

### Synthesis and Characterization of Monovalent, Divalent and Trivalent Cation Doping of Cu<sub>2</sub>Se Thin Films Using Chemical Bath Deposition Method\*

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**Abstract:** In this work, pure and Bi<sup>3+</sup>, Cd<sup>2+</sup>, Na<sup>+</sup> - doped Cu<sub>2</sub>Se thin films were prepared by chemical bath deposition (CBD) method. The effect of doping on optostructural properties was analyzed. XRD patterns show the cubic phase for pure and Bi<sup>3+</sup>, Cd<sup>2+</sup>, Na<sup>+</sup> - doped Cu<sub>2</sub>Se thin films. The doped films show higher absorption than Cu<sub>2</sub>Se in the visible region. The band gap energies of the films were found to be 1.75 eV, 1.70 eV, 3.66 eV, 2.55 eV for pure and Bi<sup>3+</sup>, Cd<sup>2+</sup>, Na<sup>+</sup> - doped Cu<sub>2</sub>Se thin films, respectively.

**Keywords:** Cu<sub>2</sub>Se thin films, Cation doping, chemical bath deposition (CBD), XRD.

## Introduction

Copper selenide is a p-type semi-conductor which is a cost-effective heterojunction solar cell used in solar energy conversion devices with high efficiency [1, 2]. Intensive research has been performed in fabrication and characterization of copper selenide in the form of thin films because of its band gap energy (1.2 eV - 2.3 eV), high optical absorption coefficient, low toxicity and relative abundance [3]. Pathan *et al.* [4] have reported a band gap energy of 2.35 eV for Cu<sub>2</sub>Se thin films. However, the bandgap is greater than the optimum value of solar cells. Hence, it is necessary to enhance the optical properties of the films to use them as a high-efficiency absorbing material.

Doping is the suitable way to tune the optical band gap, because incorporation of foreign atoms in parent material produces discrete energy levels in the intrinsic quantum energy levels, which in turn enhances the optical, electronic and magnetic properties of the host semi-conductor. These properties of a semi-conductor could be modified by doping with

divalent and trivalent metal cations due to the fact that they provide extra electrons, which enhances or modifies the properties [5]. Recently, trivalent Bi<sup>3+</sup> - doped SnS thin films showed the lowest resistivity of  $4.788 \times 10^{-1} \Omega\text{-cm}$  [6]. Luo *et al.* reported that the addition of trivalent Bi<sup>3+</sup> ions into Mg<sub>2</sub>Si<sub>0.8</sub>Sn<sub>0.2</sub> significantly decreases thermal conductivity and increases electrical conductivity and the Seebeck coefficient [7]. Patel *et al.* stated that Mn-doped CdS nanoparticles can be used for application in dilute magnetic semi-conductors and fabrication of solar cells [8]. Kumar *et al.* [9] have reported that the optical band gap energy was decreased for divalent Cd<sup>2+</sup> - doped ZnO thin films. Mondal and Mitra (2011) reported that divalent Cd<sup>2+</sup> doping in ZnO decreases the optical bandgap [10]. Bera and Saha reported higher efficiency for divalent Zn<sup>2+</sup> - doped dye sensitized solar cells [11]. Ali *et al.* [12] reported high refractive index for Ag<sup>+</sup> - doped ZnO films. Kumar and Thangavel reported that monovalent Na<sup>+</sup> doping has modified the band gap ZnO thin films [13]. From the literature, it is found that the doping of

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monovalent, divalent and trivalent cations modifies the optical and electrical properties of semi-conductor materials. Hence, the objective of this work is to prepare monovalent ( $\text{Na}^+$ ), divalent ( $\text{Cd}^{2+}$ ) and trivalent ( $\text{Bi}^{3+}$ ) ion-doped  $\text{Cu}_2\text{Se}$  thin films by CBD method to study their optical properties

