Development of nanocoral-like Cd(SSe) thin films using an arrested precipitation technique and their application†

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Nanocrystalline cadmium sulfoselenide thin films have been synthesized using a self-organized arrested precipitation technique with different deposition times using triethanolamine as a complexing agent. Optical, structural, morphological and photoelectrochemical solar cell properties were investigated as a function of deposition time. A UV-Vis-NIR absorption study suggested a direct allowed transition type and the band gap energy decreased from 2.01 to 1.86 eV with the increase in deposition time. X-ray diffraction studies revealed that the thin films are nanocrystalline by nature with a pure hexagonal crystal structure and a calculated crystallite size of 51–68 nm. Field emission scanning electron microscopy demonstrated that the surface morphology was altered from nanoflakes to assorted nanoflakes–nanospheres and finally to a nanocoral-like morphology. X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy showed that the composition of the Cd(SSe) thin films was of good stoichiometry. Electrical conductivity and thermoelectric power measurements confirmed that the deposited films were n-type semiconductors. From J–V measurements, a highest photo-conversion efficiency of 0.57% was achieved. The significant boost in the PEC performance might be due to the improved crystallinity along with lower values of the grain boundary resistance, dislocation density and the microstrain of the Cd(SSe) thin films.

1 Introduction

The depletion of energy sources, such as fossil fuels, coal oils, and natural gas, has led to the development of new energy sources in the 21st century.1 In the last few decades, concerns about unavoidable disintegration of existing energy sources have encouraged the development of a wide variety of technologies to convert solar energy into electrical energy via cost-effective routes. As a consequence, researchers throughout the world have put their efforts into developing inexpensive and highly efficient materials for solar cell applications. In this regard, thin film-based photoelectrochemical (PEC) solar cells have a wide range of applications due to their cost-effective fabrication and easy junction formation with redox electrolytes.2 Also, PEC solar cells are assumed to be the cleanest, green energy source to accomplish the desired goals in terms of photo-conversion efficiency.3

A broad range of IIb to VIa group chalcogenides4 has been synthesized and used as semiconductor nanomaterials in PEC solar cells and optoelectronic devices.5 The main cause for the rising popularity of IIb to VIa group chalcogenides is their high absorption coefficient, high efficiency in radiative recombination and quite well-matched optical band gap within the visible region of the solar spectrum (1.0–3.0 eV).6 Cadmium selenide (CdSe, 1.7 eV) and cadmium sulfide (CdS, 2.4 eV) belong to the IIb to VIa group semiconductor materials. CdSe and CdS chalcogenide thin films are mostly used as semiconducting materials for CdTe/CdSe and CdTe/CdS heterojunction photovoltaic devices.7 They can also act as window layers in copper indium disulfide (CIS)8 as well as copper indium gallium sulfide (CIGS) thin film-based solar cells.9,10

Ternary Cd(SSe) thin films can be synthesized using a variety of techniques such as chemical bath deposition,11–13 evaporation,14–17 solvothermal route,18 sputtering19 and chemical spray pyrolysis.20
These methods demand harsh experimental conditions, toxic reducing agents, organic surface directing agents, solvents and highly sophisticated instruments. In the present effort, an arrested precipitation technique (APT) was used for deposition of high-quality Cd(SSe) (abbreviated as CSSe) thin films. APT is self-organized, cost effective, and suitable for large area deposition, and does not require sophisticated instrumentation.21,22 In addition, APT is a hybrid chemical method of the chemical bath deposition (CBD) technique in combination with the controlled chemical growth process (CCGP).23,24 CSSe thin films as semiconducting materials have been applied in various fields including PEC solar cells, wavelength-tunable nano-optoelectronic devices,25 and phototransistors.26 Taking into consideration the significant advantages described here of ternary CSSe thin films, we have synthesized ternary CSSe thin films using APT. Recently, we have successfully synthesized novel ternary and quaternary mixed metal chalcogenide thin films such as MoBi2(Se,Te)5,24 MoBiInSe5,21 using APT for PEC solar cells and thermal cooling applications.

