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Chemically Deposited $CdS_{1-X}Se_X$ Thin Films and Characterization

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Abstract : Nanocrystalline cadmium sulfoselenide ($CdS_{1-x}Se_x$; x=0.2, 0.5)thin films are successfully deposited onto a Flourine doped Tin Oxide (FTO:SnO_2 ; 18-20 Ωcm^{-2}) coated glass substrates under optimized growth conditions by chemical bath deposition technique (CBD). The as-deposited thin films were yellow-orange in colour and were vacuum annealed at a temperature of 250 ^oC for 5hour. The X-Ray diffraction (XRD) analysis reveals that the films are polycrystalline with hexagonal phase. The crystallite size of the $CdS_{0.8}Se_{0.2}$ and $CdS_{0.5}Se_{0.5}$ thin films were found to be 39.1nm and 42.2 nm respectively.The band gap of the films found to be decreased slightly with increase in composition of selenium. The surface micrographs of the films obtained from the field emission scanning electron microscope (FESEM) shows that both the films exhibitflakes-like morphology with spherical shaped nano clusters. $CdS_{0.5}Se_{0.5}$ films are relatively uniform, compact, well covered,well adherent to the substrate than compared to $CdS_{0.8}Se_{0.2}$ thin films.The surface wettability test showed hydrophilic and hydrophobic nature of $CdS_{0.8}Se_{0.2}$ and $CdS_{0.5}Se_{0.5}$ thin films respectively. The Photoelectrochemical (PEC) analysis reveals that thin film of $CdS_{0.5}Se_{0.5}$ is more photoactive than $CdS_{0.8}Se_{0.2}$ thin film.
Keywords : Thin films, cadmium sulfoselenide, chemical bath deposition, flakes-like morphology, PE.

Introduction

In recent times II-VImetal chalcogenides[1] and alloys have received considerable attention of researchers due to the significant progress in the deposition techniques as well as their wide applications in the optoelectronic devices used in the UV-VIS and near IR regions of electromagnetic spectrum. Cadmiumsulfoselenide(CdSSe) is a ternary alloy metal chalcogenide has the band gap lies between that of CdS and CdSe. Its band gap can be tuned almost covering the entire visible range of electromagnetic spectrum. This shows that CdSSe is a promising candidate to achieve wavelength tunable emission. CdSSe is a highly photosensitive material and finds its applicability in various practical applications such as in optical filter, photovoltaic, photoelectrochemical devices, photoconductors and other optoelectronic devices[2-3].$CdS_{1-x}Se_x$ thin films are deposited by various methods such as screen printing, spray pyrolysis, epitaxial growth, chemical bath deposition(CBD)[4-7]etc. Among all the methods, chemical bath deposition is a simple, convenient, inexpensive technique and can be used for large area deposition. In the present work $CdS_{1-x}Se_x$ is depositedon fluorine doped tin oxide (FTO:SnO_2, 18-20Ωcm^{-2})coated glass substrates using chemical bath deposition method and a comparative study between $CdS_{0.8}Se_{0.2}$ and $CdS_{0.5}Se_{0.5}$ has been made in order to understand the effect of selenium composition on structural, morphological, optical, photoelectrochemical properties of the $CdS_{1-x}Se_x$thin films by modulating the chemical composition(x=0.2, 0.5).

