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DEPENDENCE OF BAND GAP ON DEPOSITION PARAMETERS IN CdSe SINTERED FILMS

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II-VI semiconductors form an important class of opto-electronic materials. CdSe is a promising material for the fabrication of photovoltaic devices. Polycrystalline CdSe films have been deposited onto ultra clean glass substrates by sintering process. The optical band gap of these films was determined by reflectance measurements in wavelength range 400-850 nm. The band gap of these films was observed to increase with increase in sintering temperature and sintering time separately. The crystal structure and lattice parameter of these films were determined from x-ray diffractograms. The films were polycrystalline in nature having cubic zinc blende structure.

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Keywords: Sintering, reflection spectra, band gap, x-ray diffractogram, grain size

1. Introduction

II-VI compounds in general and cadmium chalcogenides in particular have created intense scientific and technological interest. They have been investigated from the points of view of basic physics as well as of device technology for various applications. They show a high efficiency of radiative recombination, high absorption coefficients and direct band gaps corresponding to a wide spectrum of wavelengths from ultraviolet to infrared regions [1-4]. Many of these semiconducting compounds form a continuous series of solid solutions that allow the physical properties to be controlled smoothly and the structural parameters to be optimized by changing their molar composition. $Zn_xCd_{1-x}Se$ in thin film form has great potential in the fabrication of superlattice structures [5] and phosphor material for television screens [6]. Thin layers of $CdSe_xTe_{1-x}$ may effectively be used in solar control coatings on glazings of buildings in tropical climate for lowering the interior temperature [7,8]. $A^{II} B^{VI}$ semiconductors have been playing a major role in opto-electronic device owing to their potential applications. This system is a promising material for opto-electronics in the far-infrared region of spectrum and for thermoelectric transducers at medium high temperature [9]. The evaluation of optical band gaps and refractive indices of semiconductors is of vital importance for the design of integrated optic devices such as switches, filters and modulators [10].

The potential of cadmium chalcogenides for low cost photovoltaic power generation has stimulated many efforts around the world to develop such devices. This development has met with many successes in higher efficiency such as device uniformity and reproducibility, large size modules fabrication of stacked junctions to exploit the solar spectrum effectively and cost reduction. CdSe is one of the prominent materials due to its near optimum direct energy gap and high absorption coefficient. It has become interesting and important (with some additives) because of its major contributions to light emitting diodes, solar cells, photodetection, light amplification, lasers, electrophotography and photo electrochemical cells [11-17]. The sintering technique, because of its less complexity and process simplicity is considered to be a versatile technique [18-20]. The aim of present work is to study the variation of optical and structural properties with sintering temperature and time.

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2. Experimental

CdSe films were deposited on ultra clean micro glass substrates by sintering technique [21, 22]. The thickness of the films was measured by a weight difference method and found to be 5 micron approximately. As starting material for CdSe films, we used commercially available CdSe fine powder of 5N purity. In an appropriate amount of cadmium selenide, we added cadmium chloride (10% of the weight of CdSe) as an adhesive and ethylene glycol (few drops) as a binder, and mixed thoroughly. The slurry thus prepared was screen printed on glass substrates, which have been cleaned by soap solution, embry powder, isopropyl alcohol and finally washed with distilled water. The samples thus prepared were dried at 120 ^{0}C for 4 hours in open air. The reason for drying the samples at lower temperature was to avoid the cracks in the samples. The removal of organic materials take place at about 400 ^{0}C. $CdCl_2$ is hygroscopic and its melting point is 568 ^{0}C. However, the evaporation of $CdCl_2$ starts above 400^{0}C. Therefore, sintering temperature can not be less than 400 ^{0}C. To obtain good quality and stable sintered films, the sintering temperature and sintering time were optimized. The films so obtained were sintered at 450, 500 and 550 ^{0}C for 20 minutes separately; and at 450 ^{0}C for 10, 15 and 20 minutes separately; in air ambient in a quartz tube furnace having temperature controller and timer. These sintered films were kept in a dessicator for 24 hours in order to stabilize their behaviour. The uniformity and adhesion of the films were better and no pinholes or cracks were apparent. X-ray diffraction patterns show no peaks of CdSe oxidation. No $CdCl_2$ phase has also been observed.