To the best of our knowledge, there is no particular report available on the novel synthesis of nanocoral-like CSSe thin films using APT. Most complexing agents used are flammable, carcinogenic and toxic by nature.29,30 We have selected triethanolamine (TEA) as a stable complexing agent. Moreover, we have demonstrated their PEC performance with a highest conversion efficiency of 0.57%. Also, the comprehensive growth mechanism for the formation of the CSSe thin films was discussed.

2 Experimental

2.1 Materials and methods

All chemicals were of analytical reagent (AR) grade and used without further purification. Cadmium sulfate hydrate (CdSO₄·H₂O) (98%, S-D Fine Chem.), thiourea (H₂N–CS–NH₂) (99%, S-D Fine Chem.), sodium selenite (Na₂SeO₃) (96%, Sigma Aldrich), sodium hydroxide pellets (NaOH) (99%, S-D Fine Chem.), sulfur powder (99%, S-D Fine Chem.). The substrates were ultrasonically cleaned using detergent followed by methanol treatment and finally cleaned with acetone and deionized water. Herein, the CSSe thin films were deposited onto bare as well as ITO-coated glass substrates (sheet resistance 20–25 Ω cm⁻²) using simple APT.

2.2 Deposition of CSSe thin films

In a typical synthesis, the Cd–TEA complex reacts with the S²⁻ and Se⁴⁻ chalcogen ions, which are released slowly via dissociation of H₂N–CS–NH₂ and Na₂SeSO₃ at alkaline pH 10.4, and a temperature of 50 ± 2 °C. A solution of 0.05 M of the Cd–TEA complex was used as a source for Cd²⁺ ions, where cadmium sulfate was triturated with TEA as the complexing agent for 6 h to form a clear solution of the Cd–TEA complex. Sodium selenosulfite (Na₂SeSO₃) was prepared by refluxing selenium metal powder with anhydrous sodium sulfite at 90 °C for 8 h.

Nucleation and thin film formation are mainly dependant on the different preparative parameters such as complexing agent, precursor concentration, pH, deposition time and temperature of bath. These parameters were optimized during the initiative stage of thin film deposition. The precursor concentration was kept constant at 0.05 M and the deposition time was varied from 1.00 to 1.50, 2.00, and 2.50 h. After each interval of deposition time, the film thickness was checked using a surface profiler. It could be seen that, for the terminal growth of the films, the film thickness remains constant after 2.50 h. At the same time, the peeling of the substrate on an irregularly grown surface and without an increase in film thickness was observed with a further increase in deposition time. So, we have studied the effect of deposition time for up to 2.50 h. The effect of deposition time on the thickness of the thin films is explained in detail in the ESI.† In the terminal growth phase, all the deposited thin films were dark orange-red in colour and well adherent to the substrate surface. The deposited films, formed using different deposition times, were correspondingly designated as, CSSe₁, CSSe₂, CSSe₃ and CSSe₄. The optimized preparative parameters are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Sample code</th>
<th>Deposition time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CSSe₁</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>CSSe₂</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>CSSe₃</td>
<td>2.00</td>
</tr>
<tr>
<td>4</td>
<td>CSSe₄</td>
<td>2.50</td>
</tr>
</tbody>
</table>

2.3 Characterization of the thin films

The thickness of the deposited thin films was measured using surface profiler (AMBIOS XP-1). Optical absorption spectra were recorded using a UV-Vis-NIR spectrophotometer (Shimadzu, UV-1800). Structural properties were confirmed using an X-ray diffractometer (Bruker AXS, D8) using Cu Kα (λ = 1.5418 Å) radiation for 2θ ranging from 20° to 80°. The surface morphology and the elemental composition of the as-deposited thin films were investigated using field-emission scanning electron microscopy (FESEM) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer (Hitachi, S-4700). Elemental information concerning the as-deposited CSSe thin films were collected using an X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Multilab-2000) with a multi-channel detector, which can endure high photon energies from 0.1–3.0 keV. Electrical conductivities (ECs) were measured using the two probe method. Thermoelectric power (TEP) measurements were conducted under the conditions of maximum temperature difference and minimum contact resistance using a C/T meter apparatus (Teleph-France).
PEC measurements were carried out using a semiconductor parameter analyzer (Keithley SCS-4200 Semiconductor) characterization unit in the dark and under illumination using a 500 W tungsten filament lamp (intensity 30 mW cm$^{-2}$) with a sulfide/polysulfide redox electrolyte. The PEC cells were fabricated using the standard two-electrode configuration, comprised of a glass-ITO/Cd(SSe) (active surface area of 1 cm$^2$) photoelectrode and graphite as the counter electrode. All measurements were performed at room temperature (300 K) in air.