Experimental

In the experiment for the synthesis of $CdS_{0.8}Se_{0.2}$ thin films, the chemical bath with 0.5M, 20 mL cadmium sulfate ($3CdSO_4.8H_2O$) was taken in a 50 mL beaker. 30% liquid ammonia was added to it slowly drop by drop till pH 11.80 was obtained. Initially white precipitate is seen, the precipitate disappears upon excess addition of ammonia. 0.5M, 16 mL of thiourea ($CS(NH_2)_2$) was added to it and stirred well. Freshly prepared 0.5M, 4mL sodium selenosulphite (Na_2SeSO_3) solution was added to the previous solution and stirred well. Precleaned FTO substrates (50cmx0.3cmx1cm) are immersed into the chemical bath in the vertical position using a substrate holder. The chemical bath was then placed in constant temperature water bath maintained at a temperature of 75^{o}C. The contents of the bath are stirred slowly at a uniform rate using a magnetic stirrer. After 90 minutes the substrates were removed from the bath washed with double distilled water (DDW) and dried in air. Similar procedure was employed to deposit $CdS_{0.5}Se_{0.5}$thin films by using 0.5M, 10 mL $CS(NH_2)_2$) and 0.5M, 10mL Na_2SeSO_3 solution at fixed volume and concentration of cadmium sulfate under the same growth conditions. The as deposited films of $CdS_{1-x}Se_x$ were yellow-orange in colour. The films were then vacuum annealed at a temperature of 250^{o}C for 5hour.CdSSe-1 and CdSSe-2 are the sample nomenclature for $CdS_{0.8}Se_{0.2}$and $CdS_{0.5}Se_{0.5}$ samples respectively.

Results and Discussion

Structural Analysis:

Fig-1 shows the XRD patterns for CdSSe-1 and CdSSe-2 samples. The XRD pattern reveals that both the thin films are polycrystalline and are in hexagonal phase[JCPDS data sheet No.00-040-0837]. The grain size(D) was calculated using scherrer's equation for (002) plane. The structural parameters are calculated and tabulated in **Table-1**. With the increase of selenium composition from x=0.2 to 0.5, the grain size was found to increase from 39.1nm to 42.2nm and a slight decrease in dislocation density and microstrain was observed[8-9]. This shows the improvement in crystallinity of CdSSe-2 films.

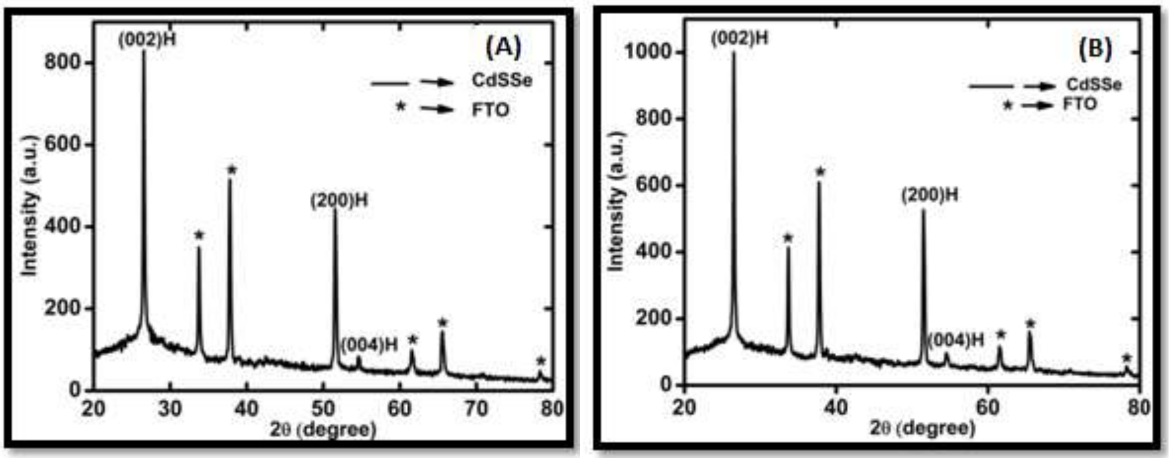

Fig-1: XRD patterns for (A) CdSSe-1(B) CdSSe-2

Table-1: Calculated values of structural parameters of $CdS_{1-x}Se_x$

Sample Id	β (FWHM) For (002) plane	$D = \frac{0.9\lambda}{\beta\cos\theta}$ (nm)	$\rho = \frac{1}{D^2}$ (lines/m²)	$N = \frac{t}{D^3}$ (m^{-2})	$\varepsilon = \frac{\beta\cos\theta}{4}$	Lattice constant (Å)	
						(exp)	(std)
CdSSe-1	0.20886	39.1	$6.54x10^{14}$	$2.78x10^{15}$	0.051	a=4.090	a =4.154
						c =6.710	c=6.764
CdSSe-2	0.19357	42.2	$5.6x10^{14}$	$1.928x10^{15}$	0.042	a =4.099	a =4.154
						c=6.728	c =6.764

