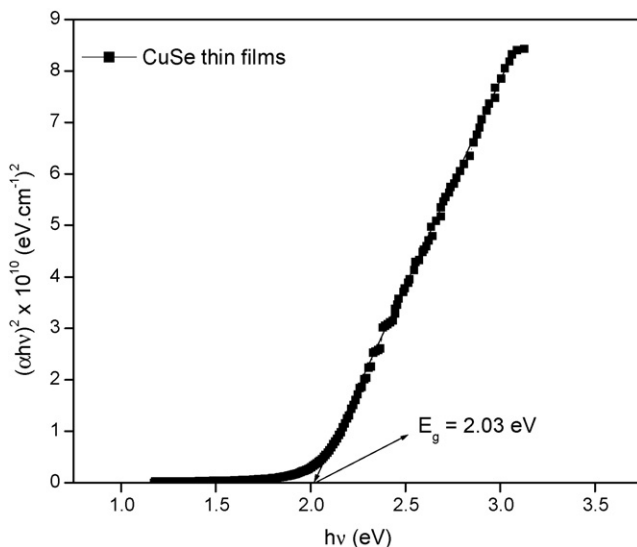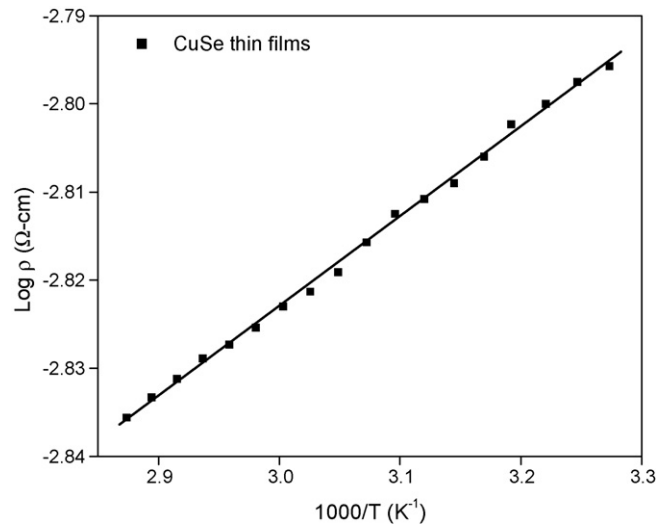Fig. 7. Plot of $\log \rho$ vs. $1000/T$ for CuSe thin films.

where $\rho$ is the resistivity at temperature $T$, $\rho_0$ is a constant, $K$ is Boltzman's constant, $T$ is the absolute temperature and $E_a$ is the activation energy.

The high-temperature conductivity is a thermally activated mechanism, which is attributed to the thermal excitation of charge carriers from grain boundaries to the neutral region of the grains.

In this case, activation energy was calculated from linear portion of the graph and is found to be 0.20 eV. Lower activation energy in our case might be due to slightly higher atomic percentage of copper. This could be further attributed to high reactivity of copper ions with available anions. Due to high reactivity larger atomic percentage of copper ions would be incorporated in composition, which leads to higher conductivity, and in turn, lower activation energy. The decrease in resistivity with increase in temperature confirms the semi-conducting behaviour of the film. The room temperature electrical resistivity was found to be $1.6 \times 10^{-3}$ $\Omega$ cm, which is quite lower than



Fig. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for CuSe thin films.
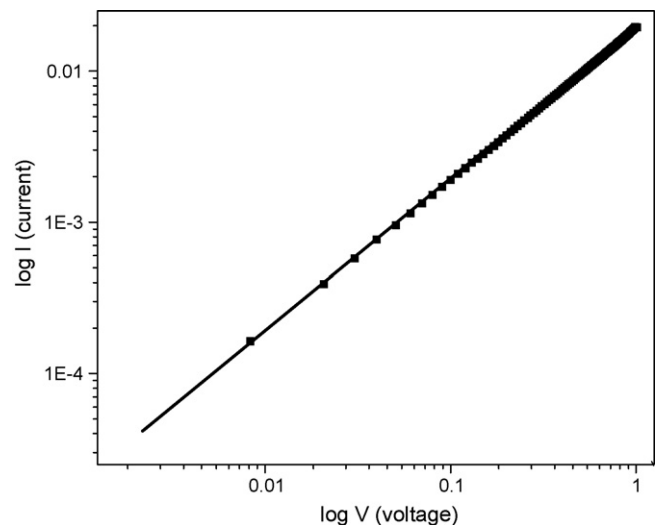


Fig. 8. $\log I$–$\log V$ characteristics curve for CuSe thin films.

the reported value [29]. Fig. 8 shows the dark logarithm *I–V* characteristics curve for the film deposited at room temperature. The linear nature from the plot suggests the ohmic nature of the copper selenide thin films. The resistivity was found to be $1.4 \times 10^{-3} \, \Omega$ cm from *I–V* curve, which is approximately near to the resistivity calculated by four point probe method.

## 4. Conclusion

Thin films of CuSe have been successfully deposited by solution growth technique. Polycrystalline nature was predicted from X-ray diffraction studies. Stoichiometric films of CuSe were observed from energy dispersive analysis by X-ray studies. Scanning electron microscopy and atomic force microscopy studies revealed uniform deposition with the average grain size calculated was $144.53 \pm 10$ nm with surface roughness 13.1 nm. The optical band gap was found to be 2.03 eV. Electrical studies showed that the films are highly conducting which may be used as radiation filters and in opto-electronic devices.

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