3 Results and discussion

3.1 Growth and reaction mechanisms of the thin film formation

In arrested precipitation, metal ions are arrested using TEA as a complexing agent and are released at the optimized precursor concentration, pH and temperature. Aqueous ammonia is used to optimize the pH, by increasing the concentration of the OH$^-$ ions, the relative molecular area and the solubility of the chalcogen ions (S$^{2-}$, Se$^{2-}$) in the reaction solution. Generally, at higher temperatures, a large number of metal ions is released and the reaction rate increases which causes bulk precipitation rather than the desired thin film formation. So, at the initial stage, we have optimized the deposition temperature, the precursor concentration and the pH to 50 ± 2 °C, 0.05 M and 10.4, respectively, to achieve high-quality, pinhole-free CSSe thin films. APT is based on the Ostwald ripening law. According to this law, the rate of the reaction between metal ions along with chalcogen ions can be controlled using stable complexing agents (in our case TEA).

The smaller nuclei or embryos come towards each other to form less stable crystals which readily convert into large crystals. As the deposition time increases, the additional metal ions will be released, which cause the dissolution of the smaller particles and the formation of well-grown stable large crystals. The formation of the thin film occurs, when the ionic product (Kp) exceeds the solubility product (Ksp) of the metal ions and the multi-nucleation process occurs next to the ion-by-ion condensation of the metal ions onto the substrate surface. When all the metal ions and chalcogen ions in solution vanish with the increase in deposition time, the film’s thickness remains constant, called the terminal thickness of the deposited thin film. Generally, a slow reaction rate results in the formation of good-quality and adherent thin films. Hence, our developed arrested precipitation technique is effective compared with routine chemical bath processes. The comprehensive growth mechanism for the formation of the CSSe thin films is depicted in Scheme 1.

![Scheme 1](image-url) Comprehensive growth mechanism of the CSSe thin films.
A plausible reaction pathway for the formation of the cadmium sulfoselenide thin films is summarized as follows.

Initially, the Cd\(^{2+}\) ions are released due to the dissociation of the Cd–TEA metal complex, as shown in reaction (1).

\[
\text{(NH}_4\text{)}_4[\text{Cd}_2\text{N(CH}_3\text{)CH}_2\text{OH}]_2 + 6\text{H}_2\text{O} \\
\text{pH 10.4} \xrightarrow{T = 50 \degree \text{C} \pm 0.5} \text{Cd}\^{2+} + [2\text{N(CH}_3\text{)CH}_2\text{OH}]_2 + 4\text{NH}_4\text{OH} + 2\text{OH}^-
\]

(1)

Further, at alkaline pH, sodium selenosulfite dissociates into sodium sulfate and the highly active HSe\(^{-}\)/C₇⁰ species. This highly active species quickly converts into Se\(^{2-}\)/C₇⁰ ions (reactions (2) and (3)).

\[
\text{Na}_2\text{SeSO}_3 + \text{OH}^- \xrightarrow{\text{pH 10.4}} \text{Na}_2\text{SO}_4 + \text{HSe}^- 
\]

(2)

\[
\text{HSe}^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Se}^{2-}
\]

(3)

At the same time, thiourea dissociates to release S\(^{2-}\) ions, as shown in reactions (4) and (5).

\[
\text{H}_2\text{N-C\text{=NH}_2} + \text{OH}^- \xrightarrow{\text{pH 10.4}} \text{H}_2\text{S}^- + \text{H}_2\text{N-C\text{=NH}_2}
\]

(4)

\[
\text{HS}^- + \text{OH}^- \rightarrow \text{S}^{2-} + \text{H}_2\text{O}
\]