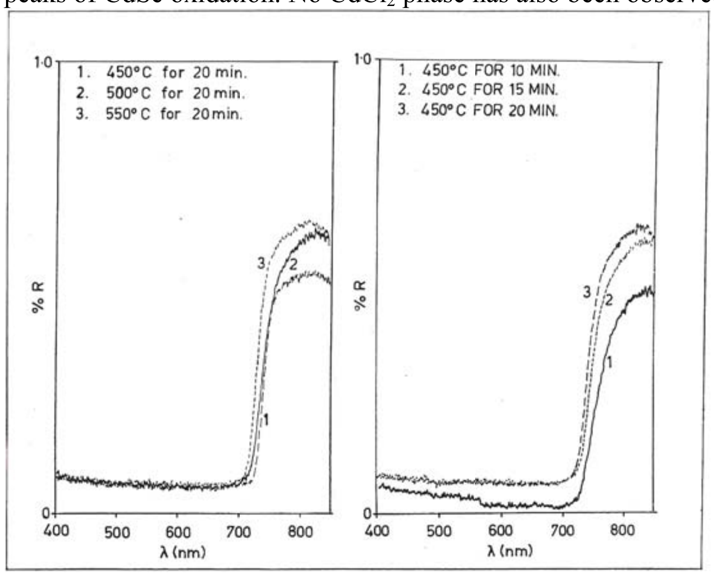

Fig. 1. Reflection spectra of CdSe films sintered at (a) 450, 500 & 550 ^{o}C for 20 min. (b) 450 ^{o}C for 10, 15 & 20 min.

Reflection spectra of the films were recorded at room temperature in the wavelength range of 400-850 nm using UV-VIS-NIR double beam spectrophotometer (Hitachi U 3400). A sample holder was mounted in front of the monochromator, which has two sample positions. The first position has the sample film and the other has a clean glass substrate as a reference. X-ray diffractograms of the films were obtained at room temperature by employing an x-ray diffractometer Philips PW 1140/09. The copper target was used as a source of CuK_{α} radiation with λ = 1.5405 Å. The scanning angle (2θ) was in the range of 20-70^0.

3. Results and discussion

The optical band gap of a film was determined by reflection spectra (optical reflectance versus wavelength trace). According to Tauc relation [23], the absorption coefficient (α) for direct band gap semiconductors is given by

$$\alpha h\nu = A\,(h\nu - E_g)^{1/2} \tag{1}$$

where A is the constant which is different for different transitions and E_g is the band gap. Absorption coefficient may be written in terms of reflectance as [24]

$$2\alpha t = \ln\,[(R_{max} - R_{min})/(R - R_{min})] \tag{2}$$

where t is the thickness of the film and R is the reflectance for any intermediate energy photon (hν). The reflectance falls from R_{max} to R_{min} due to the absorption of light by the material. Variation of $(\alpha h\nu)^2$ versus hν is plotted and the straight line portion of these plots are extended on hνaxis to obtain the values of optical band gap of the samples. Fig. 1(a) represents the reflection spectra of CdSe films sintered at 450, 500 and 550 ^{0}C for 20 minutes in air atmosphere and fig. 1(b) represents the reflection spectra of CdSe films sintered at 450 ^{0}C for 10, 15 and 20 minutes in air atmosphere. It is observed from those figures that reflectance decreases with decrease in wavelength. Sudden fall of reflectance at particular wavelength indicates the presence of optical band gap in these films. In fig. 2(a) & 2(b), we plotted graphs between $[h\nu \ln\{(R_{max} - R_{min})/(R - R_{min})\}]^2$ and hν for the determination of band gaps of above mentioned CdSe sintered films. It has been observed that these plots are linear in the high energy region indicating the band to band direct type of transitions in these films. From fig. 2(a), the value of band gaps come out to be 1.672, 1.686 and 1.714 eV for CdSe films sintered for 20 minutes at 450, 500 and 550 ^{0}C respectively. From fig. 2(b), the value of band gaps come out to be 1.662, 1.666 and 1.672 eV for CdSe films sintered at 450 ^{0}C for 10, 15 and 20 minutes respectively. From fig 1(a) & 2(a), it is observed that as the sintering temperature increases, keeping the sintering time constant, there is the shifting of sharp downfall towards the lower wavelength upto a certain extent, showing the corresponding increase in the band gap of film material. From fig 1(b) & 2(b), it is clear that as the sintering time increases, keeping the sintering temperature constant, there is the shifting of sharp downfall towards the lower wavelength upto a certain extent, showing the corresponding increase in the band gap of film material. It is quite clear that the effect of the variation of sintering temperature on band gap is more than that of sintering time. The increase in band gap of CdSe films with increase in sintering temperature or sintering time may be due to the increase in grain size and hence the improvement in the crystallinity of the films with increase in sintering temperature/sintering time. It may be understood in the following section.

