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# STRUCTURAL, MORPHOLOGICAL AND OPTICAL STUDIES OF CdSe THIN FILMS FROM AMMONIA BATH

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Cadmium selenide thin films were deposited on glass substrate using chemical bath technique for different bath temperatures 313 K, 333 K and 353 K. Polycrystalline nature of the material was confirmed by X-ray diffraction technique and various structural parameters were calculated. The spherical shaped clusters and the presence of elemental constituents were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). The optical properties were revealed by UV-Visible transmittance spectra and the band gap energy was determined.

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*Keywords:* Thin films; CdSe; X-ray diffraction; Scanning electron microscopy; Optical properties

## 1. Introduction

The II-VI binary semiconducting compounds belonging to the cadmium chalcogenide family (CdS, CdSe, CdTe) are considered to be very important materials for photovoltaic applications [1-3]. Nanocrystalline form of these groups has been a rapidly growing area of research due to its non-linear optical properties, luminescent properties, quantum size effect and other physical and chemical properties. CdSe is a promising photovoltaic material because of its high absorption coefficient and nearly optimum band gap energy for the efficient absorption of light and conversion into electrical power [4]. CdSe has been extensively investigated for its potential applications in photoelectrochemical (PEC) solar cell, optoelectronic devices and gamma ray detectors [5-7]. CdSe is an important material for the development of various modern technologies of solid state devices such as high efficiency thin film transistors and light emitting diodes. Other areas of successful applications include photo-detectors, light amplifiers, lasers, gas sensors, large-screen liquid crystal display and photoluminescence response [8]. Semiconductor devices based on CdSe thin films strongly depend on the structural and optical properties of the films obtained from various experimental conditions. A direct band gap range of 1.65 eV-1.84 eV has been reported for CdSe by various authors [9-10] and its photosensitivity gives it an edge over other semiconducting materials. Several physical and chemical techniques are available for the growth of CdSe thin films. CdSe thin films have been deposited using different techniques such as electrodeposition [11-12], molecular beam epitaxy [13], spray pyrolysis [14], successive ionic layer adsorption and reaction method [15], vacuum deposition and chemical bath deposition [16]. Among these methods chemical bath deposition has several overriding advantages with other

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techniques such as uniform film deposition, control of thickness, precise maintenance of deposition temperature, low cost [17-18]. The deposition parameters are usually optimized to obtain specularly reflecting films with a good adherence to the substrate [19-21].

In the present investigation, chemical bath deposition of cadmium selenide thin films has been reported. Structural characterization from XRD, EDAX, SEM and optical characterization from UV-Vis were carried out.

## 2. Experimental details

### *2.1 Film Preparation*

Chemical bath deposition technique was adopted for the preparation of cadmium selenide (CdSe) thin films. The chemicals used for the preparation were analytical grade cadmium acetate (99 %), selenium powder (99.5 %) and sodium sulphite (98 %).

The reaction mixture was prepared by adding ammonia ($NH_3$) solution in 0.1 M of cadmium acetate [$(CH_3COO)_2$ Cd. $2H_2O$] till a pH of 11 is attained. To the precursor cadmium acetate-ammonia solution, 5 ml of freshly prepared sodiumselenosulphite ($Na_2SeSO_3$) diluted with 5 ml of distilled water was added drop by drop under continuous gentle stirring using magnetic stirrer at about 80 ± 1 rpm. Sodiumselenosulphite was prepared by refluxing 4 gms of selenium powder with 12 gms of anhydrous sodium sulphite ($Na_2SO_3$) in 50 ml of double distilled demineralised water for 4 hours at 80 ± 0.5 °C. Thoroughly cleaned glass substrates were vertically immersed at the centre of the reaction bath.

The deposition of the film was carried out at bath temperatures 313 K, 333 K and 353 K. The bath temperature was controlled using a digital thermostat connected with Pt-100 thermocouple. The colourless bath turned orange in colour and then to orange-red as time progressed. The time of deposition was optimized as 130 minutes. After deposition, the substrates were rinsed in distilled water and dried. The films were then annealed in air at a temperature of 553 K for 15 minutes. During annealing the colour of the film changed from orange to red then to dark brown. Films prepared by this method were uniform, well adherent to the substrate, smooth and reflecting.