(5)

when the ionic product of the Cd\(^{2+}\), S\(^{2-}\) and Se\(^{2-}\) ions exceeds the solubility product of Cd(SSe) in the reaction bath, which results in a slow ion-by-ion condensation of the metal and the chalcogen ions on the basis of the Ostwald ripening law.

\[
\text{Cd}^{2+} + 1/2\text{S}^{2-} + 1/2\text{Se}^{2-} \xrightarrow{T = 50 \pm 2 \degree \text{C}} \text{Cd(SSe)}
\]

(6)

3.2 Optical absorption studies

Fig. 1(a) shows the optical absorption spectra of the CSSe thin films recorded using a UV-Vis-NIR spectrophotometer in the wavelength range 350–1100 nm. Fig. 1(a) clearly shows that the maximum optical absorption is observed at around 650–750 nm. The enhancement in the absorption spectra is due to the considerably improved crystallinity for all CSSe thin films. The absorption coefficient for all samples is found to be in the order of 10\(^5\) to 10\(^6\) cm\(^{-1}\). The fundamental absorption, which corresponds to the electron excitation from the valance band to the conduction band, can be used to determine the value of the optical band gap energy. Optical data were demonstrated using the following eqn (7):\(^{33}\)

\[
\alpha = \frac{A(h\nu - E_g)^n}{h\nu}
\]

(7)

where \(A\) is a parameter that depends on the transition probability, \(h\) is the Planck constant, \(E_g\) is the optical band gap energy of the material, and the exponent \(n\) depends on the type of transition. The values of \(n\) for the direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions are 1/2, 2, 3/2 and 3, respectively.

The optical band gap energy values of the CSSe thin films were obtained by plotting the graph of \((zhv)^2\) vs. the photon energy \((h\nu)\), as shown in Fig. 1(b). The linear nature of the plots suggests a direct and allowed type of transition. The band gap energy decreases from 2.10–1.86 eV with the increase in deposition time. The optical band gap values are in good agreement with reported values.\(^{10}\) The obtained band gap energies are summarized in Table 2. The optical absorption study revealed that the optical absorption shifts towards the red shift region and decreases the optical band gap energies due to the increase in thickness of the CSSe thin films with the increase in deposition time (1.00–2.50 h).

3.3 Structural studies

Crystal quality and structural analyses were carried out by recording X-ray diffraction patterns in the range of 2\(^\theta\) to 80\(^\circ\). Fig. 2 shows the X-ray diffraction patterns of the CSSe thin films. The broad and intense peaks in the XRD patterns confirm that all samples are nanocrystalline by nature.\(^{21}\) The major diffraction peaks centred at 2\(^\theta\) = 26.10\(^\circ\), 30.43\(^\circ\), 31.50\(^\circ\),
In a typical X-ray diffraction pattern of the CSSe thin films, all peaks appear at identical positions with amendments to the intensity and broadening of the diffraction peaks, which indicates the creation of pure phase materials with an improved crystal quality with increasing deposition time. Also, no other peaks are observed which reveals that the material has a pure phase. The observed broadening of the diffraction peaks may be due to strain or microstrain. Further, the average crystallite sizes were calculated using the Scherrer formula (eqn (8)):

\[
D = \frac{0.94\lambda}{\beta \cos \theta}
\]  

where \( D \) is the crystallite size, \( \lambda \) is the wavelength of X-ray radiation (1.5406 Å), \( \beta \) is the full-width-at-half-maximum (FWHM) in radians, and \( \theta \) is Bragg’s angle. The calculated crystallite sizes are ranging from 51 to 68 nm with the increase in deposition time. This enhancement in the crystallite size with the minimum interfacial energy is beneficial for improving the photon conversion efficiency. \(^{38,39}\) From the calculated crystallite sizes (\( D \)), dislocation densities (\( \delta \)) and microstrains (\( \varepsilon \)) for all samples were determined using eqn (9) and (10) and the data are summarized in Table 2.

\[
\delta = \left( \frac{1}{D^2} \right)
\]

\[
\varepsilon = \left( \frac{\beta \cos \theta}{4} \right)
\]

