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## Thickness dependent properties of hot wall deposited CdSe films

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The study of thickness dependent properties of hot wall deposited cadmium selenide (CdSe) films will provide valuable insight in to the material characteristics, because of its multifaceted application. CdSe films prepared under various deposition techniques have been extensively investigated from the standpoint of various potential applications such as photo conductors, solar cells, thin film transistors, gas sensors, acousto optic devices, vidicons, photographic photoreceptors etc. [1–5]. Presently this material has become important because of interest in the optical devices where band gap modulation through alloying has been exploited. For any device application, a detailed knowledge of the dependence of the structural, optical, surface stability and dielectric parameters on thickness along with the deposition conditions is a must. Recently hot wall deposition method has gained importance due to its simplicity, economical viability, growth under thermodynamic equilibrium condition and its contribution for the growth of epitaxial films with smooth surfaces. Keeping above factors in mind CdSe films are deposited by hot wall technique and for first time a summary of various parameters like grain size ( $D$ ), dislocation density ( $\delta$ ), strain ( $\epsilon$ ), band gap ( $E_g$ ), refractive index ( $n$ ), extinction coefficient ( $k$ ), laser damage threshold energy density ( $\alpha$ ), dielectric constant ( $\epsilon'$ ) and composition are determined and its dependence on thickness is presented here as a ready reference.

The hot wall experimental setup used for CdSe (99.999%, Aldrich Chemical Co., USA) films preparation was the same as reported earlier [6]. The main feature of the system was the heated linear quartz tube (0.01 m diameter), which served to enclose and direct the vapor from the source to the substrate. The source, wall and substrates were heated independently. CdSe films were deposited on well cleaned glass substrates under a vacuum of  $5 \times 10^{-5}$  Torr with a vacuum coating unit (Hind Hivac 12A4 model, Bangalore). The source, wall and substrates are maintained around 1000 K, 900 K and 400 K respectively in order to get near stoichiometric films [7]. The structure of the films was analyzed using an X-ray diffractometer (Jeol 8030, using  $\text{Cu K}\alpha$  radiation with  $\lambda = 0.15418$  nm). The composition analysis (EDAX) has been carried out on representative films using JSM 35 CF Jeol model SEM. Thicknesses of the films were determined by gravimet-

ric method using a Metler micro balance. The thicknesses of some films were verified by the calculations from interference patterns in the transmittance spectra.

The optical transmittance spectra are recorded from 400 to 2500 nm wavelength using double beam UV-VIS-NIR spectrophotometer (Hitachi, U-3400) at room temperature with unpolarized radiation. The substrate absorption is compensated by placing an identical substrate in the reference beam.

For laser damage studies a  $1.06 \mu\text{m}$  laser radiation (pulse width, 3 ns; single shot) from a Q-switched Nd-doped yttrium aluminum garnet laser ((Quanta Ray DCR-11) was focused to a diameter of about 1 mm using a convex lens onto the surface of the sample kept away from the focal point of the lens. The detailed experimental procedure has been already reported [8]. Laser energy was measured for each laser pulse using an on-line pulsed laser energy meter (Delta Development) triggered in synchronization with the laser pulse. The damage sites were examined with a metallurgical microscope (Versamet-2, Union 7596, Japan) and the threshold damage location was identified. From the measured energy and the area of the damage, the threshold energy density has been calculated.

The dielectric studies on CdSe films are carried out by forming metal–semiconductor–metal (MSM) structure. CdSe is deposited on the conducting ITO (indium tin oxide) substrate. In the capacitor, ITO acts as bottom electrode and aluminum coated on the surface of CdSe acts as top electrode. The series capacitance and the dissipation factor of the respective films in the frequency range 10 kHz are measured using a Hewlett Packard (4275A) digital multi frequency LCR meter. All the measurements were carried out in a vacuum of  $5 \times 10^{-3}$  Torr.

For the photo-electro chemical measurements a three electrode system with platinum as counter electrode and SCE (saturated calomel electrode) as the reference electrode was connected to an EG & G PARC chemical impedance analyzer (Model 398). A 1 mol.  $\text{Na}_2\text{SO}_4$  solution was used as the electrolyte. The capacitance was measured at 1 KHz while varying the DC potential from  $-200$  to  $1000$  mV.