### Experimental Procedure

Pure and  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films were prepared by chemical bath deposition method. The following A.R. grade chemicals were used: copper chloride ( $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$ ), bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), cadmium chloride ( $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ ), selenium (Se), sodium sulphite ( $\text{Na}_2\text{SO}_3 \cdot 5\text{H}_2\text{O}$ ), acetone, HCl, ammonia, glass substrates and distilled water. The substrate cleaning was performed by immersion in chromic acid. Then, the substrates were washed with double distilled water and immersed in HCl solution for etching process for 15 min. The washed substrates were immersed in a 2-propanol solution, then the solution was placed in an ultrasonic bath for 15 min. The ultrasonic bath gives the scrubbing effect on the substrates and removes dust particles from the substrates. Finally, the substrates were washed with double distilled water and cleaned with acetone. Then, they were used for thin film deposition.

Sodium selenosulphate ( $\text{Na}_2\text{SeSO}_3$ ) was prepared by refluxing of 0.1 M of selenium and 0.25 M sodium sulphite dissolved in 400 ml distilled water at  $70^\circ\text{C}$  for 6 hrs. After refluxing, the collected sodium selenosulphate solution was cooled to room temperature. Then, it was filtered and used for the deposition process.

0.1 M of  $\text{CuCl}_2 \cdot 5\text{H}_2\text{O}$  was dissolved in 40 ml distilled water. Ammonia solution was added drop by drop into the copper solution under constant stirring. The color of the solution changed from light green to blue, which indicates the formation of  $\text{Cu}(\text{OH})_2$ , followed by  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex. Further, the blue colour solution turns into deep blue while adding excess ammonia into the solution. Finally, an amount of 40 ml of freshly prepared sodium selenosulphate ( $\text{Na}_2\text{SeSO}_3$ ) solution was slowly added to the Cu complex solution. The colour of the solution again changed to dark green and then to brown, which indicates the formation of  $\text{Cu}_2\text{Se}$ . The pre-cleaned microscope glass substrates (75mm x 25mm) were vertically immersed in the solution and

deposition was carried out at  $70^\circ\text{C}$  for 2 h. The  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films were deposited by adding  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_3 \cdot 5\text{H}_2\text{O}$  into the  $\text{CuCl}_2$  solution, respectively. Afterwards, the substrates were removed from the bath solution and washed several times using distilled water. The deposited films were annealed at  $200^\circ\text{C}$  for 2 h for further characterization.

The prepared pure and doped films were characterized using XRD, FESEM and DRS techniques. X-ray diffraction (XRD) patterns were obtained using a PANalytical X'PERT-PRO diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5460 \text{ \AA}$ ). The diffraction patterns were collected in the range of  $2\theta = 10^\circ - 80^\circ$ . To investigate the surface morphology and roughness of the particles, Field Emission Scanning Electron Microscopy (FESEM) was carried out using FEI - QUANTA-FEG 250. Diffuse Reflection Spectroscopy (DRS) spectra were recorded using a UV-400 PC series UV-visible spectrometer.

### Results and Discussion

Fig. 1 shows the XRD patterns of pure and  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films. In the diffraction patterns, the polycrystalline peaks seen at  $2\theta = 26.77^\circ$  (111),  $44.41^\circ$  (220),  $52.60^\circ$  (311),  $64.97^\circ$  (400),  $71.66^\circ$  (331),  $81.78^\circ$  (422) and  $98.87^\circ$  (440) belong to the cubic structure of  $\text{Cu}_2\text{Se}$  and are in good agreement with the standard JCPDS card no. 65-2982. It is also noticed that no extra peaks were observed for the substitution of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$  - doped  $\text{Cu}_2\text{Se}$  thin films, indicating that the films were in single cubic phase, whereas additional peaks were observed for  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films. The intensity of the primary (220) peak was suppressed and shifted toward lower angle due to doping; hence, the crystallinity of the films was deteriorated (Fig 2). The (220) plane is shifted towards the lower angle for  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films (Fig. 2). The shift is due to the higher ionic radii of  $\text{Bi}^{3+}$  (1.17 Å),  $\text{Cd}^{2+}$  (1.09 Å) and  $\text{Na}^+$  (1.16 Å) than that of  $\text{Cu}^+$  (0.91 Å). The crystalline size of doped films was slightly reduced in comparison to the pure  $\text{Cu}_2\text{Se}$  thin films (Table 1). A similar result (peak shift) was observed by Peng *et al.* [14] for Zn, Mn, Ni, Fe, In and Sm-doped  $\beta\text{-Cu}_2\text{Se}$ . These results confirm the incorporation of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$  and  $\text{Na}^+$  ions in the cubic structure of  $\text{Cu}_2\text{Se}$ .

