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Effect of Deposition Time on Optostructural and Photoelectrochemical Properties of Cd(SSe) Thin Films Deposited By Facile Route

Chemistry

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Sandip K. Jagadale S. B. Patil College of Engineering, Indapur, Pune 413106

Popatrao N. Bhosale Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur- 416004,

Raghunath K. Mane Smt.K.R.P. Kanya Mahavidyalaya, Uran-Islampur, 415409 Tal.Walwa, Sangli,

ABSTRACT

In the present investigation, we have synthesized nanocrystalline cadmium sulphoselenide Cd(SSe) thin films on ultrasonically cleaned bare and FTO coated glass substrate using facile, cost effective arrested precipitation technique (APT) at different time intervals (1h,1.5h, 2h and 2.5h). The absorption spectrum shows a strong absorption in the 300-1100 nm wavelength range with band gap variation in the range of 2.05 eV to 1.87 eV. The X-ray diffraction (XRD) patterns shows nanocrystalline nature with crystallite size 58 nm to 76 nm and exhibits pure hexagonal crystal structure. The scanning electron microscopy (SEM) demonstrates formation of well adherent, pinhole free thin films with mixed nanosphere nanopetal like morphology. Energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) showed that the composition of Cd(SSe) thin films is good agreement with stoichiometry. Finally these prepared thin films tested for photoelectrochemical (PEC) performance in sulphide / polysulphide electrolyte and results are promising.

INTRODUCTION

The demand for the energy of the world is ever growing due to modern civilization and industrialization. To meet this demand of energy the conventional energy sources such as fossil fuels, natural oil, coal, etc. are mostly used which causes fast depletion of these reservoirs and also their combustion causes environmental pollution due to release of gases such as CO_2 and SO_2. Solar energy is the clean, inexpensive and more efficient renewable energy option for future energy demand. The photovoltaic solar cells convert sunlight directly into electricity and often used in many optoelectronic devices such as calculators and watches, etc. In last few decades, thin film based solar cells (TFSC) [1] have been commercialized due to their low cost of fabrication, high throughput processing techniques and ease of junction formation with a redox electrolyte to convert solar energy into electricity [2].

A variety of physical and chemical techniques have been employed for the synthesis of ternary Cd(SSe) thin films [3-6]. In the present investigation, APT was used for synthesis of nanocrystalline Cd(SSe) thin films at different deposition time. Intention of present research work is to deposit nanocrystalline Cd(SSe) thin films at different deposition time and also to study the influence of deposition time on optostructural properties and its application in photoelectrochemical solar cell.

Experimental details

All chemicals used in this work were analytical reagent (AR) grade and used without further purification. Cadmium sulfate hydrate ($CdSO_4.3H_2O$) (99 % Mereck), thiourea (NH_2-CS-NH_2) (99 % Mereck), and Sodium selenosulfite (Na_2SeSO_3) were used as precursor for Cd^{2+} , S^{2-} and Se^{2-} ions respectively. Sodium selenosulfite (Na_2SeSO_3) was prepared by refluxing selenium metal powder (99.5 % Lobachemie) and sodium sulfite (Na_2SO_3) (99 % Lobachemie) at 90°C for 9 hrs. The excess concentration of Na_2SO_3 over selenium prevents the oxidation of selenide and its reprecipitation as selenium. The pH of reaction bath was maintained by ammonia (NH_3) (25 %, Thomas Baker) and triethanolamine (TEA) used as complexing agent. For measuring the PEC performance, we have used a sulfide/polysulfide redox electrolyte prepared by crushing sodium sulfide (Na_2S) (55-58 % Thomas Baker), sodium hydroxide pellets (NaOH) (99 %, S-D Fine Chem.) and sulfur powder (99 %, S-D Fine Chem.) together and finally diluted to 50ml volume by double distilled water. Well cleaned commercial glass slides were used as substrate for thin film deposition.