Optical Study:

The UV-Visible spectroscopy was used to study the optical properties of CdSSe-1 and CdSSe-2 thin films using UV-VIS spectrophotometer in the wavelength range 300-900nm at room temperature.

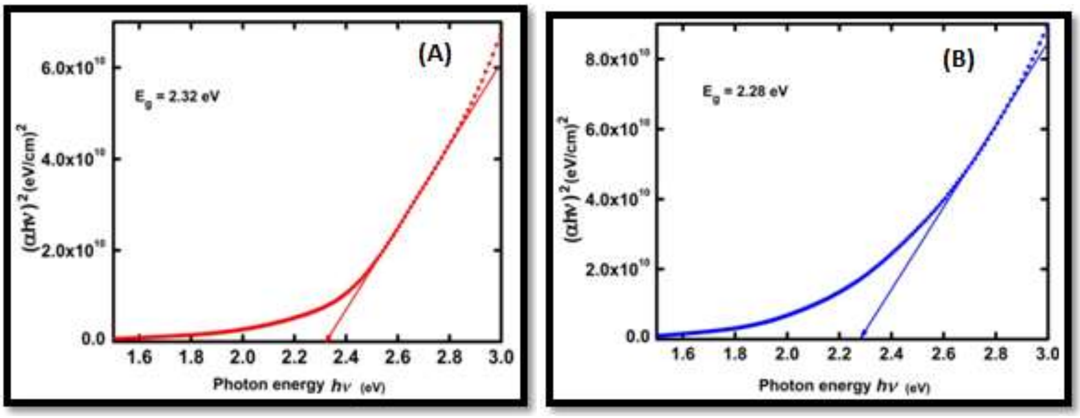

Fig-2: Plot of $(\alpha h\nu)^2$versus hν for (A) CdSSe-1 (B) CdSSe-2

Fig-2 shows the plot of $(\alpha h\nu)^2$versus hν for the CdSSe-1 and CdSSe-2 sample. The band gap was found to decrease from 2.32 to 2.28eV with the increase of x from 0.2 to 0.5[10].

Surface Morphological Analysis:

The surface morphology of $CdS_{1-x}Se_x$ thin film was carried out using FESEM. **Fig-3** shows the FESEM micrograph of both CdSSe-1 and CdSSe-2 thin film exhibiting nanoflakes-like morphology[11]. CdSSe-1 film has voids, non uniform surface morphology with the presence of spherical shaped nano clusters. However the micrograph of CdSSe-2 film shows comparatively uniform surface morphology, the film is compact, well covered and adherent to the substrate.