The lower values of \( \delta \) and \( \varepsilon \) are observed for all samples with the increase in deposition time. This endorses the decrease in defect levels and grain boundaries due to the enhancement in crystallite size. \(^{40,41}\)

The decrease in \( \delta \) and \( \varepsilon \) indicates a lower level of lattice imperfections \(^{42-44}\) and the formation of high-quality CSSe thin films with the increase in deposition time. The lattice parameters for the hexagonal crystal structure (\( a = b \neq c \)) were calculated using the following eqn (11).

\[
\frac{1}{d} = \frac{4}{3} \left( \frac{h^2 + k^2 + \frac{k^2}{a^2}}{a^2} \right) + \frac{I^2}{c^2}
\]

The lattice parameters were found to be \( a = b = 4.2595 \) Å and \( c = 6.8410 \) Å. These lattice parameters are in good agreement with the standard JCPDS data (49-1459). An increase in crystallite size was correlated to a decrease in the band gap with increasing the deposition time. \(^{45,46}\)
3.4 Morphological studies

The surface morphology and the composition of the deposited CSSe thin films were characterized using FESEM and EDS. Fig. 3 shows the FESEM micrographs of the CSSe thin films at low and high magnification with the increase in deposition time. The FESEM micrographs show that uniform, well-adhered, pinhole-free thin films were deposited over the entire substrate surface. Fig. 3(a) and (b) show the FESEM images for the CSSe thin films deposited for 1.00 h. A beaded nanoflake-like morphology is evident from the low magnification image (Fig. 3(a)). From Fig. 3(b), it is observed that numerous grown nanoflakes over the entire substrate surface are interconnected with each other. These nanoflakes have an average thickness of ~80 nm. Fig. 3(c) and (d) show the FESEM images for the CSSe thin films deposited for 1.50 h. The construction of an assorted nanoflake–nanosphere morphology is indicated in Fig. 3(c). From the higher magnification image (Fig. 3(d)), it can be seen that the assorted nanoflakes–nanospheres have an average thickness of ~50 nm. The decrease in thickness might be due to the construction and aggregation of the assorted nanoflakes–nanospheres with the increase in deposition time. Fig. 3(e) and (f) show the FESEM images for the CSSe thin films deposited for 2.00 h. A complete conversion from the assorted nanoflakes–nanospheres to a nanocoral-like morphology is observed from Fig. 3(e). The higher magnification image (Fig. 3(f)) clearly shows that the single nanocorals have an average size of ~220 nm. Fig. 3(g) and (h) show the FESEM images for the CSSe thin films deposited for 2.50 h. The formation of large-size nanocorals, due to the aggregation of the small-size nanocorals, is observed from Fig. 3(g). From Fig. 3(h), it is seen that the aggregated nanocorals are of ~400 nm in size. The FESEM micrographs signify an evolution of morphology from interconnected nanoflakes to assorted nanoflakes–nanospheres and to a finally nanocoral-like morphology.

The formation of the nanocoral-like morphology is demonstrated in Scheme 2. The formation of such a nanocoral-like

![Scheme 2](image-url)
morphology is observed to occur via the assembly of a large number of small nanospheres. These small nanospheres are interconnected with each other which leads to the formation of nanocorals. The right side of Scheme 2 shows the image of a nubbly-like texture. A nubbly-like texture is nothing but an irregularly grown surface. It is evident from Scheme 2 that the nubbly-like texture is reflected in the nanocoral-like morphology as shown on the left side of the scheme. This nanocoral-like morphology is favourable for the absorption of large amounts of solar radiation because of its high surface to volume ratio.47

