

## Grain size dependent optical band gap of CdI<sub>2</sub> films

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**Abstract.** The thermally evaporated stoichiometric CdI<sub>2</sub> films show good *c*-axis alignment normal to substrate plane for film thickness up to 200 nm. The optical absorption data indicate an allowed direct interband transition across a gap of 3.6 eV in confirmation with earlier band structure calculations. However, part of the absorption data near band edge can be fitted to an indirect band gap of 3 eV. The dependence of band gap on film thickness (> 200 nm) can be explained qualitatively in terms of decreasing grain boundary barrier height with grain size.

**Keywords.** Optical properties; thin films; halides.

### 1. Introduction

The cadmium iodide is a layer structured compound with a hexagonal unit cell, in which each hexagonal sheet of Cd atoms sandwiched between two similar sheets of I atoms, the Cd atoms being octahedrally coordinated (Hulliger *et al* 1976). The stacking of these three sandwiched sheets form the three-dimensional compound. CdI<sub>2</sub> is a well known polytype material having as high as 200 polytypes out of which only very few are commonly occurring (Trigunayat 1991). The possibility of different stacking sequences of three layer sandwiches along the third direction due to the weak bonding between layers leads to polytype structure. The reported studies on CdI<sub>2</sub> concerning structure and optical properties are scattered. The optical absorption measurements carried out on single crystal samples were fitted to an indirect gap of 3.2 eV (Greenaway and Nitsche 1965) and many subsequent reports indicate an indirect band gap of similar values (Lee *et al* 1969; Takemura *et al* 1975). However, the band structure calculations show the presence of both direct and indirect band gaps, the difference between the two is only about 0.3–0.6 eV (McCanny *et al* 1977; Bordas *et al* 1978; Robertson 1979; Coehoorn *et al* 1985; Pollini *et al* 1986). The electronic structure determined by optical reflectivity on CdI<sub>2</sub> crystals shows allowed direct transition of 4.3 eV at 30 K and forbidden direct transition of 3.8 eV at 300 K (Pollini *et al* 1986). However, there are very little studies on CdI<sub>2</sub> films regarding their optical properties (Brahms 1965; Nakagawa *et al* 1987; Kondo *et al* 1994, 1998a). Therefore, we thought it worthwhile to carry out the optical studies on CdI<sub>2</sub> films in order to understand the material better as it is a basic

isostructural compound to many halides and chalcogenides.

### 2. Experimental

The CdI<sub>2</sub> thin films were grown on glass substrates at room temperature by thermal evaporation using a molybdenum boat at a pressure better than 10<sup>-6</sup> Torr. The starting material was analar grade powder, which was pelletized for evaporation. The quartz crystal thickness monitor was used for monitoring the film thickness during evaporation. Uniformity and thickness of the film was subsequently checked and confirmed by DEKTAK IIA surface profiler. The deposition rate was slow (2–4 nm/s) as higher deposition rates led to nonuniform film growth and low sticking. Films up to 100 nm were completely transparent and become translucent for higher thicknesses. The films of thickness below 50 nm were nonuniform, discontinuous and above 600 nm peel off the substrate. Small pieces of 0.5 × 0.5 cm were cut for various measurements so as to carry out various analyses on the same film. The structural studies of the films were carried out by X-ray diffraction analysis (PHILIPS X-Pert model PW-1830 generator diffractometer). The film composition was found to be stoichiometric as determined by EDAX (JEOL-840). The optical absorption measurements were carried out in UV/VIS region using Shimadzu UV-260 spectrophotometer.

### 3. Results and discussion

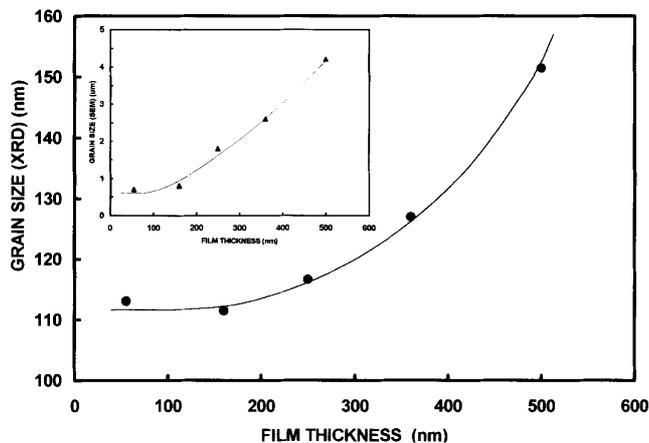
All CdI<sub>2</sub> thin films grown at room temperature were polycrystalline and stoichiometric (as per X-ray diffraction and EDAX analysis) irrespective of the film thickness.

