A comparative study on CdSe synthesized at low temperature

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Abstract. CdSe is a well-known semiconductor which finds applications as photoconductors, photovoltaic cells and other optoelectronic devices. In this paper structural studies and carrier concentration measurements of vacuum evaporated CdSe films obtained by using CdSe synthesized by simple precipitation technique are presented.

Keywords. II–VI semiconductor; CdSe; thin film.

1. Introduction

The II–VI semiconducting compounds viz. sulphides, selenides and tellurides of cadmium find applications as photoconductors (Buragohain and Barua 1987) and electro optical devices (Yukami *et al* 1986). Amongst the chalcogenides, CdSe exhibits maximum photoconductivity. In view of this, CdSe is being actively investigated. Earlier workers synthesized CdSe by several methods (Trekhora 1975; Ostrovskaya *et al* 1976). However, only a few have adopted the direct synthesis method (mixing of both the elements). For laboratory investigations, the most convenient way of obtaining high purity compounds, is by synthesis from elements. In the case of vapour phase reactions, this is usually rather difficult and from many points of view, impractical. On the other hand, synthesis by reaction of the molten elements may be either too slow for practical purposes (Reisman and Birkenblitt 1963) or too rapid (Korneeva *et al* 1960), thus causing detonations. To avoid these difficulties, a novel method was adopted for the first time to synthesize CdSe. The results obtained on evaporated films prepared using the synthesized CdSe are reported in this paper.

2. Experimental

In the present method, CdSe has been obtained by the reaction of a mixture containing cadmium and selenium solvents in the presence of a reducing solution. This technique consists of preparing a reducing solution and also the corresponding elemental solvents. All the chemicals used here are of analytical reagent grade. The reducing solution was prepared from 4 g of tartaric acid, 60 ml of hydrazine hydrate, 30 ml of distilled water and 50 ml of ammonia. 1.12 g of cadmium in 24 ml of 1:4 nitric acid and 0.79 g of selenium in 28 ml of aqua regia were the source for the elemental solvents. The cadmium solution was added first to the reducing solution at 363 K and then the selenium solution was added. A precipitate was formed at the bottom of the flask. This was filtered and washed with distilled water and the process was continued till the pH of the filtrate was found to be neutral. Then again it was washed with hot KOH to remove unreacted selenium. Finally, it was kept at 573 K in argon atmosphere for 5 min. CdSe films were thermally evaporated on cleaned glass and Ti substrates kept at room

temperature. The deposition conditions are summarized below:

Vacuum	10^{-5} Torr
Source temperature	1073 K
Source of substrate separation	12 cm
Deposition time	5 min
Source material	CdSe
Substrates	Glass and titanium

Figure 1. X-ray diffractogram of synthesized CdSe.

For comparison, films were also made by using the commercially available CdSe (M/s Koch-Light, UK).

2.1 Characterization

The possible impurities observed in the synthesized CdSe were estimated using atomic absorption spectrophotometer (AAS) (Perkin-Elmer model 380). Using Jeol JDX model 8030 ($\text{CuK}\alpha$, $\lambda = 1.541 \text{ \AA}$). X-ray diffractograms were recorded. Optical studies were carried out in the wavelength range of 550–800 nm by using Hitachi U-3400 spectrophotometer. The absorbance of the CdSe films for each wavelength can be obtained by using this spectrophotometer. The substrate absorption, if any, was corrected by introducing an uncoated glass substrate of the same size in the reference beam.

The absorption coefficient α is calculated by using the relation

$$\alpha = \frac{2.303 A}{t}, \quad (1)$$

where A is the absorbance value at a particular wavelength and t the thickness of the film. The film thickness is estimated by adopting a nondestructive technique, namely the gravimetric method (Yeh and Blakeslee 1963). Here t for the films are $0.31 \mu\text{m}$ (synthesized CdSe) and $0.309 \mu\text{m}$ (commercial one).

Table 1. Elemental analysis (in ppm).

