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# Synthesis and Characterization of Cadmium Selenide Nanocrystalline Thin Films Prepared Using Novel Chemical Approach

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**Abstract:** Chemical bath deposition, also known as solution growth technique, is presently attracting considerable attention. In this method, when cationic and anionic solution is mixed together and if ionic product exceeds or become equal to the solubility product, precipitation occurs as ions combine on the substrate and in the solution to form nuclei. It is relatively inexpensive, simple and convenience for large area deposition, where the precipitation is controlled through use of suitable metal complexing agents and the amount of anions in the bath is controlled through setting of appropriate chemical equilibrium. Cadmium Selenide thin films were deposited using Chemical bath deposition (CBD) method on glass substrate at room temperature. Characterization was done by x-ray diffraction method, the scanning electron microscope (SEM) and the energy dispersive x-ray analysis (E-DAX). X-ray diffraction study indicates the hexagonal structure. The band gap was found to be 1.82eV. The E-DAX peaks shows the presence of Cadmium, which is much more than Selenium, which implies that the CdSe films are rich in cations.

**Keywords:** Nanocrystalline thin films, Chemical bath deposition, X-Ray diffraction, Scanning electron microscopy.

## 1 Introduction

CdSe is an II-VI binary semiconductor compound. It is a promising photovoltaic material because of its high absorbance coefficient and nearly optimum band gap energy, which is essential for efficient absorption of light and converting it into electrical power. A direct band gap range of 1.65eV to 1.84eV has been reported for the CdSe nanocrystalline material by various authors [1-2]. Among all the metal selenides, CdSe has attracted much attention of many researchers as it finds immense potential in photoelectronic and photovoltaic devices.

Semiconductor devices based on CdSe thin films strongly depend on the structural, optical and electrical properties of the films obtained from various experimental techniques. In recent years, CdSe nanoparticles have been synthesized using different methods such as spray pyrolysis [3], electrochemical deposition [4], molecular beam deposition [5], laser ablation [6], chemical bath deposition [7] and SILAR method [8]. Of these methods, the CBD and SILAR techniques can be used to deposit uniform thin films over large area having complex geometries. These methods do not require any sophisticated and expensive instruments for the deposition of thin films. It is easy to handle, inexpensive and capable of yielding good quality thin films. CdSe thin films grown by using CBD technique have been investigated by number of researchers for their structural, optical and electrical properties. The properties of these films depends on the optimization of various parameters such as chemicals used for the preparation of the films, concentration, pH of the solution, deposition time and temperature. The purpose of this research work is to investigate structural, crystallographic properties, electrical and optical properties of the chemically deposited thin films of CdSe on glass substrate obtaibnbbned at room temperature using the CBD technique.

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## 2 Experimental Details

Thin films of CdSe were deposited on glass substrates using the chemical bath deposition method at room temperature. Glass substrates of commercial quality were used as substrates for the deposition of CdSe thin films. The substrates were first cleaned with HCl, acetone, double distilled water and was ultrasonically cleaned. The cleaned glass slides were placed vertically on the walls of the beaker containing the deposition mixture for the deposition of the film.

A solution of Sodium selenosulphite ($Na_2SeSO_3$) which is used a source of $Se^{2-}$ ions were prepared by the following procedure. Sodium selenosulphite ($Na_2SeSO_3$ ) was prepared by refluxing 5.54 gms of Sodium Sulphite ($Na_2SO_3$) with 0.214gms of Selenium powder in 55ml of double distilled water for 5hrs at 70± 0.5 $^{O}$C.The reaction mixture was prepared by slowly adding 25% ammonia ($NH_3$) solution used as a complexing agent in 0.05M of Cadmium Acetate[$(CH_3COO)_2Cd.2H_2O$] till the solution becomes clear. The pH of the solution was 11.2, which was recorded using a pH meter. The solution was slowly stirred for 5min with the help of a magnetic stirrer. Freshly prepared solution of Sodium selenosulphite was added to the beaker containing the Cadmium Acetate solution and again stirred for 5min. Glass substrates was immersed into the chemical bath solution for a deposition time of 50-60 hrs at room temperature. The bath was colourless at the start but turned orange and then to orange red as time progressed. After deposition, the films were washed with double distilled water to remove the loosely adhered particle and then finally dried in air. The thin film deposited on the glass substrate were orange red in colour, uniform, well adherent to the substrate, smooth and reflecting.

The thickness of the film was calculated by weight difference method using a microbalance. The crystal structure of the sample was studied from the XRD spectra using X-ray diffractometerPW-3710 using monochromatic CuKα radiation (1.5406$^{o}$A) in the range of 2θ from 20-80$^{o}$ at the scan rate of 4$^{O}$/min. The microstructure and surface morphology was analyzed by taking Scanning Electron micrograph using SEM (model S-2400 Hitachi) for different magnifications.

Optical characterization was done by recording absorption spectra of the sample using a double beam spectrophotometer (Hitachi-220). The optical spectra was recorded in the wavelength of 500-900 nm. The electrical resistivity was calculated by using the d.c. two point probe method.