3.5 Compositional analysis

XPS analysis was carried out to determine the surface composition of the CSSe₄ thin film, as shown in Fig. 4. A typical XPS survey spectrum (Fig. 4(a)) of the CSSe₄ thin film indicates the presence of cadmium (Cd), sulfur (S), selenium (Se), carbon (C), and oxygen (O). The binding energies recorded in the XPS analysis were corrected to take into account specimen charging by setting C1s to 285.02 eV. The high-resolution core level spectrum for Cd(3d) is shown in Fig. 4(b). The two peaks in the Cd(3d) core level spectrum arise from Cd3d₅/₂ at a binding energy of 405.03 eV and from Cd3d₃/₂ at 412.18 eV. The S(2p) spectrum (Fig. 4(c)) shows two relevant peaks for S2p₃/₂ at a binding energy of 160.5 eV and S2p₁/₂ at 161.7 eV. The high-resolution core level spectrum for Se(3d) is shown in Fig. 4(d). The core level spectrum for Se(3d) was fitted yielding a single peak at the binding energy of 54.10 eV. The values of the binding energies for Cd, S and Se are at their respective positions for the Cd⁺⁺, S²⁻ and Se²⁻ states. It means that Cd⁺⁺, S²⁻ and Se²⁻ exist in the as-deposited CSSe thin films with the stoichiometric formula Cd(SSe).

Quantitative analysis was carried out to confirm the atomic percentages of Cd, S and Se in the as-deposited CSSe₄ thin film.

Fig. 4 (a) XPS survey spectrum of the CSSe₄ thin film, (b) high-resolution core level XPS spectrum of Cd, (c) high-resolution core level XPS spectrum of S, (d) high-resolution core level XPS spectrum of Se.
by recording the EDS pattern. Fig. 5 shows a representative EDS spectrum of the as-deposited CSSe₄ thin film. From Fig. 5, it is observed that the peaks at 3.13, 2.50 and 1.38 keV confirm the presence of Cd, S and Se in the as-deposited thin film, respectively. The inset of Fig. 5 shows tabulated data of the expected and the actual atomic percentage for Cd, S and Se. The small amount of divergence of the actual atomic percentage from the expected atomic percentage of Cd, S, Se might occur due to trace inclusions of oxygen into the films from atmospheric contamination and during the transfer of the films. The data in the table (inset of Fig. 5) confirm that the actual atomic percentages of the elements are in good agreement with the expected atomic percentages.

### 3.6 Electrical studies

Electrical conductivity is essential for studying the electrical transport properties of the synthesized materials. Fig. 6 shows a plot of $\ln \sigma$ vs. $1000/T$ for the CSSe thin films with the increase in deposition time. From the plots (Fig. 6), it is observed that with the increase in temperature the conductivity increases for all samples. This increase in conductivity indicates that the CSSe thin films are semiconductors by nature. The activation energies were estimated using eqn (12) as follows:

$$\sigma = \sigma_0 e^{(\frac{E_a}{kT})}$$

(12)

where $\sigma$ is the conductivity of sample, $\sigma_0$ is the temperature-independent part of the conductivity, $E_a$ is the activation energy, $k$ is the Boltzmann constant, and $T$ is the temperature in Kelvin. It is observed that the activation energy decreases with the increase in deposition time which confirms the high electrical conductivity of the CSSe thin films. Table 4 summarizes the values of the activation energy for the CSSe thin films.

**Table 4**

<table>
<thead>
<tr>
<th>Elements</th>
<th>Expected atomic %</th>
<th>Actual atomic %</th>
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<tr>
<td>Cd</td>
<td>50</td>
<td>54</td>
</tr>
<tr>
<td>S</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>Se</td>
<td>25</td>
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</tbody>
</table>

Thermoelectric power (TEP) measurements assess the difference between thermally generated voltages resulting from a temperature difference across the hot and cold ends of the semiconducting material. The plots of thermo EMF vs. temperature for the CSSe thin films are shown in Fig. 7. The negative polarity of the generated thermo EMF indicates that all CSSe thin films are n-type semiconductors. The carrier concentration and the mobility for all samples were calculated using eqn (13) and (14) as follows:

$$\log n = \left[\frac{2}{3}\log T - 0.005\text{TEP} + 15.719\right]$$

(13)

$$\mu = \frac{\sigma}{n e}$$

(14)
where \( \mu \) is the mobility, \( n \) is the carrier concentration and \( e \) is the electronic charge. From Table 4, it can be seen that the carrier concentration increases exponentially and the mobility decreases with the increase in deposition time. The increase in carrier concentration and decrease in mobility might be due to a low level of anti-structural defects present in the deposited thin films.\(^{51,52} \) The carrier concentrations and the mobilities are summarized in Table 4.

