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Chemosynthesis, characterization and PEC performance of $CdZn(SSe)_2$ thin films by arrested precipitation technique (APT)

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In the present work, we have used simple, cost effective arrested precipitation technique (APT) to deposit $CdZn(SSe)_2$ thin films. Preparative conditions were optimized during the initial stage of experimentation to obtain good quality $CdZn(SSe)_2$ thin films. The as-deposited film was studied for its structural, morphological, optical, and compositional analysis by XRD, SEM, UV-Vis-NIR spectrophotometer and EDSanalysis techniques respectively. XRD analysis revealed that the film was polycrystalline in nature and exhibit hexagonal crystal structure. The SEM micrograph shows the formation of spherical surface morphology. EDS results confirm the presence of Cd, Zn, S and Se elements in the synthesized thin film. The band gap value of thin film was calculated from the absorption spectra which is found to be 1.8 eV. From J–V measurements, photo-conversion efficiency is found to be 0.07%.

Keywords: arrested precipitation technique, thin films, XRD, photoconversion efficiency.

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1. Introduction

The II-VI compounds are becoming interesting and important because of their major applications in solar cells [1] and opto-electronic devices [2]. A variety of techniques presently used for the synthesis of cadmium and zinc chalcogenide semiconductor thin films [3–8]. In all these methods, APT is self organized, cost effective, suitable for large area deposition [9] and is presently usedby us to prepare $CdZn(SSe)_2$ thin films. In the present investigation, we propose the synthesis, growth mechanism, optostructural, morphological, compositional and photoelectrical properties of quaternary $CdZn(SSe)_2$ thin films by arrested precipitation technique (APT).

2. Experimental details

All the chemicals used in the present investigation are of AR grade and used as received without further purification. The cadmium sulfate hydrate ($CdSO_4{\cdot}3H_2O$), zinc sulfate hydrate ($ZnSO_4{\cdot}7H_2O$), thiourea (NH_2–CS–NH_2), and sodium selenosulfite (Na_2SeSO_3), were used as precursors for Cd^{2+},Zn^{2+}, S^{2-}, Se^2-ions. Ammonia is used to maintain pH of reaction bath and triethanolamine (TEA) was used as a complexing agent. For measuring the PEC performance, sulfide/polysulfide redox electrolyte is used. The solution of sodium selenosulfite was prepared by refluxing selenium metal powder with Na_2SO_3 at 90 °C for 9 h. Commercial glass slides and FTO were used as the substrate for thin film deposition. In the APT method, metal ions of the precursors are arrested using a stable organic complexing agent (in this case triethanolamine) in alkaline medium. All the preparative parameters such as pH of reaction bath, precursor concentration and temperature are optimized initially to 10.8 ± 0.2, 0.1 M and 55 ± 2 °C respectively, to obtain good quality thin films.

The optical absorbance was measured using UV-Visible NIR-spectrophotometer (Hitachi model 330, Japan) in the wavelength range 300 – 1100 nm. The structural analysis is doneby X-ray diffraction (XRD) analysis[Brukers AXS Analytical Instruments. Model D2 PHASER] with Cu Kα target for the 2θ ranging from 10 ° to 100 °.The compositional analysis of deposited thin film was determined by energy dispersive X-ray analysis (EDS) attached to scanning electron microscope (SEM). (JEOL-JSM-6360A). J–V measurements (PEC) were recorded on semiconductor characterization instrument (SCS-4200 Keithley, Germany) using a two electrode configuration.

3. Results and discussion

3.1. Reaction mechanism for thin film formation

In the present investigation, we have successfully deposited $CdZn(SSe)_2$ thin films by arrested precipitation technique. APT is based on Ostwald ripening law [9]. The mechanism is given below. In an alkaline medium, Cd-TEA and Zn-TEA complexes slowly release Cd^{2+} and Zn^{2+}-ions at pH 10.8 ± 0.2.

$$(NH_4)_4[Cd2N(CH_2-CH_2-O)_3]+6H_2O \rightarrow Cd^{2+}+[2N\,(CH_2-CH_2-OH)_3]+4NH_4OH+2OH^- \quad (1)$$

$$(NH_4)_4[Zn2N(CH_2-CH_2-O)_3]+6H_2O \rightarrow Zn^{2+}+[2N\,(CH_2-CH_2-OH)_3]+4NH_4OH+2OH^- \quad (2)$$

Na_2SeSO_3 and thiourea dissociates in an alkaline medium to produce Se^{2-} and S^{2-}ions respectively

$$Na_2SeSO_3+OH^- \rightarrow Na_2SO_4+HSe^-$$

$$HSe^-+OH^- \rightarrow Se^{2-}+H_2O \quad (3)$$

$$(NH_2)_2C{=}S+OH^- \rightarrow (NH_2)_2C{=}O+HS^-+H_2O$$

$$HS^-+OH^- \rightarrow S^{2-}+H_2O \quad (4)$$

The overall reaction is . . .

$$Cd^{2+}+Zn^{2+}+Se^{2-}+S^{2-} \rightarrow CdZn(SSe)_2. \quad (5)$$

3.2. Optical study

The optical absorption was measured at room temperature for the $CdZn(SSe)_2$ thin films at wavelengths ranging from 300 – 1100 nm. The linear nature of the optical absorption plot confirms the direct allowed transition and is obtained by using formula given in [9].