## 3 Reaction Mechanism

Deposition of CdSe thin films takes place only when the ionic product of $Cd^{2+}$ and $Se^{2-}$ ions exceeds the solubility product of CdSe.

$$Se + Na_2SO_3 \rightarrow Na_2SeSO_3$$

Sodium selenosulphite ($Na_2SeSO_3$) in alkaline solution gives $Se^{2-}$ ions as

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

$$HSe^- + OH^- \leftrightarrow Se^{2-} + H_2O$$

When ammonia is added to cadmium acetate 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 and forms the complex cadmium tetra-amine ions,

$$(CH_3COO)_2Cd.2H_2O + 4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+} + CH_3COO)_2^{2-} + 2H_2O$$

Finally, the CdSe thin film formation takes place

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

## 4 Result and Discussion

### *4.1 Structural analysis*

The crystal structure and orientation were studied by X-ray diffraction. CdSe thin films can be in the form of hexagonal (wurtzite) structure or cubic (zinc-blende) structure. The hexagonal state is more stable phase while the cubic is the metastable phase.

Fig.1 shows the x-ray diffractometer of cadmium selenide thin film prepared at a substrate temperature 300K. It reveals the existence of (002), (102), (201) and (202) planes of reflections of hexagonal structure(JCPDS 080459) .The presence of large number peaks shows that the films are polycrystalline .The low intensity peaks observed in the XRD pattern of the sample under study shows that the films are fine crystallites or nanocrystalline in nature. The lattice constants from the

XRD were found to be a=4.299$^0$A and c= 7.01$^0$A.

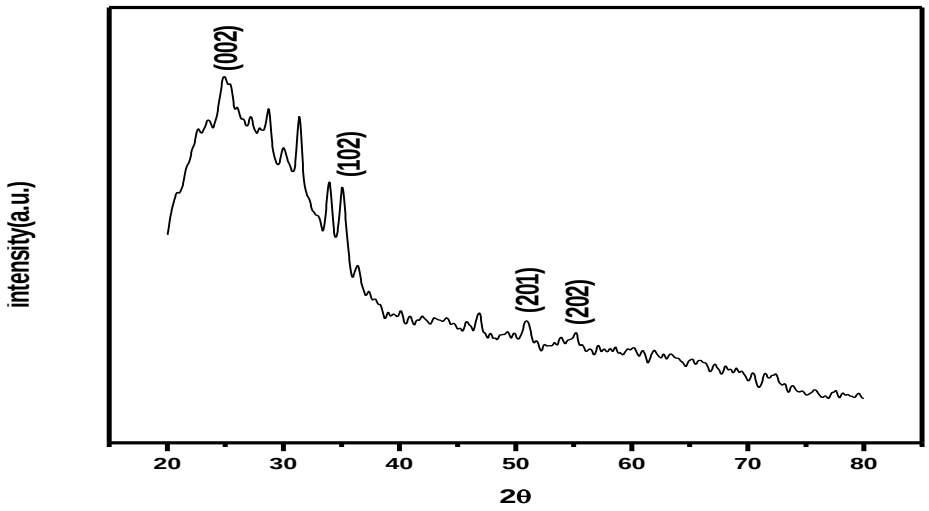


**Fig.1** X-ray diffraction pattern of CdSe thin film (300K).

The average crystallite size of the material was calculated from the XRD data by using the Scherrer's relation [18]

$$D = \frac{0.94\lambda}{\beta cos\theta}$$

Where λ = 1.5406 Aº for CuKα, β is the full width at half maximum (FWHM) of the peak and θ is the diffraction/Bragg's angle. The average crystallite size of the as deposited CdSe thin film was found to be 20.75nm.

## *4.2 Scanning Electron Microscope (SEM)*

The surface morphology of the films was observed by the SEM images.

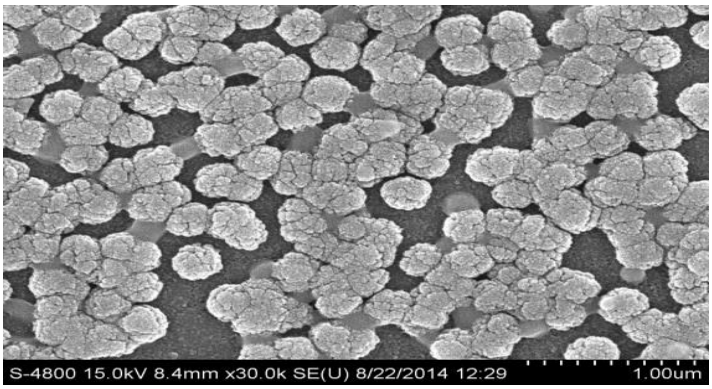


**Fig. 2** The SEM micrographs of CdSe film grown on glass substrate at 300K.

Fig.2 shows the SEM pattern of the CdSe film with deposition time of 50h at 300K. From the SEM micrograph, it is observed that the films were homogeneous, without cracks or holes and covers the entire surface of the glass substrate. Fig. 2 shows the small spherical nano sized grains which indicates the nanocrystalline nature of the CdSe thin films. In addition, the quantitative analysis of the films grownat room temperature was carried out by using the Energy Dispersive X-ray analysis (EDAX). The EDAX was recorded in the energy region 0-14KeV. The atomic percentage ratio of CdSe was found to be 19.28 : 1.99 showing that the content of cadmium is more than that of selenium, which implies that CdSe film is rich in cations. Thus it is an n-type material which can be used as an window layer in photovoltaic cells. The presence of silicon in EDAX is due to the Si content in the glass substrate.