3.7 Photoelectrochemical (PEC) properties

PEC performance of all CSSe thin films was measured using the standard two-electrode configuration. Fig. 8 shows the \( J–V \) curves of the PEC cells, formed using the CSSe thin films as the working electrode, with an active area of 1 \( \text{cm}^2 \), and graphite (G) as the counter electrode. All \( J–V \) measurements were performed under light illumination using a 500 W tungsten filament lamp (intensity 30 mW cm\(^{-2} \)) in an 0.5 M sulfide/polysulfide redox electrolyte. In all samples, the characteristic \( J–V \) curve in the dark shows ideal diode-like rectifying characteristics for the PEC cells. Upon illumination, the \( J–V \) curves were obtained in the fourth quadrant, indicating the generation of electricity which is a distinctive PEC solar cell characteristic.\(^{50} \)

Also, for all CSSe thin films, the magnitude of photocurrent increases by way of the negative polarity region, demonstrating that the materials are n-type semiconductors.\(^{51,52} \) This result is in good agreement with the observed TEP results. The photoresponses of all samples were obtained by forming the subsequent cell configuration:

Glass-ITO/Cd(Se)/polysulfide electrolyte, \([\text{Na}_2\text{S–NaOH–S}]_{\text{aq}}/\text{G.}\)

The solar cell parameters such as fill factor (FF) and conversion efficiency (\( \eta \% \)), were calculated using the relations (15) and (16) as follows:\(^{53} \)

\[
\text{FF} = \left( \frac{J_{\text{sc}} \times V_{\text{oc}}}{P_{\text{in}}} \right) \quad (15)
\]

\[
\eta(\%) = \left( \frac{J_{\text{sc}} \times V_{\text{oc}} \times \text{FF} \times 100}{P_{\text{in}}} \right) \quad (16)
\]

where \( J_{\text{sc}} \) is the short-circuit current density and \( V_{\text{oc}} \) is the open circuit voltage. \( J_{\text{max}} \) and \( V_{\text{max}} \) are the maximum current density and the maximum voltage, and \( P_{\text{in}} \) is the input light intensity (30 mW cm\(^{-2} \)). From the \( J–V \) measurements, the obtained values of \( J_{\text{sc}} \) for the samples CSSe\(_1\), CSSe\(_2\), CSSe\(_3\) and CSSe\(_4\) were 0.247, 0.311, 0.366 and 0.454 mA cm\(^{-2} \) and the corresponding values of \( V_{\text{oc}} \) were 755, 758, 777 and 782 mV, respectively. The values of the series resistance \( (R_s) \) and the shunt resistance \( (R_{sh}) \) for all samples were determined from the slope of the power output characteristics using eqn (17) and (18) as follows:\(^{53} \)

\[
\left[ \frac{df}{dP} \right]_{V=0} = \frac{1}{R_s} \quad (17)
\]

\[
\left[ \frac{df}{dV} \right]_{P=0} = \frac{1}{R_{sh}} \quad (18)
\]

\( R_s \) varies from 429 \( \Omega \) to 255 \( \Omega \) for the CSSe\(_1\) to the CSSe\(_4\) thin films, respectively. At the same time, a decrease in \( R_{sh} \) from 8103 \( \Omega \) for CSSe\(_1\) to 4189 \( \Omega \) for the CSSe\(_4\) thin films is observed. \( R_s \) is based on the resistance of the metal contact, ohmic contact and the junction depth, whereas \( R_{sh} \) depends on the crystal defects. Ideally, \( R_s \) and \( R_{sh} \) should be 0 \( \Omega \) and infinite, respectively.\(^{51} \) \( R_s \), \( R_{sh} \), FF and \( \eta \) (%) for all CSSe thin films are summarized in Table 5.

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Fig. 7 Plots of thermo EMF vs. temperature for the CSSe thin films, prepared with various deposition times.