Synthesis of thin films

Preparative parameters such as precursor concentration, complexing agent, pH, bath temperature and deposition time were optimized initially and the deposition time was varied from 1.0 to 1.5, 2.0, and 2.5 h. In a typical synthesis, an appropriate volume of 0.05 M [Cd-TEA] solution was taken in a 100ml beaker. The pH of the mixture was adjusted to 11 by dropwise addition of ammonia followed by addition of adequate volume of 0.1 M Na_2SeSO_3 and 0.1 M $(NH_2)_2C=S$ solution to the reaction mixture with constant stirring and then the reaction mixture was stirred for 2 min to get a homogeneous colorless solution. Previously cleaned glass and fluorine-doped tin oxide (FTO) coated glass substrates were mounted vertically on substrate holder with a constant rotation of 45±5 rpm. At this stage nucleation centers are formed on substrate surface at 55 ± 2°C followed by ion by ion condensation mechanism which results in formation of well adherent, uniform and pinhole free thin film on substrate surface [7]. After desired deposition time, the substrates were withdrawn from the reaction bath, sufficiently rinsed with double-distilled water and dried at room temperature and correspondingly designated as CSS1, CSS2, CSS3 and CSS4. It could be seen that, for the terminal growth of the films, the film thickness remains constant after 2.5 h. So, we have studied the influence of deposition time for up to 2.5 h.

Characterization of the thin films

The thickness of as deposited thin films was measured by using surface profiler (AMBIOS XP-1). UV-Vis-NIR absorbance spectra were measured using a model Shimadzu UV 1800 in the wavelength range 300 nm to 1100 nm. The crystal structure of the thin films were analyzed by X-ray powder diffraction (XRD) with Rigaku, D/MAX Ultima III XRD spectrometer (Japan) using Cu-Kα radiation ($\lambda = 1.5418$ Å) in 20° to 80° 2θ range. The surface morphology elemental composition of Cd(SSe) thin films were assessed by scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) analyzer (JEOL-JSM- 6360A). Elemental composition of Cd(SSe) thin films can obtained by energy dispersive X-ray spectroscopy (EDS) analyzer (JEOL-JSM- 6360A) and X-ray photoelectron spectroscopy. The PEC performance were measured in dark conditions and under irradiation of light using a 500 W tungsten filament lamp (intensity 30 mW/cm²) at an electrochemical workstation (AUTOLAB PGSTAT 100 potentiostat) with two electrode configuration, the Cd(SSe) thin film acts as a photoanode with working area 1 cm^2, graphite as a counter electrode and 0.5 M sulphide/polysulphide as redox electrolyte.

Results and discussion

Growth and reaction mechanism for thin film formation

In the present investigation, APT method is used to deposit Cd(SSe) thin films at different deposition time (1.0, 1.5,2.0 and 2.5 h). In APT, formation of metal complex and controlled release of metal ions is a key step in growth of desired material, hence release of metal ions was controlled by arresting them using organic complexing agent triethanol ammine (TEA). Release of these metal ions takes place at the optimized reaction conditions as precursor concentration 0.05M (Cd-TEA), 0.1 M thiourea,0.1M Na_2SeSO_3, pH 11 and temperature to $55^o \pm 2^oC$ respectively, to achieve good quality thin films. APT is based on the Ostwald ripening law [8]. Overall stepwise thin film formation process involves, diffusion of smaller nucleus present in vicinity to form less stable crystals, that are readily converted in to larger stable particles, and further thin film formation takes place by the growth of metal chalcogenide accordingly slow ion- by-ion condensation [9]. The formation of Cd(SSe) thin films occurs when the ionic product (K_p) of ions exceeds the solubility product (K_{sp}) of metal chalcogenide. As deposition time increases the concentration of metal ions and chalcogen ions in solution decreases, it results in non-noticeable change in the film thickness (film thickness remains constant), called the terminal thickness of the deposited thin film [10]. The possible reaction mechanism for the formation of Cd(SSe) thin films is discussed below.

Initially, in alkaline medium Cd-TEA complex slowly releases Cd^{2+} ions at pH 11 and temperature 55 ± 2 °C

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

In alkaline medium Na_2SeSO_3 dissociates to release HSe^- species which immediately converts into Se^{2-} ions

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

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

At the same time $(NH_2)_2C{=}S$ dissociates in alkaline medium to produce S^{2-} ions

$$(NH_2)_2C{=}S + 2OH^- \rightarrow (NH_2)_2C{=}O + S^{2-} + H_2O \ (3)$$

Overall possible reaction is as follows,

$$Cd^{2+} + \frac{1}{2}S^{2-} + \frac{1}{2}Se^{2-} \longrightarrow Cd(SSe) \ \ldots (4)$$