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However, the earlier report (Yu 1967) on the structure of CdI<sub>2</sub> films shows that thinner films (< 100 nm) are amorphous and thicker films tend to crystallize, while as per Kondo *et al* (1998b), the CdI<sub>2</sub> films grown at substrate temperature < 300 K are amorphous and those either grown or annealed above 300 K are polycrystalline. Our X-ray diffraction data is in agreement with ASTM No. (12–574) and with the earlier report (Bringans and Liang 1981). The XRD analysis shows a high degree of orientation with the basal plane parallel to substrate and *c*-axis normal to substrate plane as indicated by the total absence of (001), (101) or (111) reflections. Earlier studies (Yu 1967; Bringans and Liang 1981) have also observed this kind of *c*-axis alignment in CdI<sub>2</sub> films. However, a small amount of (111) reflection and other non zero 1-reflections were observed for higher film thicknesses than 160 nm. This indicates a slight misalignment among the grains. We have determined the average grain size from the full width at half maximum (FWHM) of the most intense peak using the Scherrer formula (Cullity 1978) as a function of film thickness as shown in figure 1. The inset of figure 1 shows for comparison the grain size dependence on thickness as determined by SEM.

The optical absorption measurements were carried out on a large number of samples of various thicknesses. Figure 2 shows some representative optical absorbance curves as a function of wavelength for different thicknesses. The wavy nature of the absorbance away from the fundamental absorption edge is due to the interference fringes arising from the substrate–film and film–air interfaces. The fringes smoothen out as film thickness increases. The steep rise in the absorbance near the absorption edge hints at a direct type transition. The absorption coefficient *a* was calculated by

$$a = (2.303A)/t, \quad (1)$$



**Figure 1.** Grain size variation with thickness of CdI<sub>2</sub> films determined from the full width at half maximum of most intense X-ray diffraction peak using Scherrer formula. Inset shows similar variation as determined from scanning electron graph.

where *A* is the absorbance and *t* the film thickness, neglecting the reflection coefficient, which is negligible and insignificant near the absorption edge. The dependence of *a* on *hn* near the band edge is shown in figure 3 for 250 nm thick film. In a crystalline or polycrystalline material both direct or indirect optical transitions are possible depending on the band structure of the material. Assuming parabolic bands, the relation between *a* and *E<sub>g</sub>* for a direct transition is given by (Mott and Davis 1979)

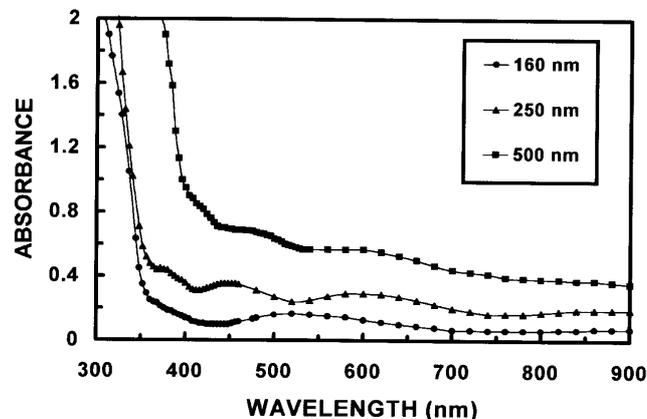
$$ahn = \text{constant} (hn - E_g)^n, \quad (2)$$

and for indirect transition by (Mott and Davis 1979)

$$ahn = \frac{A(hn - E_g + E_p)^n}{\exp(q_D/T) - 1} + \frac{B(hn - E_g - E_p)^n}{1 - \exp(-q_D/T)}, \quad (3)$$

where *E<sub>p</sub>* is the phonon energy assisting the transition, *q<sub>D</sub>* the Debye temperature and *A*, *B* are constants. For a direct transition *n* = 1/2 or 3/2 depending on whether the transition is allowed or forbidden in quantum mechanical sense. Similarly, *n* = 2 or 3 for indirect allowed and forbidden transition respectively. The usual method of determining band gap is to plot a graph between (*ahn*)<sup>1/*n*</sup> and *hn* and look for that value of *n* which gives best linear graph in the band edge region. Obviously, there will be a single linear region in direct transition and two linear portions in indirect transition as can be seen from (2) and (3). We plotted (*ahn*)<sup>1/*n*</sup> vs *hn* for CdI<sub>2</sub> films for various thicknesses and the best fit was obtained for *n* = 1/2 indicating a direct allowed transition as shown for 250 nm thick film in the inset A of figure 3.