Fig. 8 \( J–V \) characteristics of the CSSe thin films.
The highest conversion efficiency obtained was 0.57% for the sample CSSe4. A literature survey on Cd(SSe) thin films shows that the obtained conversion efficiency is comparable with other reports on Cd(SSe) thin films deposited using highly sophisticated physical techniques.10

Good-quality, highly adherent and densely packed CSSe thin films are favourable for the absorption of sufficient light radiation and the generation of photoelectrons. These generated photoelectrons transfer from the nanocrystalline, pinhole-free and well-adhered compact layer to the conducting substrate. Table 5 indicates a boost in PEC performance for samples CSSe3 and CSSe4 compared to samples CSSe1 and CSSe2. This is because the nanocoral-like surface morphology consists of interconnected and well-grown nanocorals which increases the surface area in contact with the electrolyte. Also, samples CSSe3 and CSSe4 have better crystallinity, a lower dislocation density and microstrain. This improved crystallinity significantly reduces the grain boundary resistance. This reduced grain boundary resistance effectively retards the recombination of electron–hole pairs. In addition, the effective decrease in Rs for the CSSe3 and CSSe4 thin films causes an enhancement in PEC performance. While the CSSe1 and CSSe2 samples show a nanoflake or an assorted nanoflake–nanosphere-like morphology, which have a high dislocation density and microstrain as compared to the CSSe3 and CSSe4 thin films. As a result, the low conversion efficiencies of the CSSe1 and CSSe2 thin films follow from considerable grain boundaries in the nanoflake or the assorted nanosphere-like morphology. Hence, it is concluded that the improvement in conversion efficiency of the nanocoral-like CSSe thin films is due to the crystalline nature of the material, the lower values of Rs, the grain boundary resistance and the decrease in dislocation density and microstrain as compared to the nanoflake and the assorted nanosphere-like morphologies.

However, compared to other surface morphologies such as self-assembled nanoflower and micro-nano branch structures, the obtained nanocoral-like morphology of the Cd(SSe) thin film demonstrates a low conversion efficiency which may be due to two reasons.

(1) The shaggy structured nanocoral-like surface morphology contains a limited surface area compared to other self-assembled nanoflower and micro-nano branch structured morphologies of Cd(SSe) thin films.

(2) The nanocoral-like morphology is closely packed by a variety of small grown nanospheres. However, the surface of the nanocorals in between the small nanosphere edges may contain some defect-induced surface states. These defects act as a trap for current carriers and result in a low conversion efficiency (0.57%) compared to other hierarchical morphologies.

The above results on the synthesis of the CSSe thin films using APT are promising for the development of solar cell devices. So, we are trying to deposit Cd[S1–Se3] thin films by varying the bath composition and to engineer novel surface morphologies. Such morphologies may contain fewer defect-induced surface states, which might reduce the number of surface traps for current carriers. These studies are underway in our laboratory.

4 Conclusions

In conclusion, we have first time reported facile, cost-effective, simple and hybrid APT method for deposition of nanocrystalline Cd(SSe) thin films. Opto-structural, morphological and photoelectrochemical studies concluded that TEA as the complexing agent plays a crucial role in the growth process. The band gap energy is decreased from 2.01 to 1.86 eV, while the films thickness is increased from 535 to 793 nm, as a function of the deposition time. The XRD patterns of the as-deposited thin films illustrated the formation of nanocrystalline materials with a pure hexagonal crystal structure. The crystallinity was improved with an average crystallite size from 51 to 68 nm with the decrease in dislocation density and microstrain in the CSSe thin films. The morphology changed from nanoflakes to assorted nanoflakes–nanospheres and finally to a nanocoral-like morphology with nearly stoichiometric CSSe thin films. Such a nanocoral-like morphology is beneficial for the effective increase in photocurrent and efficiency of photoelectrochemical solar cells. All samples were shown to be semiconductors with n-type conductivity, confirmed by EC and TEP measurements. The highest conversion efficiency obtained was 0.57% for the CSSe4 thin film. This might be due to low values of Rs and a reduced grain boundary resistance. These results are promising for the effective application of CSSe thin films that significantly help to enhance the light harvesting efficiency.

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Notes and references


