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Influence of thickness and substrate temperature on electrical and photoelectrical properties of vacuum-deposited CdSe thin films

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Abstract

Polycrystalline cadmium selenide thin films are prepared in different thicknesses and substrate temperatures by vacuum deposition technique. The XRD patterns recorded for the CdSe thin films show that these films are polycrystalline in nature and crystallise in the hexagonal form. The crystallinity increases with increase in substrate temperature. The optical measurements reveal that the CdSe thin films possess direct band gap and the band gap energy decreases with the increase of thickness and substrate temperatures. The electrical conductivity measurements show that they possess three different activation energies in the temperature range 298 to 118 K. The steady-state photoconductivity measurements reveal that the photocurrent varies linearly with the applied voltage and the photocurrent obeys a power law of the form, $I_{ph} \propto F^{\gamma}$, where γ is a constant. The transient photoconductivity measurements show that the decay process is very rapid in the beginning followed by a slow process.

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1. Introduction

Among II-IV compounds, CdSe has been investigated for its potential applications in the field of light amplification [1], photoelectrochemical cells [2], optoelectronic devices [3,4], thin film transistors [5], and gamma ray detectors [6]. A wide range of electrical properties has been reported for CdSe. In the reported electrical properties of CdSe, the predominant scattering mechanism has been attributed to ionised impurity scattering [7], intercrystalline potential barrier scattering [8] or a combination of both. Gupta and Deh [9] also obtained a combination of both conduction due to the presence of oxide impurities for their CdSe thin films prepared by electroless deposition. The photoconductivity of the photodetectors depends on the method of preparation [10] and sensitisation [11]. Several workers [12,13] have studied the oxygen adsorption and desorption energies in CdSe thin films. Samanta et al. [14] have studied the photoconductivity of the as-grown thermally evaporated CdSe thin films. In this paper, the influence of thickness and substrate temperature of CdSe thin films on structural, electrical and photoelectrical properties of the vacuum-deposited films is presented.

2. Experimental details

Thin films of CdSe were deposited from CdSe powders (Aldrich, 99.99%) using a Hind Hivac Vacuum Coating Unit (model 12-A4) at different thicknesses and substrate temperatures on glass substrates. The vacuum was kept at 10^{-4} Pa and the rate of deposition was maintained at 2-3 nm s⁻¹. The films were found to be uniform, porous free and adhered well with the glass plates. CdSe thin films were prepared for three different thicknesses at room temperature (RT) and at two different substrate temperatures. The thickness of the thin films was measured by optical method.

The X-ray diffraction pattern for the CdSe powder sample and the thin films were recorded in JEOL JDX 8030 X-ray diffractometer using Cu K α radiation. The XRD pattern of the CdSe powder sample reveals that it is in hexagonal form with the cell dimensions a = 4.307(3) Å and c = 7.03(1) Å.

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The optical spectra were recorded in the wavelength region 400-2000 nm using UV-Vis-NIR spectrophotometer (Hitachi V-3400). The XPS spectra were recorded in an ES-CALAB MK II spectrometer (VG Scientific Ltd., UK) with Mg Ka radiation of energy 1253.6 eV. The electrical conductivity measurement was carried out from liquid nitrogen temperature to 573 K by van der Pauw technique. The photoconductivity measurements were carried out at RT by two probe technique using a halogen lamp source of 100 W. The light intensity was measured using lux meter (model Lutron LX-101).

3. Results and discussions

3.1. Structural properties

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The XRD patterns of vacuum-deposited CdSe thin films prepared at RT having thicknesses 0.343, 0.403, and 0.497 µm are shown in Fig. 1A, 1B and 1C, respectively. The broad peak appearing at low angle is due to the glass substrate itself. The observation of X-ray peaks in all the three CdSe thin films indicates that the vacuum-deposited films are polycrystalline in nature. Table 1 lists the observed *d*-values with the standard JCPDS *d*-values for CdSe thin films. The observed *d*-values are in good agreement with the standard values for the hexagonal structure. In the

ntensity (Counts) B n 100 С 10.0 30.0 50.0 70.0 Anale 20

Fig. 1. XRD patterns of CdSe thin films of thicknesses: (A) 0.343 µm, (B) 0.403 µm and (C) 0.497 µm prepared at RT.