### *2.2 Film kinetics*

Deposition of CdSe thin film occurs when the ionic product of $Cd^{2+}$ and $Se^{2-}$ ions exceeds the solubility product of CdSe. $Cd^{2+}$ and $Se^{2-}$ ions in the solution control the rate of precipitation and film formation. The steps involved in the chemical deposition of CdSe thin film are as follows, the hydrolysis of sodiumselenosulphite proceeds via the chemical reactions

$$Na_2SeSO_3 + OH^- \longleftrightarrow Na_2SO_4 + HSe^-$$
$$HSe^- + OH^- \longleftrightarrow Se^{2-} + H_2O$$

When ammonia is added to $Cd^{2+}$ salt solution, $Cd(OH)_2$ is produced and starts precipitating when the solubility product of $Cd(OH)_2$ is exceeded, but dissolves in excess of ammonia solution to form the complex cadmium tetra-amine ions,

$$(CH_3COO)_2 \text{ Cd. } 2H_2O + 4\ NH_3 \longleftrightarrow [\text{ Cd } (NH_3)_4\ ]^{2+} + (CH_3COO)_2^{2-} + 2H_2O$$

Finally, the CdSe thin film formation takes place

$$[Cd\ (NH_3)_4]^{2+} + Se^{2-} \longleftrightarrow CdSe + 4NH_3$$

At intermediate temperature (333 K), the ions get sufficient time to condense on the substrate surface and therefore large amount of material gets deposited on the substrate giving maximum layer thickness. At relatively higher temperatures, more and more ions are released but all the ions do not get chance to adsorb on the substrate surface, they settle down at the bottom of the reaction container decreasing the film thickness [22].

### *2.3 Characterization*

The CdSe films were structurally characterized by X-ray powder diffraction using a JEOL JDX services instrument with $CuK_{\alpha}$ radiation ($\lambda$=1.5406 Å). The microstructures of these samples were characterized using Hitachi S-3400 equipped with an EDAX spectrometer. The optical properties of CdSe films were measured using UV-Vis spectrophotometer (JASCO V-530 dual beam).

## 3. Results and discussion

### *3.1 Structural analysis*

The structural elucidation of CdSe film for the bath temperatures 333 K and 353 K are presented in Fig. 1 (a), (b) with the diffraction 2θ from 20 to 70 °C. The observed *d* spacing and the respective prominent peaks correspond to reflections from (111), (220) and (311) planes which coincide well with JCPDS data [23]. Therefore it has been concluded that the deposited CdSe thin films are polycrystalline in nature with cubic structure.

The lattice parameter (a) for cubic structure is determined using the relation

$$a= d\sqrt{h^2+k^2+l^2} \quad (1)$$

where, d is the spacing between the planes in the atomic lattice, hkl are the Miller indices.

The grain size (D) for CdSe thin films are calculated using Scherrer's formula,

$$D = k\lambda / \beta\cos\theta, \quad (2)$$

where, the constant k is the shape factor, taken as 0.94, $\lambda$ is the wavelength of X-rays (1.5406 Å for $CuK_{\alpha}$), θ is the Bragg's angle and β is the full width at half maximum.

The dislocation density (δ) has been evaluated from Williamson and Smallman's formula,

$$\delta = 1/D^2 \ \text{lines/ m}^2. \quad (3)$$

The micro strain (ε) is obtained using the relation

$$\varepsilon = \beta \cos\theta / 4. \quad (4)$$

All these parameters are calculated and presented in Table 1.

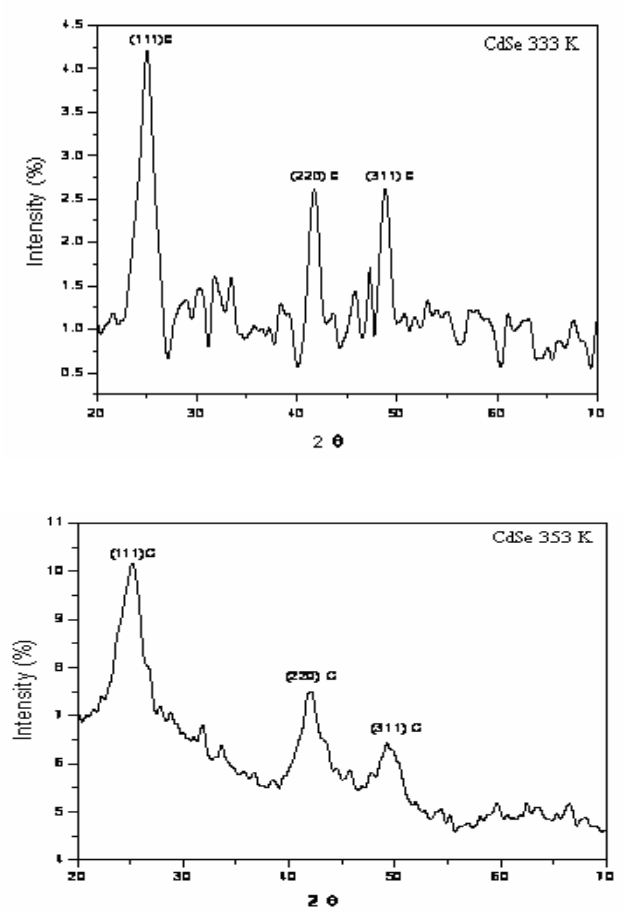


*Fig. 1 (a) XRD pattern of CdSe thin film (333 K), (b) XRD pattern of CdSe thin film (353 K)*