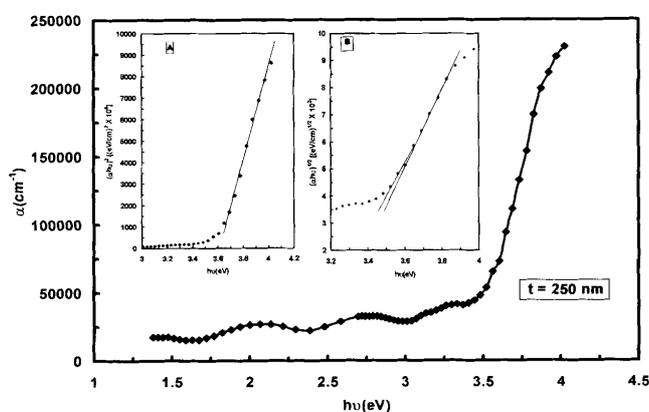
In earlier reports (Greenaway and Nitsche 1965; Lee *et al* 1969), the absorption data on single crystals were fitted to *n* = 2 to obtain an indirect gap of 3.2 eV by the plot of (*a*)<sup>1/2</sup> vs *hn*. Using their data of *a* vs *hn*, we have found that the best fit is obtained for *n* = 1/2, i.e. a direct transition. A peak corresponding to a direct band to band tran-



**Figure 2.** The optical absorption spectra for different thicknesses of CdI<sub>2</sub> films.

sition (at room temperature) has been identified in the reflectivity spectra at 3.8 eV (Greenaway and Nitsche 1965) and at 4.3 eV (at 30 K) (Pollini *et al* 1986). The energy band structure calculations (McCanny *et al* 1977; Bordas *et al* 1978; Robertson 1979; Bringans and Liang 1981; Coehoorn *et al* 1985; Pollini *et al* 1986) clearly show the existence of both direct and indirect band gaps of similar magnitudes, the difference between the two is about 0.3–0.6 eV. However, the band structure (Coehoorn *et al* 1985) and band gaps (Slater 1956) of CdI<sub>2</sub> are shown to be insensitive to its polytypes. Therefore, we can realize that both indirect and direct band gaps exist in CdI<sub>2</sub> and they are separated by just 0.3–0.6 eV. Since indirect gap is just less than direct gap, it lies near the onset of direct gap and can hardly be noticed in  $(ahn)^2$  vs  $hn$  plot of much dominated direct transition. Therefore, the part of the optical absorption data near the knee or tail of the direct absorption edge have to be replotted as  $(ahn)^{1/2}$  vs  $hn$  to determine indirect gap as shown in the inset B of figure 3. However, we still believe that the optical absorption data reveals clearly a direct band gap showing the best fit to  $n = 1/2$ . Thus determined value of  $E_g$  (indirect) agrees well with earlier experimental results as well as band structure calculations. Our value of  $E_g$  (direct) of 3.6 eV determined for thicknesses  $\leq 250$  nm agrees well with the predicted value of 3.8 eV from band structure calculations.

However, both types of band gaps showed thickness dependence as shown in figure 4. In general, thickness dependence of band gap can arise due to one or combined effect of the following causes: (i) a large density of dislocations, (ii) quantum size effect and (iii) the change in barrier height due to change in grain size in polycrystalline films. However, first one looks reasonable cause in the present case with small contributions from dislocation density as well. As the thickness of the films in the present study is quite large, the quantum size effect can completely be ruled out. The decreasing band gap with grain