CdSe films of various thicknesses were deposited onto well-cleaned glass substrates using quartz tube length of 0.15 m. The XRD analysis revealed that the

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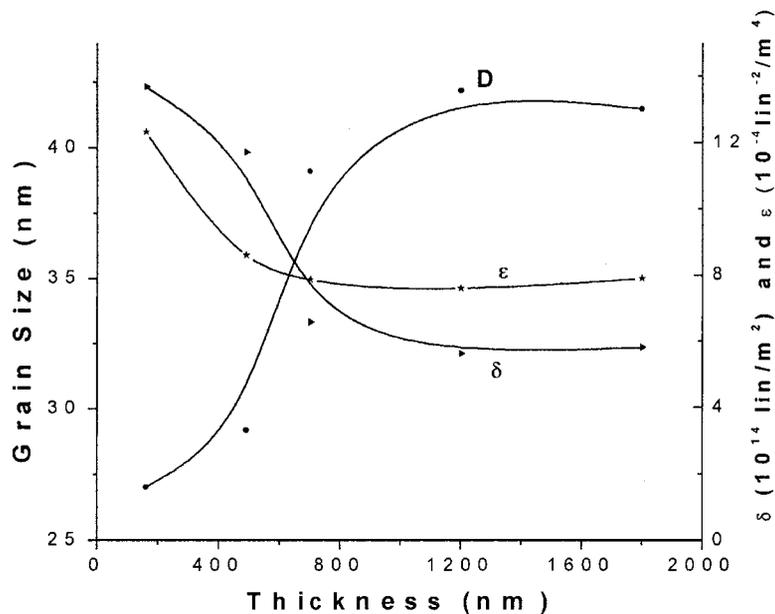


Figure 1 Variation of grain size, dislocation density and strain with thickness.

films are polycrystalline in nature possessing wurtzite structure. The film thickness strongly affects the X-ray diffraction pattern. For lower thickness, the films have random particle orientation, and as the film thickness increases, the (002) diffraction peak becomes more and more dominant [6]. From Fig. 1 it is observed that the crystallite size ( $D$ ) increases but the dislocation density ( $\delta$ ) and strain ( $\epsilon$ ) decreases with increase of film thickness. A similar trend of the dependence of grain size, dislocation density and RMS strain on the thickness has been reported by Pal *et al.* [9] for vacuum deposited CdSe films on glass substrates. When thickness increases the average grain size increases and reaches saturation. Lopez-Otero [10] have reported that the size of grains does not increase indefinitely with thickness but reaches a level where average grain size begins to oscillate with increased thickness and it becomes difficult to analyze experimentally for PbTe films.

A decrease of grain size with increase in the content of cadmium on the basis of composition has been

reported by Dufresne and Brodie [11]. Even one atomic percent increase in cadmium has a significant effect on the crystallite size. In the present investigation at higher thickness we have observed a slight decrease of grain size which needs further detailed investigation. The increase of cadmium content in the films at higher thicknesses has been confirmed from composition analysis. Fig. 2 clearly shows the dependence of composition on the film thickness. It is found that as the thickness increases the cadmium content slightly increases, which would have influenced the crystallite size. Also, since selenium is a low melting point element, there is every possibility that resulting film will be selenium deficient. The sticking coefficients of the elements also contribute to this state of affairs, that is,  $S_{Cd} > S_{Se}$ , where  $S$  is the sticking coefficient [12].

It is found that  $(\alpha h\nu)^{1/2}$  versus  $(h\nu)$  did not lead to straight lines over any part of the optical spectrum, thus supporting the direct band gap (where  $\alpha$  is the

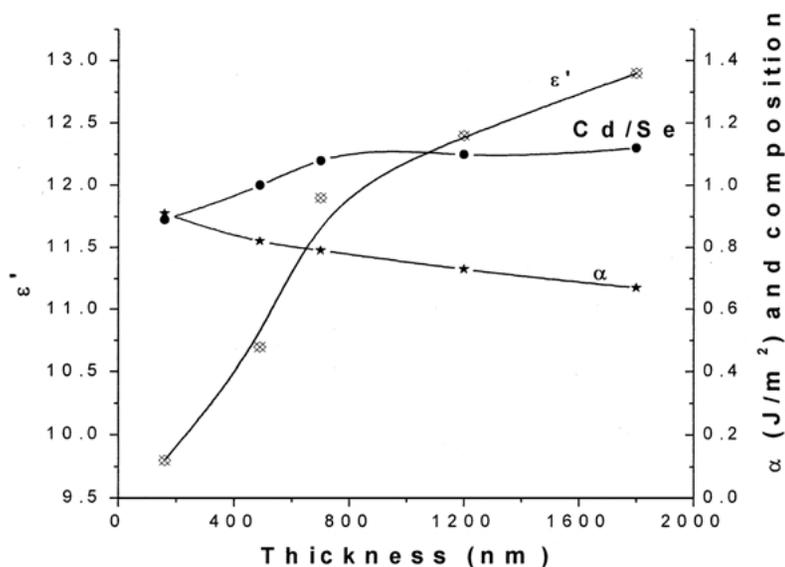


Figure 2 Variation of dielectric constant ( $\epsilon$ ), laser damage threshold energy density ( $\alpha$ ) and composition (Cd/Se) with thickness.