Optical absorption studies

Optical absorption spectra of the Cd(SSe) thin films recorded using UV-Vis- NIR spectrometer in the wavelength range 300-1100nm for different deposition time as shown in Fig.1(a). The Fig 1(a) clearly indicates that light maximum absorption is observed at around 550 nm to 650 nm wavelength range. This enhancement in light absorption for CSS1 to CSS4 samples is due to considerable improvement in crystallinity, which is clearly seen in X-ray diffraction patterns [11]. To confirm the band edge transition in the sample, the optical data were demonstrated by using following equation (5) [12].

$$(\alpha) = \frac{A(h\nu - Eg)^n}{h\nu} \qquad (5)$$

Where is absorption coefficient, ‘A’ is parameter that depends upon transition probability, ‘’ is photon energy, Eg is optical band gap energy of material and ‘n’ depends on the type of transition. Optical band gap energy values of the Cd(SSe) thin films were obtained by plotting $(\alpha h\upsilon)^2$ *vs* hυ (photon energy) and by extrapolating the linear portion of the absorption edge to the energy axis as shown in Fig.1(b). The linear nature of the plots over a wide range of photon energy suggests a direct allowed type of transition [13]. As well the band gap energy decreased from 2.05 eV to 1.87 eV with the increase in deposition time. Optical absorption study revealed that the optical absorption shift towards red shift region and decreases band gap energy values due to the increase in crystallinity and improvement in film thickness.

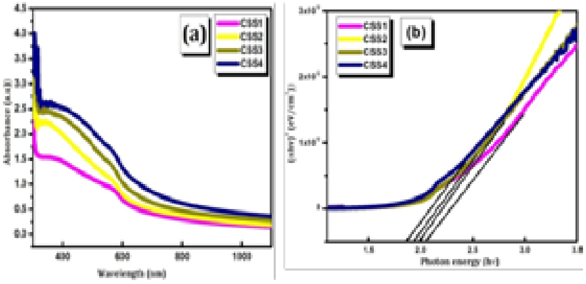

Figure 1: (a) Absorption spectra of Cd(SSe) thin films at different deposition time (b) Plots of $(\alpha h\upsilon)^2$ (eV/cm^2) vs. the photon energy hυ (eV)

3.3 Structural studies

Fig.2 shows the X-ray diffraction pattern of all samples deposited at different deposition time. The intense peaks in XRD pattern confirms that all Cd(SSe) thin film sample are nanocrystalline in nature [14]. Six distinct reflections centered at 2θ = 26.09, 30.43, 31.56, 42.83, 50.02 and 51.80 can be index to (002), (101), (102), (110), (200) and (201) crystal plane respectively, corresponding to observed‘d’ values 3.410, 3.335, 2.537, 2.109, 1.821 and 1.762 Å. The observed‘d’ values from diffraction pattern were compared with standard diffraction data (JCPDS # 49-1459) confirms the formation of pure Cd(SSe) phase with hexagonal (wurtzite) crystal structure. The average grain size (D) has been determined using following Scherrer’s formula from full width at half maximum (FWHM) β of the intense peak [15].

where, ‘K’ is constant (0.94), ‘D’ is the crystallite size, ‘**λ**’ is wavelength of X- ray used, ‘β’ is full width at half-maximum (FWHM) of the peak in radian and ‘θ’ is Bragg’s angle. The calculated crystallite sizes ranging from 58 nm to 76 nm with the increase in deposition time.

Table:1
Values for the thickness, band gap, crystallite size (D), of the Cd(SSe) thin films.

Sample code	Film Thickness (nm)	Band gap (eV)	Crystallite size (nm)
CSS1	347	2.05	58
CSS2	420	2.00	64
CSS3	517	1.93	71
CSS4	561	1.87	76

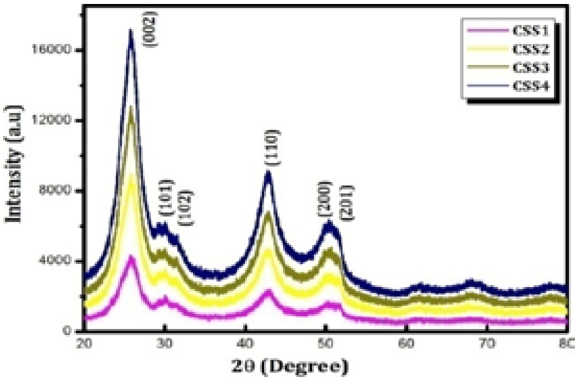

Figure.2 XRD patterns of Cd(SSe) thin films.