TABLE 1. Crystalline parameter of pure and Bi<sup>3+</sup>, Cd<sup>2+</sup>, Na<sup>+</sup> doped Cu<sub>2</sub>Se thin films.

S.No.	Sample	D (nm)	$\delta$ (lines/m <sup>2</sup> )	$\epsilon$	a (Å)	V (Å) <sup>3</sup>
1	Cu <sub>2</sub> Se	84.18	1.411 x 10 <sup>14</sup>	2.3 x 10 <sup>-3</sup>	5.73	188.12
2	Bi:Cu <sub>2</sub> Se	70.13	2.033 x 10 <sup>14</sup>	2.9x 10 <sup>-3</sup>	5.746	189.71
3	Cd:Cu <sub>2</sub> Se	69	2.06 x 10 <sup>14</sup>	4.9 x 10 <sup>-3</sup>	5.768	191.90
4	Na:Cu <sub>2</sub> Se	81	1.51x 10 <sup>14</sup>	3.4 x 10 <sup>-3</sup>	5.763	191.40

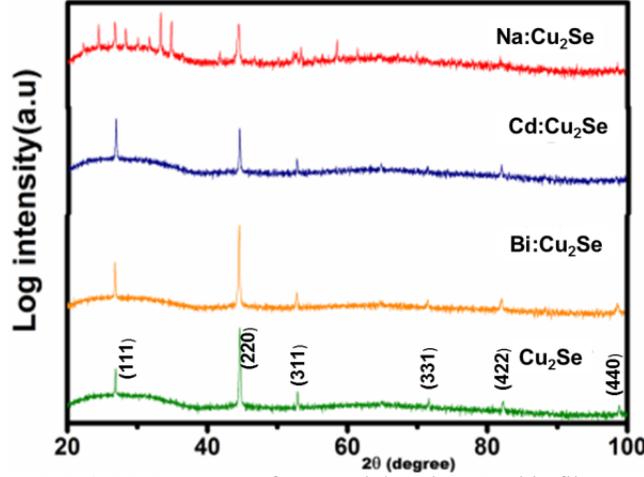


FIG. 1. XRD patterns of pure and doped Cu<sub>2</sub>Se thin films.

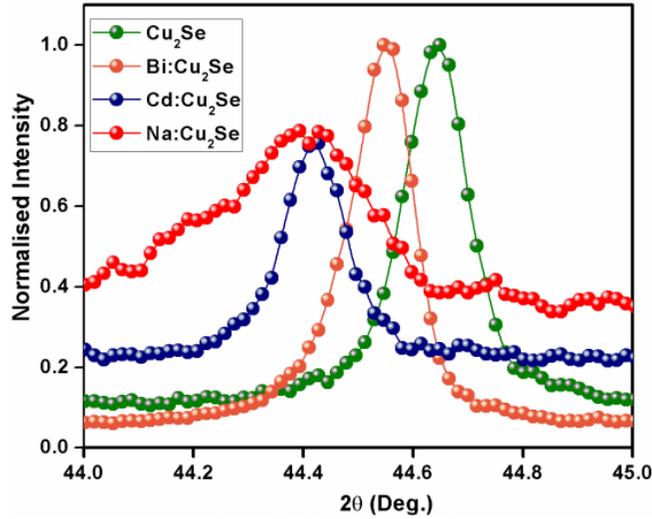


FIG. 2. Peak shift of (220) plane.