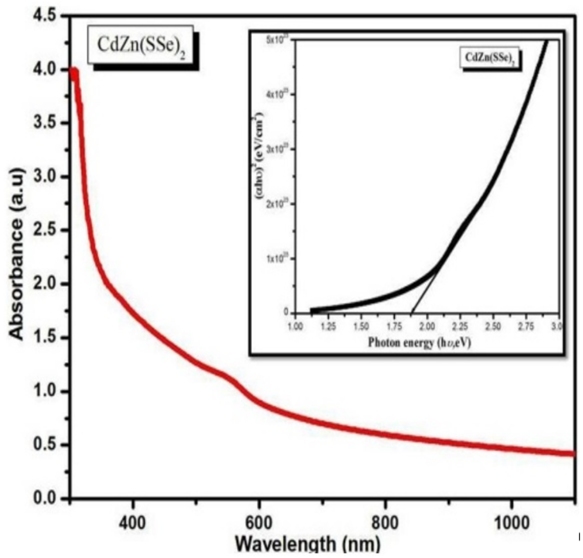

FIG. 1. Optical absorption plot and **Inset:** band gap energy plot of synthesized thin film

3.3. X-ray diffraction study

Figure 2 shows X-ray diffraction pattern of $CdZn(SSe)_2$ thin film. Four peaks observed at diffraction angle of 24.92 (100), 26.20 (100), 41.92 (110), and 71.87 (105) corresponding to 3.568, 3.396, 2.149 and 1.312 'd' values respectively. These values are matched with standard JCPDS data (card No. 80-006, 35-1469 and 77-2307). XRD data demonstrate a polycrystalline phase and a hexagonal crystal structure of $CdZn(SSe)_2$ thin film. The crystallite size, calculated by using the Debye Scherer formula, was found to be 20 nm.

3.4. SEM /EDAX studies

Figure 3 shows SEM micrograph ofsurface morphology of $CdZn(SSe)_2$ thin film which exhibits well adherent, smooth and uniform distribution of nanosphere, which cover the entire substrate surface. The average grain size is calculated by standard scale bar method, and was found to be ∼120 nm. The EDS spectrum for $CdZn(SSe)_2$ film is shown in Fig. 4. The EDS spectrum indicates the present peaks for the Cd, Zn, S and Se elements in the synthesized thin film. The spectrum also shows peak for platinum, which is used for coating the sample during analysis.