Morphological study

All SEM images clearly show the uniformity of the thin films throughout the substrate surface with well-adherent and clearly defined grains. Fig.5 (a-h) shows the SEM micrographs of thin films at low and high magnification for different deposition time.

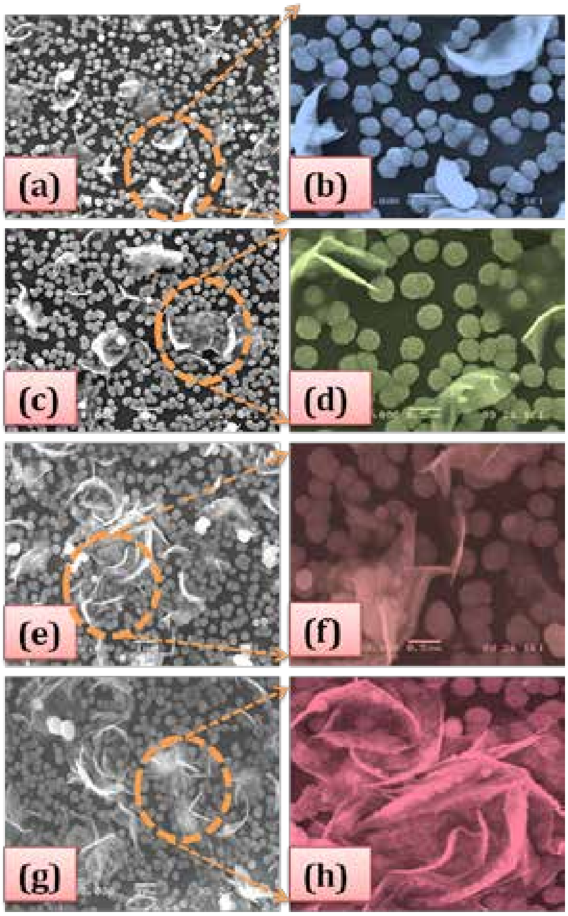

Figure.3 SEM micrograph of Cd(SSe) thin films. CSS1(a-b),CSS2 (c-d),CSS3 (e-f) and CSS4 (g-h).

The SEM micrograph of all the samples (CSS1 to CSS4) shows the formation of a densely packed smooth homogenous surface, with the formation of spherical grains mixed nanopetals and finally Rose flower like morphology that are dispersed over the entire substrate surface. SEM micrograph of sample CSS1 (Fig.3a-b) shows the presence of nanospheres with dispersed nanopetals while sample CSS2 (Fig.3 c-d) shows nanospheres with aggregated nanopetals, this aggregation of nanopetals increased to more extent in sample CCS3 (Fig.3e-f) to CSS4 (Fig.3g-h) and finally aggregation of nanopetals results in formation of rose flowers nanoparticles like morphology (CSS4). SEM images reveal that noticeable surface modification is observed as reaction time increases from 1h to 2.5 h.

Compositional study

Fig.4 indicates the representative EDS spectrum of CSS4 thin films. From Fig.4 it shows the presence of peaks at 3.13, 2.50 and 1.38 keV confirms the presence of Cd, S and Se elements respectively.

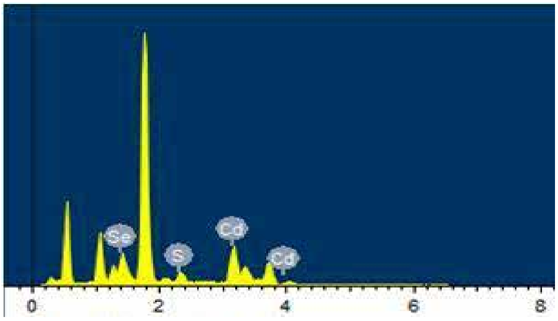

Figure.4 Energy dispersive X-ray analysis (EDS) spectrum of CSS4 samples.