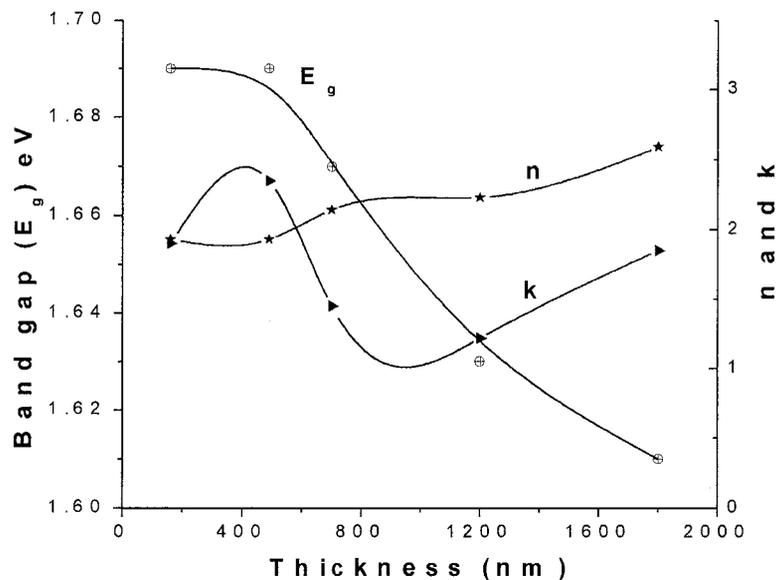


Figure 3 Variation of optical band gap ( $E_g$ ), refractive index ( $n$ ) and extinction coefficient ( $k$ ) with thickness.

absorption coefficient,  $h$  is the Planck's constant and  $\gamma$  is the frequency). The  $(\alpha h \gamma)^2$  versus  $(h \gamma)$  plots for all the films deposited on glass substrates were plotted and the straight line portion is extrapolated to cut the  $x$ -axis which gives the energy gap. The variation of  $E_g$ , refractive index ( $n$ ) and extinction coefficient ( $k$ ) with thicknesses is given in Fig. 3. It is observed that the band gap ( $E_g$ ) decreases with increase of film thickness. Similar observation of decrease in band gap with thickness was reported by Pal *et al.* [9] and Shaalan and Muller [13]. The band gaps  $E_g$  is found to vary from 1.69 to 1.61 eV. Mondal *et al.* [14] have reported band gap  $E_{g1} = 1.69$  eV for CdSe films on glass substrates which coincides with the value of  $E_g$  in the present investigation. The decrease in band gap may be attributed to an increase in particle size and decrease in strain and dislocation density. From Fig. 3 it is seen clearly that the refractive index increases with increase of film thickness and there is no monotonous change in  $k$  is observed. Similar trend is reported by Pal *et al.* [9] for vacuum evaporated CdSe films.

Fig. 2 shows the variation of threshold damage density ( $\alpha$ ) with thickness. It is observed that threshold energy density decreases with increase of film thickness. This can be explained by using the impurity dominated model proposed for dielectric films [15]. In this model a small spherical particle embedded in the material is considered. This impurity absorbs energy from the incident radiation, this absorption produces an increase in the temperature of the particles at that particular point, leading to melting, vaporization or stress fracture of the material around the impurity. Also since the damage studies were carried out in normal atmospheric air, the presence of atmospheric impurities markedly influences the damage threshold values, favoring surface absorption. A similar trend is reported for cadmium telluride [16], cadmium oxide [17], tin oxide and indium tin oxide [17] films deposited by vacuum evaporation. The decrease in threshold damage density with increasing thickness can be explained on the basis of absorption coefficient [8]. The increase in thickness

increases the absorption in the film, that is higher the absorption by the film, lower is the threshold damage density.

An important fundamental property of a semi conducting material is its relative permittivity or dielectric constant ( $\epsilon'$ ). It is observed that the dielectric constant of hot wall deposited CdSe films increases with increase of thickness (Fig. 2). In any vacuum deposited films, the growth processes produce agglomeration and hence porosity in thin films. As the thickness increases the density of voids decreases and hence the dielectric constant increases. When the films become sufficiently thick, the voids disappear and dielectric constant must become independent of thickness. Similar results were reported for other semi conducting materials [18–20]. In the present investigation, the value of dielectric constant varies from 9.8 to 12.9. Berlincourt *et al.* [21] have measured the dielectric constant of high resistivity single crystal CdSe at room temperature and reported the values around 9.7 and 10.65, which almost coincides with the results in the present investigation. Brodie and LaCombe [22] have estimated the real part of dielectric constant for high resistivity CdSe films and have reported a value of 10 at 240 K.

From the easy direction of current flow and using the thermal probe method the as deposited films are found to be  $n$ -type. The flat band potential and donor density can be determined from the change in the dark capacitance as a function of applied potential using the well known Mott-Schottky relation. A plot of  $C^{-2}$  versus the electrode potential yields a straight line with the slope containing the information on carrier density. The influence of substrate temperature on the flat band potential and carrier concentration for a 500 nm thick hot wall deposited CdSe films is already reported [23]. The flat band potential and carrier concentration of a typical CdSe film of thickness around 500 nm at room temperature were found to be  $-1.4$  V (with respect to a SCE) and  $1.73 \times 10^{18} \text{ cm}^{-3}$  respectively. These values are in good agreement with the reported values of vacuum deposited and electrodeposited CdSe films [24].

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