Material	Tl	K	Na	Fe	Pb	Cu	Zn	As	Co	Ca
CdSe (Prepared)	20	10	9	—	—	—	5	—	—	115
CdSe (Imported)	16	7	5	—	—	—	3	—	—	110

The absorption coefficient α for a band transition between parabolic bands is given by

$$\alpha = \frac{\beta}{h\nu} (h\nu - E_g)^{n/2}, \quad (2)$$

where β is the constant depending upon the transition probability, $h\nu$ the radiation energy and $n = 1$ or 4 depending upon direct or indirect transition, respectively. A

Figure 2. X-ray diffractogram of CdSe films obtained from (a) the synthesized and (b) commercially available CdSe annealed at (1) 300 K (—), (2) 573 K (----) and (3) 623 K (-·-·-).

plot of $(\alpha h\nu)^2$ or $(\alpha h\nu)^{1/2}$ against $(h\nu)$ exhibits a straight line, whose intercept on the $h\nu$ axis is the energy band gap for direct or indirect transition respectively and the slope is β . Impedance measurements were made by using PAR electrochemical analyser for the film deposited on Ti substrates. Measurements on films were carried out after annealing at 473 K in air and argon atmospheres for 5 min in separate experiments. Here a three electrode system with Pt as the counter electrode, CdSe on Ti as the working electrode and SCE as the reference electrode was used. 1 M (Na_2SO_4)

Table 2. Crystallite size of the films.

Film deposited from	Crystallite size ($\text{\AA}$)		
	Film annealed at		
	300 K	573 K	823 K
CdSe (Prepared)	210	215	326
CdSe (Imported)	300	322	626

Figure 3. Mott-Schottky plot for CdSe films annealed at 473 K in (1) air and (2) argon atmospheres.

was used as the electrolyte. DC potential in the range of + 700 to – 200 mV corresponding to the two frequency ranges 1 and 10 kHz was applied to the films (area of the film is 0.15 cm²). Capacitance of the films was computed from the observed values of z'' (imaginary part of the impedance which is equal to $1/(2 \times 3.14 \times \text{frequency} \times \text{capacitance})$).

3. Results and discussion

X-ray diffractogram of the prepared CdSe (figure 1) exhibited almost all the reflections corresponding to single phase hexagonal CdSe. The prominent peaks were observed at $2\theta = 23.9^\circ$, 25.4° , 27.08° , 35.1° , 41.8° , 45.78° and 49.6° having reflections (100), (002), (101), (102), (110), (103) and (112) having reflectivity. The reflections observed in figure 1 are in agreement with ASTM data (ASTM standards). From the diffuse

Figure 4. Variation of α^2 with photon energy ($h\nu$) CdSe films obtained by using (1) the synthesized (●) and (2) commercially available CdSe (○).

reflectance spectra it was observed that the energy band gap value is 1.74 eV. The purity of the synthesized CdSe was examined by AAS and compared with that of the commercial one, as given in table 1. The results shown in table 1 clearly suggest that CdSe prepared in the laboratory is of comparable purity to the commercially available one.

The X-ray diffractogram as grown films and those annealed at 573 and 823 K in air exhibit a peak at $2\theta = 25.1^\circ$ with a preferred orientation in the (002) direction, as shown in figure 2, indicating the preferential growth of crystallites in this direction. It is also seen from figure 2 that while the peak width decreases with annealing temperature, the peak height increases. These results were obtained on the cleaned glass substrate without any application of electrical/magnetic field during deposition. Similar observations were obtained in the case of both close-spaced vapour transport and conventional evaporated CdS films on glass and mica substrates. Using Scherrer's equation (Cullity 1956), the crystallite size for these films was estimated as given in table 2. The variation in crystallite size may be due to the difference in the growth rates of the films. The capacitance of the films was of the order of 10^{-6} F. Using Mott-Schottky relation (Chopra and Das 1983), the curves were drawn between $1/C^2$ against V , as shown in figure 3. From figure 3, it is observed that $1/C^2$ for the air annealed films is less than for the argon annealed films. The carrier concentration was calculated from the slope of figure 3 which was found to be in the range of 10^{21} cm^{-3} . This high value of carrier concentration may be due to the contribution of substrate through micropinholes and microcracks formed in the films during the heat treatment step (Herrasti *et al* 1990). Also the films were found to be *n*-type in nature as seen from figure 3.

Using the optical transmittance measurements, the absorption coefficient α was determined at various photon energies (Dawar *et al* 1990). In order to estimate the energy band gap, the results were plotted between α^2 and $h\nu$, as shown in figure 4. The plot is a straight line for both the films indicating the band gap to be direct. The values are 1.74 and 1.72 eV, which agree well with the values reported by other workers (Masatoshi *et al* 1988).

4. Conclusions

A novel method has been attempted for the synthesis of CdSe and it is of comparable purity to the commercial one. The present method of preparation possesses the following advantages: economically viable, does not involve the use of hazardous hydrogen selenide, impurity levels are very low, does not involve the costly imported selenourea as normally used in other techniques and involves the use of relatively low temperature i.e. 373 K. The films prepared using both the CdSe exhibit identical XRD and optical characteristics.

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