3.7 Photo electrochemical (PEC) study:

Fig.5 shows the current density–voltage (J–V) characteristics for CSS1, CSS2, CSS3 and CSS4 samples in dark and under illumination. For all the samples, J–V characteristics curves in the dark display diode like rectifying characteristics while under light illumination these photo-anodes generates electron-hole pairs on the surface of Cd(SSe) thin films resulting flow of photocurrent. PEC cell was assembled with Cd(SSe) thin films as working electrodes with an active area of 1 cm^2 and graphite as counter electrode, All J–V measurements were performed under illumination using a 500W tungsten filament lamp having a light intensity 30 mW cm^{-2} in an 0.5 M sulfide/polysulfide redox electrolyte. The following cell configuration was used to record the J-V characteristic plots.

Glass-FTO/Cd(SSe)/0.5M(Na$_2$S-NaOH-S) aq/ G

Under illumination, the J–V curves shift in the IVth quadrant, indicating the generation of electricity, which is typical of solar cell characterization. The output parameters of PEC cell such as fill factor (FF) and power conversion efficiency (◎ %) were calculated using equation (7) and (8) respectively.

Where is the short-circuit current density and is the open circuit voltage. and are the maximum current density and the maximum voltage and is the input light intensity (30 mW cm^{-2}). From the J–V measurements, the obtained values of , , , and FF are explored in Table 4. The improvement in conversion efficiency with increasing deposition time can be explained on the basis of the surface morphology and optostructural properties of Cd(SSe) thin films. As observed from the optostructural properties, sample CSS1 and CSS2 shows mixed spherical grains with dispersed nanopetallike surface morphology and low crystallinity, high dislocation density and microstrain. As a consequence, these samples have recombination problem due to grain boundaries and recombination of electron–hole pairs those results in low conversion efficiency [16]. The dispersed nanopetals in spherical grains aggregated in some extent in sample CSS3 which increases light absorption by providing more surface area While CSS4 sample shows interconnected and well-grown spherical grain with rose flowerlike morphology which is helpful for light harvesting. Also, from samples CSS1 to CSS4 crystallinity increases, this improved crystallinity significantly reduces the grain boundary resistance. The highest conversion efficiency obtained was 0.17 % for the sample CSS4.

Table:2
Solar cell parameters of the Cd(SSe) thin films.

Sample Code	J_{sc} ($mAcm^{-2}$)	V_{oc} (mV)	J_{max} ($mAcm^{-2}$)	V_{max} (mV)	FF	η (%)
CSS1	0.1803	331.0	0.1219	116.8	0.23	0.04
CSS2	0.1609	415.9	0.1016	160.6	0.24	0.05
CSS3	0.1858	374.0	0.1117	159.9	0.25	0.06
CSS4	0.2639	413.8	0.1793	141.2	0.47	0.17

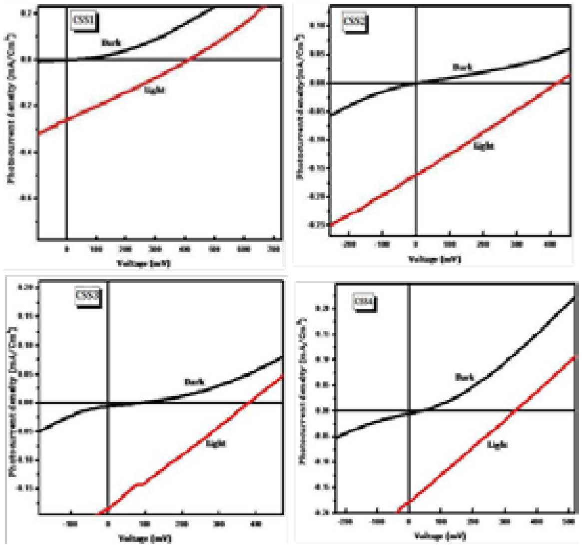

Fig.5 J-V characteristic curves for Cd(SSe) thin films.

CONCLUSIONS

In conclusions, an APT is cost effective method for deposition of Cd(SSe) metal chalcogenide thin films. From optical studies, band gap value was found in the range of 2.05 eV to 1.87 eV. The XRD study revealed the Cd(SSe) thin films formed were nanocrystalline in nature with pure hexagonal crystal structure.With increase in deposition time modification in surface morphology was observed which was found very beneficial for effective light absorption. The SEM micrograph shows the nanosphere mixed nanopetal like morphology aggregated finally into rose flower like surface. EDS analysis shows the presence of Cd, S and Se in films. From J–V measurements, a highest photoconversion efficiency of 0.17 % was obtained for the sample synthesized at higher synthesis time (CSS4).

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