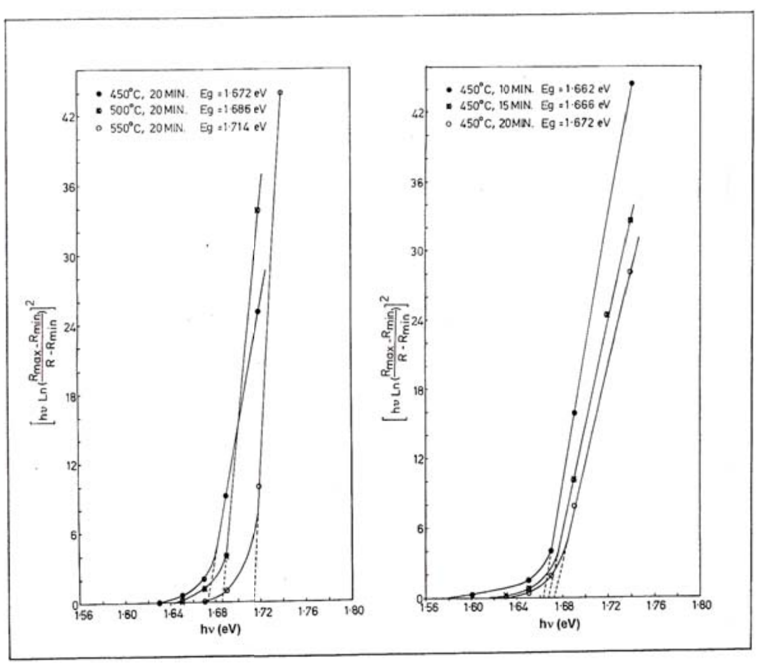

Fig. 2. Band gap determination of CdSe films sintered at (a) 450, 500 & 550 ^{o}C for 20 min (b) 450 ^{o}C for 10, 15 &20 min.

X-ray diffraction patterns of CdSe films sintered at 450, 500 and 550 ^{0}C for 20 minutes are shown in Fig. (3). The presence of sharp structural peaks in XRD patterns confirmed the polycrystalline nature of the samples. The d-values are calculated from the Bragg's relation

$$2d \sin\theta = n\lambda \tag{3}$$

by taking θ-values from the positions of the peaks of XRD (in our case n =1, λ= 1.5405 Å) The experimental d-values are in good agreement with the standard d-values from ASTM card for cubic CdSe confirming the zinc blende structure of CdSe sintered films. The place spacing d and lattice constant a are found to be 2.149Å and 3.039Å respectively for (110) plane corresponding to which highest peak is observed.