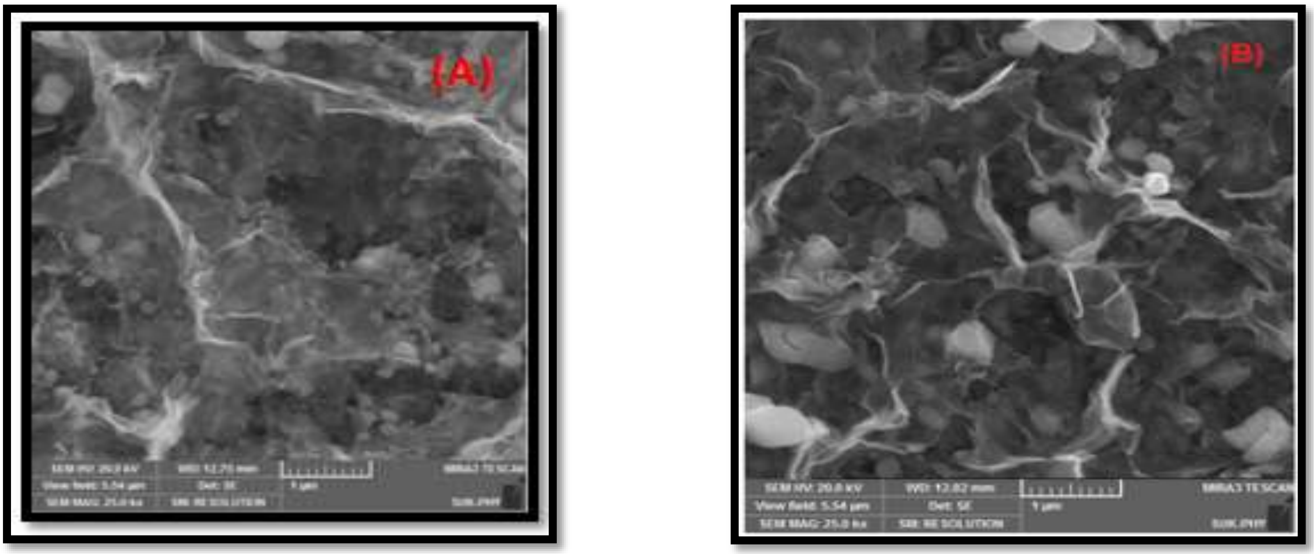

Fig-3: FESEM micrographs of (A) CdSSe-1 (B) CdSSe-2

Surface Wettability Study:

The surface wettability study of $CdS_{1-x}Se_x$films was carried out by measuring water contact angle to the$CdS_{1-x}Se_x$ thin film. **Fig-4** shows the captured water drop image on the CdSSe-1 and CdSSe-2 samples. The mean contact angle for CdSSe-1 is 75° while, it is 95° for CdSSe-2 sample. This shows that the surface of CdSSe-1 sample is hydrophilic and that of CdSSe-2 is hydrophobic in nature[12].Hence the adsorption is stronger for CdSSe-2 sample than CdSSe-1 sample. The enhancement in the contact angle for CdSSe-2 sample indicates the decrease in the surface energy of the sample.

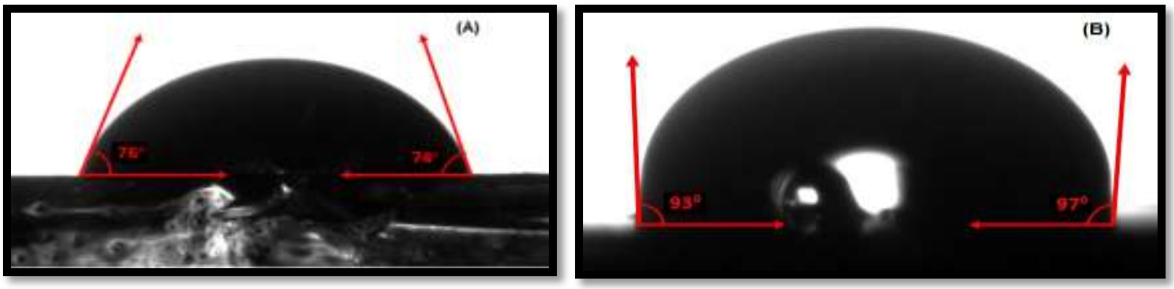

Fig-4: Captured waterdrop image(A) CdSSe-1 (B) CdSSe-2

Photoelectrochemical Analysis:

In the photoelectrochemical study of the $CdS_{1-x}Se_x$ thin film, a photoelectrochemical cell was fabricated with $CdS_{1-x}Se_x$ thin film having area $1cm^2$ as photoelectrode and graphite as counter electrode respectively. 1M polysulfide electrolyte (1M (NaOH) +1M (Na_2S) + 1M (S)) was used as an aqueous redox electrolyte in the PEC cell.