The crystalline size was estimated by using Scherrer formula [15]:

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

where  $\beta$  is full width at half maximum (FWHM),  $\lambda$  is the wavelength of X-ray source and  $\theta$  is the Bragg's angle. Dislocation density ( $\delta$ ) was evaluated by the following formula [15] to

obtain information about the amount of defects in the films:

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

The micro-strain can be calculated from the following relation [15]:

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

The calculated values of crystalline size, dislocation density and microstrain were tabulated in Table 1. It is clear, from Table 1, that the crystalline size of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  is smaller than that of pure  $\text{Cu}_2\text{Se}$ . This is attributed to the incorporation of foreign atoms in the parent network that alters the nucleation step during particle growth, limiting the nucleations, which consequently reduces the crystalline size. The dislocation density and stress are found to increase for doped samples. The result is evident for the substitution of  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  ions into the Cu sites. The lattice parameter  $a$ , and the cell volume were calculated

using the unit cell software (method of TJB Holland & SAT Redfern 1995). The calculated values are presented in Table 1. The lattice parameter,  $a$  is found to increase after doping, which confirms the incorporation of larger dopants into smaller Cu sites.

Fig. 3 shows the FESEM images of pure and  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  films. The films show that the well defined, almost similar size particles, were uniformly distributed over the entire surface without any observable voids.

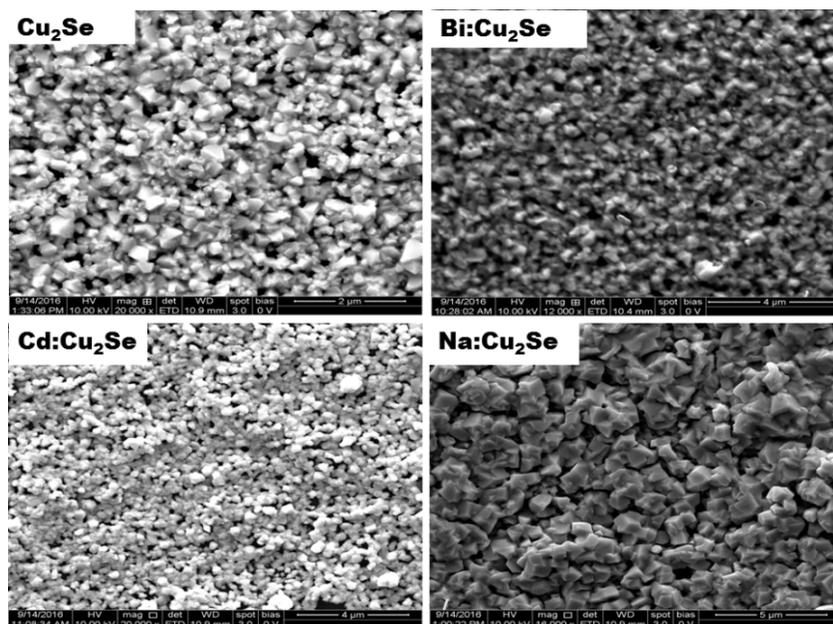


FIG. 3. FESEM images of pure and doped  $\text{Cu}_2\text{Se}$  thin films.

Fig. 4 shows the DRS absorption spectra of pure and  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  films. All films showed higher optical absorption than  $\text{Cu}_2\text{Se}$  in the visible region. The increase in absorbance may be due to the overgrowth of particles on the film surface, which implies scattering losses as suggested by Saima Mushtaq *et al.* (2016) [16]. The calculated band gap values of  $\text{Cu}_2\text{Se}$  and Bi, Cd, Na - doped  $\text{Cu}_2\text{Se}$  films were found to be 1.75 eV, 1.70 eV, 3.66 eV and 2.55 eV, respectively (Fig. 5). It is obviously visible that doping tailors the band gap of the parent material. The  $\text{Cd}^{2+}$  and  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$

films show higher band gap values than those of the other films due to the higher carrier concentration that moved the optical edge towards lower energy and broadened the energy gap. The dopant may dominantly contribute to the width of localized states within the optical band of  $\text{Cu}_2\text{Se}$ . Introduction of  $\text{Cd}^{2+}$  and  $\text{Na}^+$  into  $\text{Cu}_2\text{Se}$  increases the width of the localized states, hence resulting in increasing the band gap. Similar trends of these results were reported for trivalent  $\text{Sb}^{3+}$  - doped  $\text{ZnO}$  and trivalent  $\text{Al}^{3+}$  - doped  $\text{ZnS}$  films studied by other researchers [5, 17].