*Table 1. Structural parameters of Cdse Thin Film.*

| Material (temp. in K) | 2θ (degree) | d (spacing) Å | (β) FWHM | (hkl) | Lattice (a) Å | Grain Size(D) nm | density (δ) $x10^{15}$ lines/$m^2$ | Micro strain (ε) $x10^{-3}$ |
|---|---|---|---|---|---|---|---|---|
| | 25.3436 | 3.51438 | 1.170 | 111 | 6.0870 | 7.2701 | 18.9193 | 4.9798 |
| CdSe (333 K) | 42.1084 | 2.11360 | 1.160 | 220 | 5.9781 | 7.6660 | 17.0160 | 4.7226 |
| | 49.8257 | 1.8286 | 1.152 | 311 | 6.0647 | 7.9430 | 15.8499 | 4.5579 |
| | 25.2062 | 3.53030 | 1.152 | 111 | 6.1146 | 7.3818 | 18.3516 | 4.9045 |
| CdSe (353 K) | 42.0122 | 2.14887 | 1.152 | 220 | 6.0779 | 7.7167 | 16.7930 | 4.6916 |
| | 49.6925 | 1.8046 | 1.142 | 311 | 5.9851 | 8.0082 | 15.5927 | 4.5208 |

### *3.2 Surface Morphology*

SEM is a convenient and versatile method to study the microstructure of thin film. The surface morphology of CdSe thin film prepared at 333 K is shown in Fig. 2 (a), (b) of magnification 10,000 x. From the micrograph it was speculated that the agglomeration of spherical grains led to the formation of relatively big islands of spherical shape but of different size. Cracks observed on the surface region indicate that the films were less compact on glass substrate, as the kinetics of film formation on the substrate was not uniform. It can be eliminated by increasing the mass thickness of the film.

The cluster size of the CdSe particle was found to be 1.11 μm. Annealing caused the isolation of islands from each other.

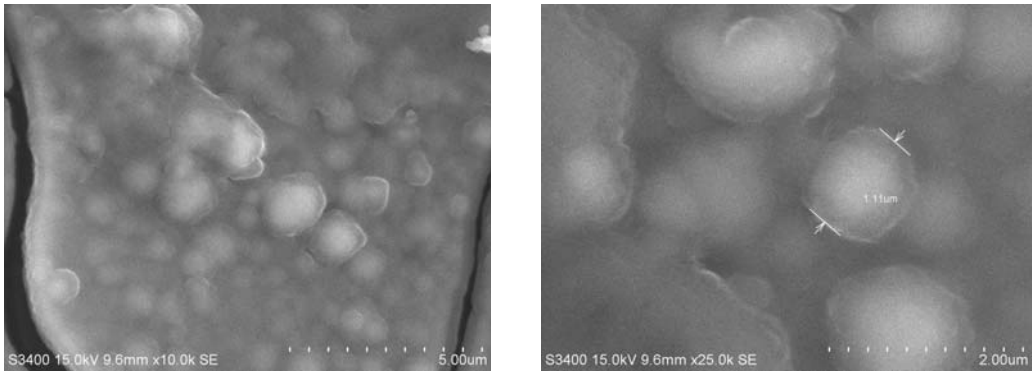


*Fig. 2 (a), (b) Surface Morphology of CdSe thin film (333 K).*

### *3.3 Energy Dispersive X-Ray Analysis (EDAX)*

The quantitative analysis of CdSe films prepared at bath temperature 333 K is shown in Fig. 3. The EDAX pattern confirms the presence of cadmium and selenide compounds. The average atomic percentage ratio of CdSe was found to be 19.57: 3.78 showing that the sample was cadmium rich. Presence of silicon in EDAX is due to the silicon content in glass substrate, since $Na_2SeSO_3$ was used as a source of selenium, a small amount of sodium is present in the film where as sulphur escapes as $H_2S$ or $SO_2$.