Table	1				
ZPD	data	for	CdSe	thin	film

Thickness (µm)	20 (°)	Ι	d (Å), measured	d (Å), standard	h k l
$T_{\rm s} = {\rm RT}$					
0.343	25.4	134	3.504	3.517	002
0.403	25.2	137	3.531	3.517	002
0.497	25.5	125	3.49	3.517	002
0.497	26.8	111	3.324	3.300	101
$T_{\rm s} = 100 ^{\circ}{\rm C}$					
0.359	20.5	120	4.329	4.307	100
	25.7	406	3.463	3.517	002
	27.4	172	3.252	3.300	101
	46.1	105	1.967	1.980	103
	50.1	68	1.819	1.836	112
	64.2	53	1.450	1.458	203
$T_{\rm s} = 200 ^{\circ}{\rm C}$					
0.213	25.2	503	3.531	3.517	002
	27.2	300	3.276	3.300	101
	45.7	177	1.984	1.980	103
	62.0	100	1.496	1.458	203

XRD patterns for these three thin films, the X-ray peak corresponding to (002) reflection is observed. It indicates that the preferred orientation lies along [002] direction in vacuum-deposited CdSe thin films. This dominant orientation in the [002] direction has been reported for spraved [15], vacuum-deposited [16] and the annealed CdSe thin films prepared by chemical bath deposition [17].

The XRD patterns of the films prepared at different substrate temperatures are shown in Fig. 2A and B, respectively.



Fig. 2. XRD patterns of CdSe thin films deposited at substrate temperatures of: (A) 100 °C and (B) 200 °C.

As expected, the crystallinity of the films deposited at higher substrate temperature is better and more number of X-ray peaks are observed. The strong X-ray peak at (002) plane indicates the preferred orientation of the crystalline grains with *c*-axis perpendicular to the plane of the substrate that makes the (002) peak relatively stronger than the other peaks. The crystallite size (grain diameter), *D*, of the crystallites can be determined using the Scherrer's formula [18]:

$$D = \frac{K\lambda}{\omega\cos\theta} \tag{1}$$

where λ is the wavelength of X-rays, θ the Bragg angle and ω the full width at half maximum in radian. *K* varies with (h k l) and crystallite shape but usually nearly equal to 1. The dislocation density (δ) is evaluated [19] using the relation:

$$\delta = \frac{n}{D^2} \tag{2}$$

where n is a factor, which equals unity giving minimum dislocation density and D the crystallite size. The crystallite

Table 2Grain size and dislocation density for CdSe thin films

S. no.	Thickness (µm)	Substrate temperature	Peak	Grain size (nm)	Dislocation density (m ⁻²)
1	0.343	RT	002	3.46	8.35×10^{16}
2	0.403	RT	002	3.48	8.25×10^{16}
3	0.497	RT	002	3.51	8.17×10^{16}
4	0.359	100 °C	002	6.87	2.11×10^{16}
5	0.213	200 °C	002	7.01	2.03×10^{16}

size and dislocation density of the CdSe thin films are calculated and given in Table 2. It is evident from the table that the grain size increases with increase in substrate temperature.

3.2. XPS study

The X-ray photoelectron spectra were recorded for the CdSe thin films prepared at a substrate temperature of $100 \,^{\circ}$ C having 0.359 μ m thickness and shown in Fig. 3. In the case



Fig. 3. XPS spectra of CdSe thin films recorded for the core levels of: (A) Cd and (B) Se.

of elemental cadmium, the $3d_{5/2}$ and $3d_{3/2}$ peaks are found in standard table at 403.7 and 410.5 eV, respectively. The XPS peaks observed at 404 and 411.8 eV in the core level spectra of cadmium coincide with $3d_{5/2}$ and $3d_{3/2}$ of the cadmium peaks available in the standard tables [20]. The selenium XPS peaks $3p_{3/2}$ and $3p_{1/2}$ are observed at 158.0 and 164.9 eV. The shift in the binding energies for Se and Cd from their standard values is due to the presence of adsorbed oxygen [21].