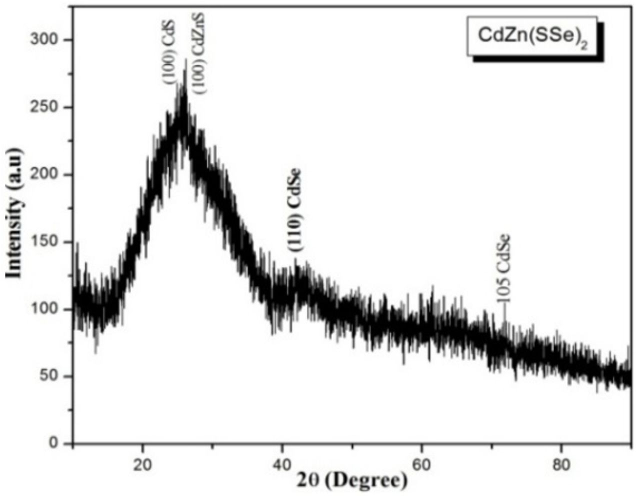

FIG. 2. X-ray diffraction pattern of $CdZn(SSe)_2$ thin film

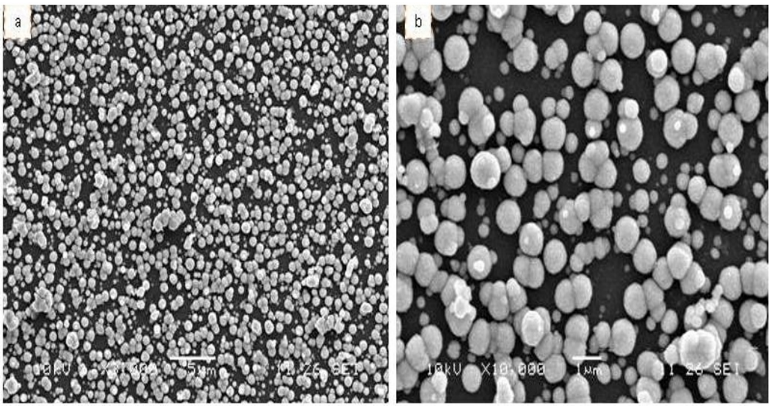

FIG. 3. SEM micrographs of $CdZn(SSe)_2$ thin film

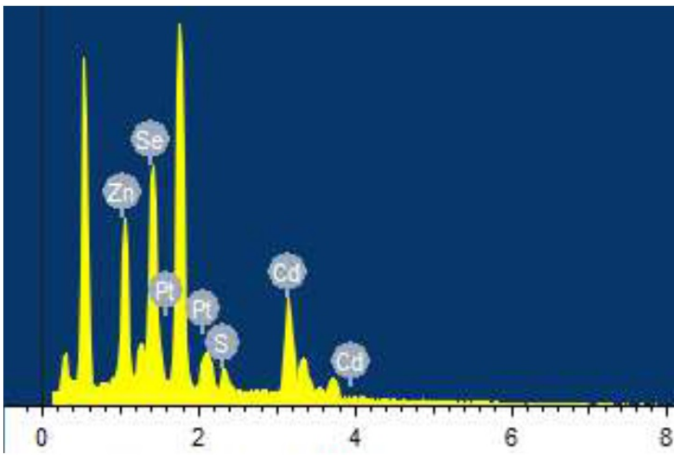

FIG. 4. EDS spectrumof $CdZn(SSe)_2$ thin film

3.5. Photoelectrochemical performance

The PEC performance of deposited $CdZn(SSe)_2$ thin film was verified using the standard two electrode configuration, both in dark and under light illumination of a 500 W tungsten filament lamp having a light intensity of 30 mW cm^{-2}, in sulphide/polysulphide redox electrolyte. The current density–voltage (J–V) characteristics ofglass/FTO/$CdZn(SSe)_2$/electrolyte/graphite were measured. J–V characteristic curve of $CdZn(SSe)_2$ thin film in dark display diode-like rectifying characteristics. Upon illumination, the magnitude of the open circuit voltage (Voc) increases with negative polarity towards the $CdZn(SSe)_2$ electrode, indicating cathodic behavior and which confirms that $CdZn(SSe)_2$ thin film is p-type. The output parameters of the PEC solar cell, i.e. light conversion efficiency (η%) and fill factor (FF), were calculated from eqn (6) and (7), respectively:

$$FF = \left(\frac{J_{max} X V_{max}}{J_{sc} X V_{oc}}\right) \tag{6}$$

$$\eta\% = \left(\frac{J_{sc} X V_{oc}}{P_{in}} X FF X 100\right), \tag{7}$$

where J_{sc} is the short-circuit current density and V_{oc} is the open circuit voltage. J_{max} and V_{max} are the maximum current density and the maximum voltage, and P_{in} is the input light intensity (30 mW cm^{-2}). From the J–V measurements, the obtained values for J_{sc}, V_{oc} and FF for the sample are 0.1917 mA cm^{-2}, 457.2 mV and 0.27 respectively. The resultant conversion efficiency for the synthesized thin film is 0.07 %.

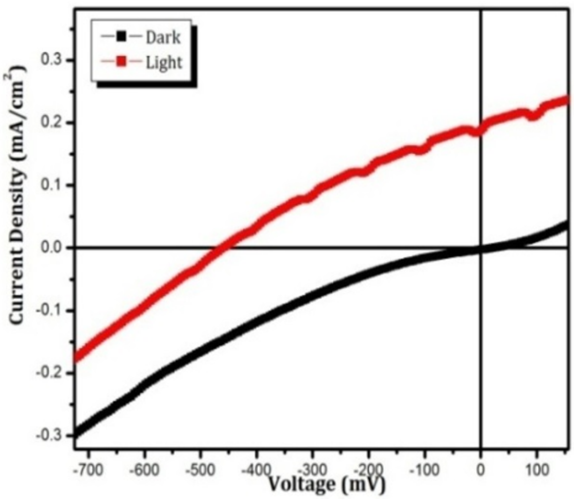

FIG. 5. J–V measurement curve of $CdZn(SSe)_2$ thin films

4. Conclusions

The arrested precipitation technique is found to be the most convenient method for the deposition of metal chalcogenide thin films. Optical band gap energy value was found to be 1.87 eV. The XRD study revealed the polycrystalline nature with purehexagonal crystal structure of the $CdZn(SSe)_2$ thin film. The SEM micrograph shows that the spherical grain structure of the surface without any pinholes.EDS results confirm the presence of Cd, Zn, S and Se elements in the synthesized thin film. The J–V measurement curve showed the efficiency of $CdZn(SSe)_2$ film to be 0.07 %. This revealed that $CdZn(SSe)_2$ thin films deposited by APT technique, showed potential as candidates for solar cell applications.

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