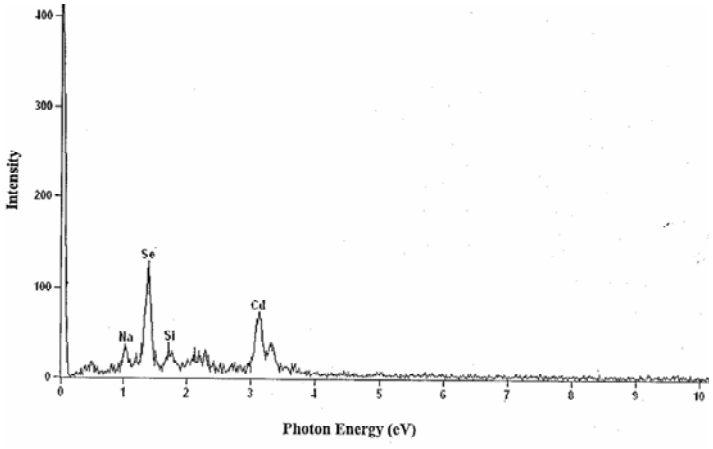


*Fig. 3 Enegry Dispersive X-ray analysis of CdSe thin film (333 K)*

### *3.4 Optical Properties*

The optical transmittance spectra of CdSe thin film is recorded as a function of wavelength in the range 400-1200 nm as shown in Fig. 4 (a). The CdSe material deposited on the glass substrate showed a transmittance of ~60 % for 313 K and is found to decrease as temperature increases along with the film thickness which shows the improvement in crystallinity. A typical plot of $(\alpha h\nu)^2$ with photon energy $h\nu$ for CdSe thin film is shown in Fig. 4 (b). The band gap energy is obtained by extrapolating the straight line portion of the graph to zero absorption coefficient. The intercept on the $h\nu$ axis gives the value of band gap energy. It was found to be 2.12 eV, 1.75 eV and 1.52 eV at bath temperatures 313 K, 333 K and 353 K respectively. The direct band gap energy was found to decrease as temperature increases along with film thickness [16]. These changes are attributed to the crystallite size - dependent properties of the band gap energy.

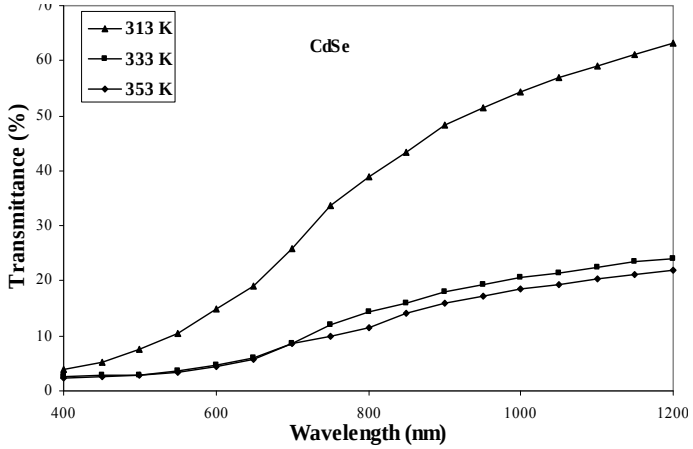


*Fig. 4 (a) Transmittance of CdSe*

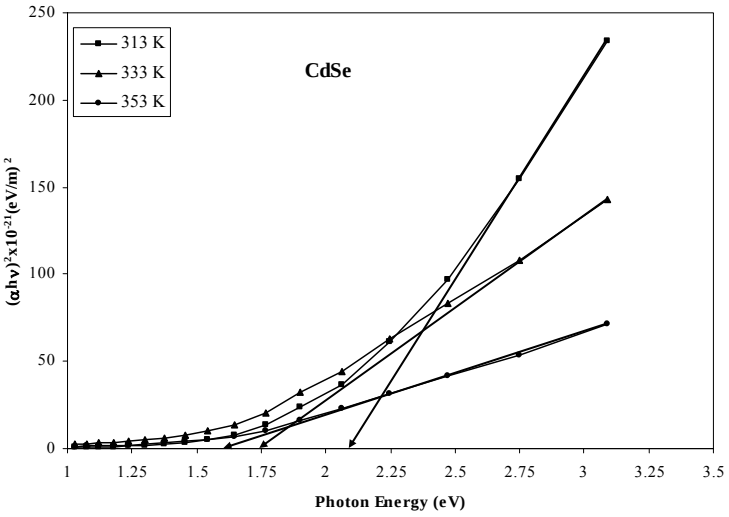


*Fig. 4 (b) Band gap energy of CdSe*

## 4. Conclusions

CdSe thin films were deposited onto glass substrate by simple economical chemical bath deposition technique at bath temperatures 313 K, 333 K and 353 K. XRD pattern confirms the

cubic structure of CdSe thin film. SEM analysis revealed the presence of spherical shaped clusters of size 1.11 μm. The presence of Cd and Se elements were confirmed from EDAX analysis. From the optical analysis the band gap energy was found to lie in the range 2.12 eV - 1.52 eV.

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