An increase in the doublet separation energy of cadmium $3d_{5/2}$ and $3d_{3/2}$ peaks is observed and it is due to the exchange splitting of 3d levels by the unpaired electrons [22]. The doublet separation energy of selenium peaks of $3p_{3/2}$ and $3p_{1/2}$ is also found to be increased compared to their standard values. It is also due to the exchange splitting of 3p levels by the unpaired electrons. The increase in the separation of doublet is associated with multiplet splitting effect.

The atomic concentration ratio (cadmium to selenium) determined using the peak area and intensity ratio, shows that the film is cadmium deficient and slightly rich in selenium. The selenium rich in CdSe thin film is due to the higher deposition rate and substrate temperature. A change of film composition from Cd rich to Se rich due to the increase in the deposition rate and substrate temperature has been reported by Chan and Hill [23]. The change of Cd rich to Se rich is also expected from the consideration of the vapour pressure curves for Cd and Se [24]. These curves show that the vapour beam becomes increasingly rich in selenium as the source temperature increases.

3.3. Optical properties

A plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdSe thin films for three different thicknesses prepared at RT is shown in Fig. 4A.



Fig. 4. A plot of $(\alpha h\nu)^2$ versus $h\nu$ for CdSe thin films of thicknesses: (A)—(a) 0.343 µm, (b) 0.403 µm and (c) 0.497 µm prepared at RT; (B) prepared at—(a) 303 K, (b) 373 K and (c) 473 K.

The direct band gap energies are evaluated by finding the *x*-axis intercepts. The band gap energies obtained for the film of thickness 0.343 µm are 1.79(4) and 1.98(1) eV, for the film of thickness 0.403 µm are 1.75(2) and 1.99(3) eV, and for the film of thickness 0.497 µm is 1.73(2) eV. The $(\alpha h\nu)^2$ versus $h\nu$ plot for cadmium selenide thin films deposited on glass substrates at different substrate temperatures is shown in Fig. 4B. The band gap energies for the films prepared at 303, 373 and 473 K are 1.79(4), 1.69(2) and 1.62(3) eV, respectively. The decrease in band gap energy with the increase in the substrate temperature can be attributed to the increase in the grain size.

3.4. Electrical conductivity

3.4.1. Below RT

The electrical conductivity for the CdSe thin film samples prepared at a substrate temperature of 200 °C and having a thickness of 0.213 µm is measured in the region 298–77 K. A plot is drawn between $\ln \sigma$ and $10^3/T$ and shown in Fig. 5A. The curve has four steps and plateaus (I–IV in Fig. 5A). These steps have been attributed to transitions from a subband of the valence band to the conduction band. Szabo and Cocivera [25] have observed similar types of plateaus and steps in the action (photocurrent) spectra and the optical absorption spectrum of the electrodeposited CdSe thin films. Thutupalli and Tomlin [26] have also observed similar plateaus and steps in the optical absorption spectrum of their vacuum-deposited CdSe thin films.

The plot shown in Fig. 5A exhibits Arrhenius behaviour in three different temperature ranges 298–218, 218–133 and 133–118 K. In these three regions, the activation energy is found to be 27.9, 9.37, and 0.54 meV. Below 118 K, the conductivity is almost constant indicating the freezing of

charge carriers. Three different activation energies of 0.029, 0.003 and 0.002 eV were reported by Gupta and Deh [9] for their CdSe thin films prepared by chemical bath deposition.