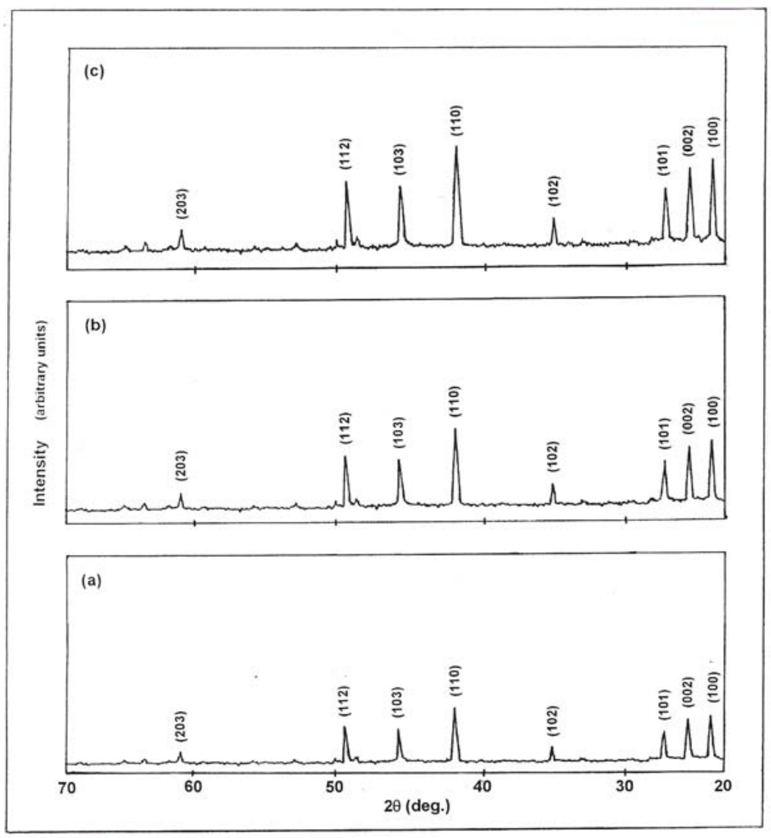

Fig. 2. X-ray diffraction of CdSe films sintered at (a) 450 ^{o}C, (b) 500 ^{o}C, (c) 550 ^{o}C for 20 min

The average grain size (D) of the crystallites can be determined by using well known Scherrer's relation [25]

$$D = K\lambda / B \cos\theta \tag{4}$$

where K (= 0.94) is a constant related to the shape of crystallites and indices of reflecting planes, λ is the wavelength of x-ray radiation, B is the full width at half maximum of the peak (in radian) and 2θ is the angle of diffraction. An increase in the intensity (peak height) was observed with increase in the sintering temperature or sintering time of the films. This increase in intensity strengthens the possibility of improved grain structure. The highest peak (110) was used to calculate the grain size of the films. The average grain size of CdSe films sintered at 450, 500 and 550 ^{0}C for 20 minutes are found to be about 4.8, 5.7 and 7.3 μm respectively. Similarly the average grain size of CdSe films sintered at 450 ^{0}C for 10, 15 and 20 minutes (XRD not shown here) works out to be around 4.1, 4.4 and 4.8 μm respectively.

The crystallite size plays an important role in the optical behaviour of a film. The effect of annealing on the crystallite size and structure is of considerable importance. It is known that in polycrystalline thin films, normal grain growth will result in randomly oriented grains with a grain size of the order of film thickness. As films get thicker, surface energy effects will be less significant and a tendency toward random grain orientation may present. The increase in optical band gap of the films with increase in sintering temperature could be related to the enhancement in crystallite (grain) size leading to a smaller number of grain boundaries. Similar reasons might be expected for increase in band gap with increase in sintering time. But in this case crystallite size does not undergo an appreciable change expect for the fact that it smoothens out irregular boundaries and decreases inter-crystalline spacing. All these observations can be attributed to the better crystalline structure of the films with increase in sintering temperature or sintering time.

4. Conclusions

Cadmium selenide films have been deposited on glass substrates by sintering technique. Sintering is very simple and less expensive technique. The band gap of CdSe films increases with increase in sintering temperature/sintering time. It may be attributed to the enhancement in grain size and hence an improvement in the crystalline structure of the films. CdSe films are polycrystalline in nature and having cubic zinc blende structure. The increase in peak intensity strengthens the possibility of improved grain structure.

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