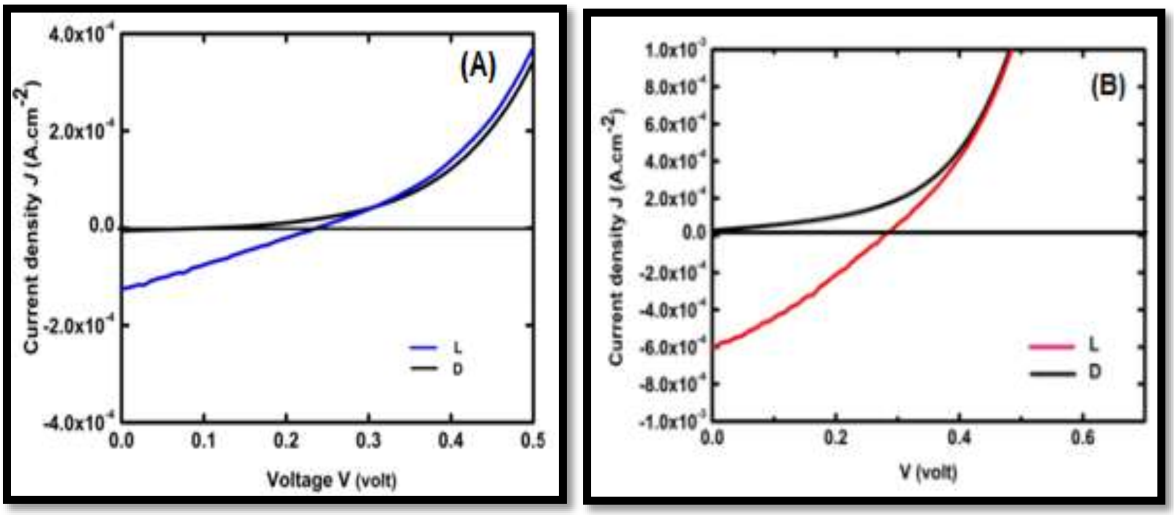

Fig-5: J-V Characteristic for (A)CdSSe-1 (B) CdSSe-2

Table-2: PEC Cell Parameters for $CdS_{1-x}Se_x$samples

Sample Id	V_{oc} (V)	J_{sc} (mA/cm^2)	J_m (mA)	V_m (V)	$FF = \frac{J_m X V_m}{J_{sc} X V_{oc}}$	$\eta = \frac{J_{sc} X V_{oc}}{P_{in}} X FF X 100$ (%)
CdSSe-1	0.24	0.13	0.069	0.103	0.23	0.01
CdSSe-2	0.29	0.60	0.053	0.129	0.30	0.10

The PEC performance of $CdS_{1-x}Se_x$photoelectrode was examined by measuring current density(J) – voltage (V) characteristics in dark as well under illumination shown in **Fig-5**. The measurements were performed under the input power of 50mWcm^{-2}. The fill factor (FF) and power conversion efficiency (η) are calculated and tabulated in the **Table- 2**.

It is observed that with the increase of selenium composition there is an improvement in the PEC performance[13]. This might be due to improved crystallinity, surface morphology along with decrease in microstrain, dislocation density and grain boundary resistance.

Conclusion

Nanocrystalline CdS_{1-x} Se_x thin films with the measurable changes in structural and optical properties are obtained using chemical bath deposition technique by modifying the chemical composition.The XRD studiesreveal the presence of polycrystalline with hexagonal structure. The increase in grain size, slight improvement in crystallinity, the reduction in dislocation density as well as microstrain was observed with the increase of selenium composition.The decrease in band gap, relatively better and uniform surface morphology, enhancement in wetting characteristics with the increase of selenium composition was observed.The slight improvement in the PEC performance of $CdS_{0.5}Se_{0.5}$ compared to$CdS_{0.8}Se_{0.2}$ confirms that $CdS_{0.5}Se_{0.5}$ is more photoactive than $CdS_{0.8}Se_{0.2}$ thin film.

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