The electrical conductivity in thin films at low temperatures have four different types of conductions [27], namely: (a) the ordinary conductivity, with activation energy ε_1 , due to the drifting of the charge carriers in the applied electric field, (b) conductivity with activation energy ε_2 due to thermally assisted hopping, (c) conductivity with activation energy ε_3 due to hopping of charge carriers due to the existence of localised states around $E_{\rm F}$ and (d) variable range hopping (VRH) conduction. In CdSe thin films, all the four types of conduction are observed such as ε_1 in the region 298–218 K, ε_2 in the temperature range 218–133 K, ε_3 in the temperature range 133-118 K and VRH below 118 K. This shows that below 218 K, the impurity conduction with activation energies ε_2 and ε_3 is dominant. In the $\ln \sigma$ against $10^{3}/T$ plot, the observed deviation in the straight line below 118K indicates the existence of VRH conduction. The first term represents the conduction in the conduction band, most likely due to singly ionised native Cd interstitial defect [28,29] having ionisation energy $E_{A1} \approx 0.014 \,\text{eV}$.

The Greaves [30] conductivity expression for VRH model applicable to low temperature is:

$$\sigma T^{1/2} = C \exp\left(-\frac{T_0}{T}\right)^{1/4} \tag{3}$$

where *C* and T_0 are constants related to the density of localised states $N(E_F)$ by:

$$T_0 = \frac{16\alpha^3}{kN(E_{\rm F})}\tag{4}$$

where α^{-1} is the measure of the spatial extension of the wave function $\exp(-\alpha x)$ associated with the localised states.



Fig. 5. A plot of: (A) $\ln \sigma$ versus $10^3/T$ in the temperature region 298–77 K and (B) $\ln (\sigma T^{0.5})$ versus $T^{-0.25}$ showing hopping conduction mechanism for CdSe thin films.



Fig. 6. A plot of $\ln \sigma$ versus $10^3/T$ from RT to 573 K for CdSe thin film of thicknesses: (A) 0.343 μ m, (B) 0.403 μ m and (C) 0.497 μ m prepared at RT.

A plot of $\ln(\sigma T^{1/2})$ versus $T^{-0.25}$ is drawn and is shown in Fig. 5B. In the temperature range 118–77 K, it is found to be a straight line indicating the validity of hopping conduction mechanism. This is in good accordance with Mott's VRH process. The slope of the curve gives the value of T_0 and is equal to 1.23×10^3 K.

3.4.2. Above RT

In cadmium selenide thin films, the conductivity measurements are carried out from RT to 573 K for various thicknesses. The $\ln \sigma$ versus $10^3/T$ curves from RT to 573 K for CdSe thin films are shown in Fig. 6. The plot obeys the relation:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{5}$$

where E_a is the activation energy, k the Boltzmann constant and T the temperature in Kelvin.

The conductivity of the films increases with increase in thickness. The observed lesser conductivity in thinner films can be explained due to lower degree of crystallinity and the small grain size. The presence of a number of defects such as structural disorders, dislocations, surface imperfections, etc. also play a role in decreasing conductivity. The activation energies obtained from the slopes of the plots are 242 meV (513–573 K) and 13 meV (312–493 K) for 0.343 μ m thick film; 216 meV (474–571 K) and 12 meV (302–473 K), 30 meV (392–452 K) and 7 meV (302–393 K) for 0.497 μ m thick film.

3.5. Photoelectrical properties

3.5.1. Steady-state photoconductivity

The steady-state photoconductivities for the CdSe thin films of thickness $0.213 \,\mu m$ prepared at a substrate tempera-

ture of 200 °C are measured by exposing the sample to three different light intensities, namely 600, 1800 and 3000 lx as shown in Fig. 7A. The photocurrent is found to be greater than the dark current and it is in the order of 10 times larger than that of the dark current in these thin films. The photoconductivity of the CdSe samples at RT is found to be 2.37×10^{-7} , 1.31×10^{-6} and 3.69×10^{-6} S m⁻¹ for the light intensities of 600, 1800 and 3000 lx, respectively. The dark conductivity at RT is 1.95×10^{-6} S m⁻¹.