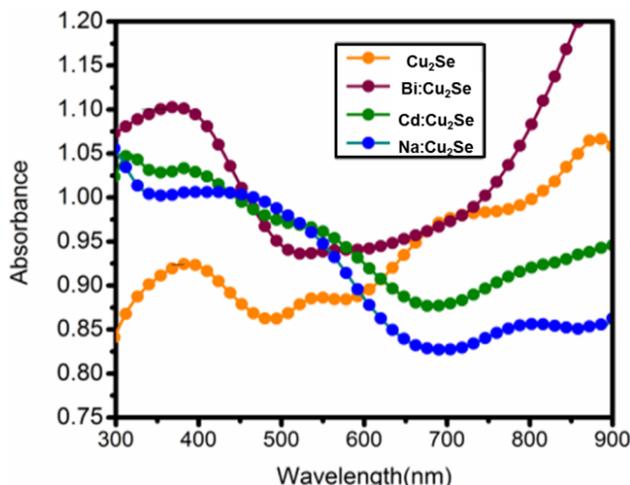


FIG. 4. Absorbance spectra of pure and doped  $\text{Cu}_2\text{Se}$  thin films.

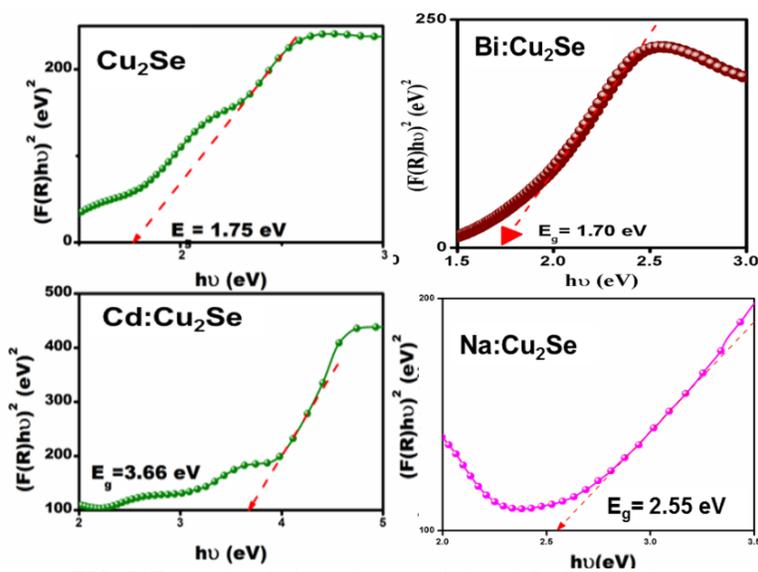


FIG. 5. Energy band plots of pure and doped  $\text{Cu}_2\text{Se}$  thin films.

## Conclusions

Pure and  $\text{Bi}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$  - doped  $\text{Cu}_2\text{Se}$  thin films with cubic phase have been deposited successfully by chemical bath deposition method and the crystalline size was decreased from 84 nm to almost 70 nm for Bi- and Cd-doped and to 81 nm for Na-doped  $\text{Cu}_2\text{Se}$  films. The films were homogeneous and uniform size particles were covering the surface. The optical absorbance study reveals that Bi-doped films show lower band gap of 1.70 eV, whereas Cd- and Na-doped films show higher values of 3.66 eV and 2.55 eV when compared to the band gap of 1.75 eV of pure  $\text{Cu}_2\text{Se}$  films.

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