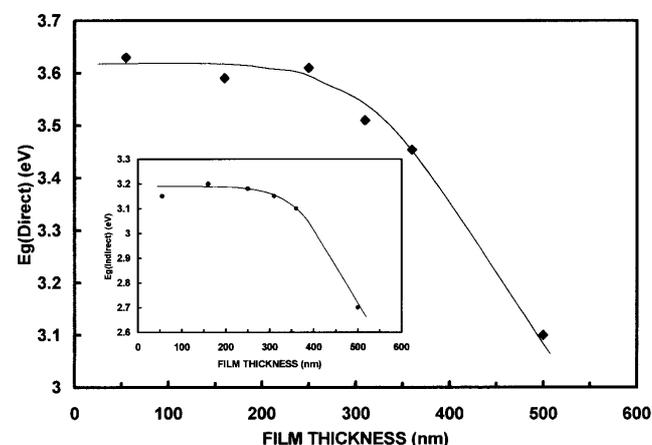


**Figure 3.** The absorption coefficient  $\alpha$  as a function of  $hn$ . The inset A shows  $(ahn)^2$  vs  $hn$  plot for the determination of  $E_g$  (direct) while inset B shows  $(ahn)^{1/2}$  vs  $hn$  plot for the determination of  $E_g$  (indirect).

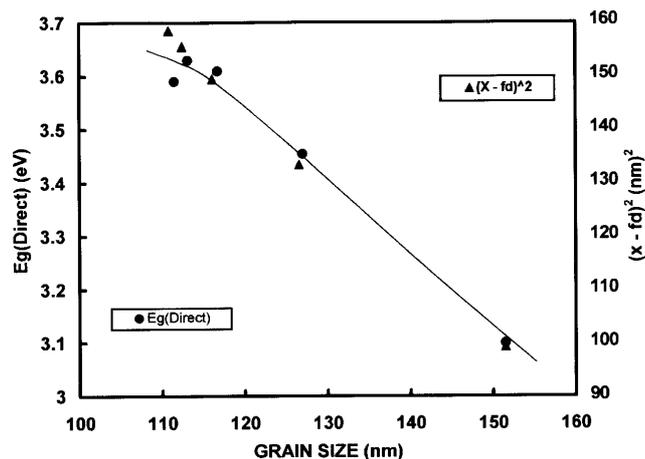
size as shown in figure 5 is exactly similar to its thickness dependence and indicates the decreasing barrier height with increasing grain size. The variation of grain boundary barrier height with grain size is given by (Slater 1956)

$$E_b = E_{b0} + C(X - fd)^2, \quad (4)$$

where  $E_{b0}$  is the original barrier height,  $C$  is a constant depending on the density of charge carriers and dielectric constant of the material,  $X$  the barrier width (20–30 nm),  $d$  the grain size and  $f$  is a fraction of the order of 1/15 to 1/50 depending on the charge accumulation and carrier concentration. We can estimate the change in barrier height as a function of grain size in CdI<sub>2</sub>. We take  $X = 20$  nm as the average barrier width,  $f = 1/15$  considering the low carrier concentration of CdI<sub>2</sub> and the grain size as a function of thickness from figure 1. Thus, the calculated variation factor  $(X - fd)^2$  as a function of grain size is compared qualitatively with the experimentally observed band gap variation with grain size in figure 5. The striking agreement indicates the dominance of barrier height contribution to the observed band gap variation with thickness. The band gap variation with either thickness or grain size is nominal for film thickness  $< 250$  nm. This could be due to the better  $c$ -axis alignment of the grains as observed in XRD for these thicknesses. As film thickness becomes larger, the misalignment among the grains starts leading to grain boundary structure. Therefore, the data for higher thickness agree better with the behaviour of grain boundary barrier height with grain sizes. It can be noted that the only earlier study focussed on the structure of films was carried out in the range 5–100 nm and showed good  $c$ -axis alignment with which our results agree very well. Therefore, we can clearly realize that the thickness dependence of optical band gap is dominated by the grain size dependence of grain boundary barrier height for film thicknesses  $> 200$  nm.



**Figure 4.** Thickness dependence of  $E_g$  (direct). Inset shows similar dependence of  $E_g$  (indirect).



**Figure 5.** The grain size dependence of band gap along with the estimated grain boundary barrier height variation factor  $(X - fd)^2$  with grain size.

#### 4. Conclusions

The cadmium iodide films show good *c*-axis alignment normal to substrate plane for film thicknesses up to about 200 nm and a slight misalignment sets in for higher thicknesses as observed by XRD. The optical absorption data fit best to direct band to band type transition indicating a direct band gap in conformity with band structure calculations. However, a smaller indirect band gap can also be determined from part of absorption data near the band edge for the purpose of comparison with earlier analyses of absorption data as well as the band structure calculations. The decreasing band gap with film thickness can be attributed to the grain size dependent grain boundary barrier height, at least for film thickness > 200 nm, consistent with XRD analysis.

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