The variation of the photocurrent with the intensity of photo excitation (*F*) is shown in Fig. 7B. The observed linear behaviour of $\ln I_{\rm ph}$ versus $\ln F$ indicates that CdSe thin films follow the power law of the form:

$$I_{\rm ph} \propto F^{\gamma}$$
 (6)

where γ is a constant and its value determines whether the recombination process is monomolecular or bimolecular. If $\gamma < 1$, the recombination process is sublinear and if $\gamma > 1$, the recombination process is supralinear. For bimolecular process, $\gamma = 0.5$ and for monomolecular process $\gamma = 1$. In the present case, γ lies between 1.68 and 2.1 at RT, indicating that the recombination is supralinear. In TiO₂–ZnO solid solutions supralinearity is reported [31] at low illumination levels. A similar supralinear recombination mechanism was also reported by Bube [32] in CdS samples. The photosensitivity of CdSe thin films is determined using the relation $S = \sigma_{\rm ph}/\sigma_{\rm d}$, where $\sigma_{\rm ph}$ is the photoconductivity and $\sigma_{\rm d}$ is the dark conductivity. The photosensitivities at RT are found to be 0.12, 0.67, and 1.89 at 600, 1800 and 3000 lx, respectively. The effect of thickness and substrate temperature on the behaviour of photoconduction is also studied. The dark current and the photocurrent measured for CdSe thin films at RT increase with the increase of the film thickness and the substrate temperatures.



Fig. 7. A plot of: (A) steady-state photoconductivity for CdSe thin films at different illumination levels and (B) $\ln I_{\rm ph}$ versus $\ln F$ for CdSe thin films.

3.5.2. Photodecay

Fig. 8A shows the transient photoconductivity measurements on the CdSe thin films of thickness $0.213 \,\mu\text{m}$ prepared at a substrate temperature of $200 \,^{\circ}\text{C}$ and light intensity of $3000 \,\text{lx}$ measured at RT. After reaching the steady-state condition, the light is switched off and the decay curve is

followed. Initially the decay is fast and then it is followed by a slow decay. The fast decay is due to the greater number of free charge carriers than that of the trapped carriers. In the first region (up to 20 s), the decay time is found to be 0.26 s. The mechanism of slow decay process has been reported due to the presence of deeper level



Fig. 8. A plot of: (A) photodecay of CdSe thin films measured at 3000 lx and (B) $\ln \tau_d$ versus $\ln t$ for CdSe thin films showing the non-exponential decay of photocurrents.

traps and explained using the concept of differential lifetime, τ_d . The lifetime for such a slow decay process can be written as [33]:

$$\tau_{\rm d} = -\left(\frac{1}{I_{\rm ph}'}\frac{{\rm d}I_{\rm ph}}{{\rm d}t}\right)^{-1} \tag{7}$$

where I'_{ph} is the maximum photocurrent at t = 0 for a given applied voltage. The decay time observed for the vacuum-deposited CdSe thin film is found to be time dependent. In order to study the dependence of τ_d with time, a plot of $\ln \tau_d$ versus $\ln t$ is drawn and shown in Fig. 8B. The plot is found to be a straight line indicating that the non-exponential decay process involved in the CdSe thin film samples. It shows that the decay law is hyperbolic. The decay obeys the power law of the form t^{-n} , with:

$$n = \frac{\mathrm{d}(\ln \tau_{\mathrm{d}})}{\mathrm{d}(\ln t)} \tag{8}$$

and the value of *n* is found to be 1.52. The extrapolation of the curve at t = 0 gives the value of the carrier lifetime and is found to be 1.42 s.

4. Conclusion

Influence of thickness and substrate temperature on the structural and photoelectrical properties of vacuum-deposited CdSe thin films are analysed. The XRD patterns indicate the preferred orientation along [002] direction in all the thin films. The grain size increases with increase in substrate temperature. The electrical conductivity measurements show that CdSe film possesses mixed conduction at low temperatures. The CdSe thin films are highly photosensitive and the photoconductivity measurement show that the photoconductivity is enhanced for the samples prepared at higher substrate temperatures.

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