## *4.3 Optical properties*

The thickness of the CdSe film is calculated using the weight difference method assuming the density of the deposited film

to be same as that of the bulk (ρ= 5.816g/cm$^3$ ).

$$t = \frac{m}{A\rho}$$

t is the film thickness, m is the mass of deposited CdSe film and A is the area of the sample. The thickness was found to 1.25μm.

The optical properties of the CdSe films were measured by using UV-visible spectrophotometer at room temperature in the wavelength range 300-1000nm. The band gap was obtained using the following equation coefficient for a semiconductor

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

Where A is a constant, α the absorption coefficient and n is equal to ½ for direct band gap semiconductors. The energy intercept of a plot $(\alpha h\nu)^2$ versus hν (Fig.3) gives $E_g$ for direct transition.

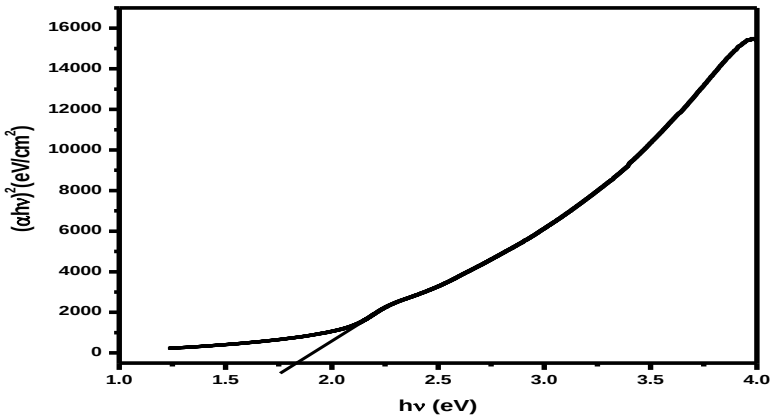


**Fig.3**. Plot of $(\alpha h\nu)^2$ versus hν for CdSe thin film.

The intercept on the hν axis gives the value of the band width of the energy gap.The energy gap is of the order of 1.82eV for CBD grown CdSe thin films, which agrees well with the standard value reported for CdSe by [9,10].

## *4.4 Electrical properties*

It was experimentally established that the thin films of some semiconductor materials was found to have stable structure if they are subjected to a heat treatment. We studied the temperature dependence of the electrical conductivity for CdSe thin films by subjecting heat treatment consisting of heating and cooling cycles within temperature range of 323K to 473K using the d.c. two point probe method. Fig. 4 shows the variation of logarithm of resistivity with reciprocal of temperature ( 1000/T).

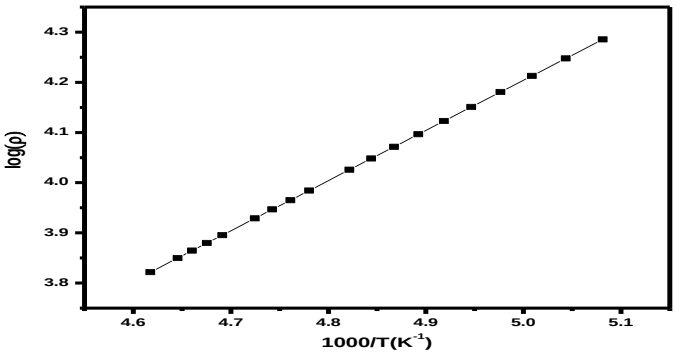


**Fig. 4.** Plot of log ρ vs. (1000/T) for CdSe thin film

It is observed that the resistivity decreases with increase in temperature, indicating the semiconducting nature of the CdSe thin film. The resistivity was found to be in the range of $10^4$Ωcm which is comparable to chemically deposited CdSe film [11]. The high value of the deposited CdSe film on glass substrate maybe attributed to the nanocrystalline nature of the thin film.

## 5 Conclusion

CdSe thin films were deposited on glass substrate by using the chemical bath deposition technique at room temperature.Red-orange colour thin films were formed on the glass substrate. The XRD pattern confirms the hexagonal structure of CdSe film. The presence of Cd and Se elements were confirmed from the EDAX analysis. The SEM micrographs revealed the presence of spherical shaped clusters of size 20.75nm. From the optical analysis, the band gap energy was found to be 1.82 eV.The electrical resitivity is of the order of $10^4\Omega$cm.

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