The Study of Optical Band Gap of CdI_2 Films

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In this paper thin film of CdI_2 were grown on glass substrate at room temperature, elevated temperature by thermal evaporation at a vacuum of about 10^{-6} Torr using molybdenum boat. The optical absorption measurements were carried out in UV/VIS region using a (Shimadzu UV-260) spectrometer. The absorption coefficient α is calculated. The thickness of film (t) vs Energy bad gap (Eg) of CdI_2 is studied. Studies show both direct and indirect nature of band gap in conformation with existing theoretically calculated band structure in literature.

Keywords: thermal evaporation, Absorption coefficient, Energy bad gap.

1. INTRODUCTION

Cadmium Iodide is an important compound having a layered structure with a hexagonal unit cell, which is a common structural type in many dihalides and MX_2 type dicohalcogenides. The basic structure consists of an infinite hexagonal sheet of Cd atoms sandwiched between two similar sheets of I atoms. These three sheet sandwiches are then stacked to from the three dimensional compound. CdI_2 is a well-known material having a number of poly types as high as 200 out of which only very few are commonly occurring. The possibility of three layer sandwiches along the third direction due to the weak bonding (van be Waals) between layers leads to various poly type structure. Absorption measurements carried out on single-crystal samples were fitted to an indirect energy gap of 3.2 eV while the reflectivity spectra reveal a direct transition at 3.8 eV. However, the band structure calculations show the presence of a direct band gap and a slightly smaller indirect band gap, the difference between the two is only 0.3 – 0.6 eV. Even after various studies. CdI_2 continues to be puzzling and interesting. Studies on CdI_2 continue to be puzzling and interesting. Studies in CdI_2 films regarding structure and optical properties are quite limited [1-10].

2. EXPERIMENT

The films of CdI_2 were grown on glass substrate at room temperature and elevated temperature by thermal evaporation at a vacuum of about 10^{-6} Torr using a molybedenum boat. The starting material was fine grade powder, which was pelletized for evaporation [1,2]. The film thickness was monitored by a quartz crystal thickness monitor during evaporation. The optical absorption measurement were carried out in UV/VIS region using a (Shimadzu UV - 260) spectrometer.

The structural and physical properties of CdI_2 films seem to depend on growth process as mentioned about at different ranges of deposition rate. This could be mainly due to its

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polytypsim nature. Among all the polytypes, 4H type is the most stable form followed by 2H type.

3. OPTICAL PROPERTIES

These are various ways in which light interact with mater e.g. absorption, reflection, scattering, emission etc. The study of optical properties of solids proved to be a powerful tool in our understanding of the electronic and atomic structure of these materials.

3.1. Ultra Violet-Visible (UV-VIS) Spectroscopy

This is the spectroscopic method to measure absorption spectra which are primarily due to light absorption resulting from the excitation of electrons or molecules [3,4]. The basic of quantitative absorption measurement is provided by the Bouguer Lambert-Beer law according to which the transmitted light intensity through a non-reflecting medium is given as

$$I = I_0 e^{-\alpha t} \tag{1}$$

Where I_0 is the incident intensity, t and α are the thickness and absorption coefficient of the medium respectively. Absorption coefficient is a measure of the energy attenuation or loss as it travels through the medium. However, if the medium is also partiality reflective then

$$I = I_0 \frac{(I-R^2)e^{-\alpha t}}{1-R^2 e^{-\alpha t}} \tag{2}$$

The velocity of light in a medium of refractive index ‘n’ can be determine by

$$v = \frac{c}{n} \tag{3}$$

Where ‘c’ is the velocity of light vacuum. However, if the medium is an absorbing one, the velocity of light in the medium becomes complex and the corresponding complex refraction index n^* is defined as

$$n^* = n + ik \tag{4}$$

where k the absorption index. The absorption coefficient α is related to the absorption index by

$$\alpha = \frac{2\omega k}{c} \tag{5}$$

The major sources of absorption in solids are its electrons [5,6]. The optical absorption of the films were recorded using Shimadzu UV/VIS spectrometer (model UV 260), which like most of the spectrometers, measures I_0 and I simultaneously. Since films were grown on glass substrate, the substrate absorption was corrected by the instrument's computer interface, taking measurements with reference to another similar glass slide. The absorbance is related to absorption coefficient for a non reflecting medium from equation (1) as

$$\alpha = \frac{2.303A}{t}\log_{10}\left(\frac{I_0}{I}\right) = \frac{2.303A}{t} \tag{6}$$

For a reflecting film in the region of strong absorption (small R and large α) near the fundamental absorption edge, α can be calculated by

$$\alpha = \frac{2.303A}{t} + \frac{4.606log_{10}(1-R)}{t} \tag{7}$$

Normally, R is very small near the absorption edge and therefore the second term in equation is neglected in determination of optical energy gap [7,8].

3.2. Optical Band Gap

The major sources of absorption in solids are (1) band-to-band transition (2) excitation (3) imperfections and (4) free carries. However, band to band transitions that can occur at the fundamental absorption edge of crystalline semiconductors, direct or indirect, depending upon the position of conduction band minima (CBM) with respect to the valence band maxima (VBM) K-space.

$$\Delta E = E_{gap} = E_{photon} = hv \tag{8}$$

It is possible however, for the two extrema (CBM and VBM) to occur at different points in K-space. An electron making transition from VBM to CBM is said to be making an indirect transition of the energy and the momentum. Conservation in such a transition can be explained by the emission or absorption of a photon (i.e. process involves a simultaneous interaction with lattice vibration [9]. The conservation of energy is given by

$$\Delta E = hv_{photon} \pm hv_{photon} \tag{9}$$

Where hv_{photon} is the energy of photon that is absorbed (plus sign) or emitted (minus sign) simultaneously with the absorption [10,11].

In a crystalline or polycrystalline material the nature of optical transition (direct or indirect) near the absorption edge can be determined by the relation between α and the optical energy gap E_g. Assuming the bands to be parabolic in nature the absorption coefficient in direct transition is related to the band gap by

$$\alpha_{\mathrm{hv}} = const.(hv - E_g)^n \tag{10}$$

And for indirect transition by

$$\alpha_{\mathrm{hv}} = \frac{\mathrm{A(hv-E_g+E_p)^n}}{\mathrm{exp}\left(\frac{\theta_D}{T}\right)-1} + \frac{\mathrm{B(hv-E_g-E_p)^n}}{1-\mathrm{exp}\ (-\theta_D/T)} \tag{11}$$

where E_p is the photon energy and θ_D is the Debye temperature. For small photon energies only second term contributes. Values that *n* can take are

n = ½, for direct allowed transition

n = 1/3, for direct forbidden (in quantum mechanical sense) transition.

n = 2, for indirect allowed transition

n = 3, for indirect forbidden transition.

The usual method for calculating band gap is to plot graph between $(\alpha_{\mathrm{hv}})^{1/n}$ and *hv* and look for the value of *n* which gives best linear graph. The value of *n* will decide the nature of the energy gap or transition involved as mentioned above. In case of direct band gap metrical the graph shows a single linear portion (as in equation 10) which is extrapolated to determine E_g (the *x*-intercept). Indirect bad gap materials show two linear portions of different slopes in $(\alpha_{\mathrm{hv}})^{1/n}$ versus *hv* plot (equation 11) giving two intercepts, viz (E_g - E_p) and (E_g + E_p) from which E_g can be determined.

We have carried out optical absorption/transmission measurement on a large number of samples of CdI_2 films. Some representative optical absorbance curves as a function of wavelength are shown for films of different thickness in Figure 1. 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 [12].

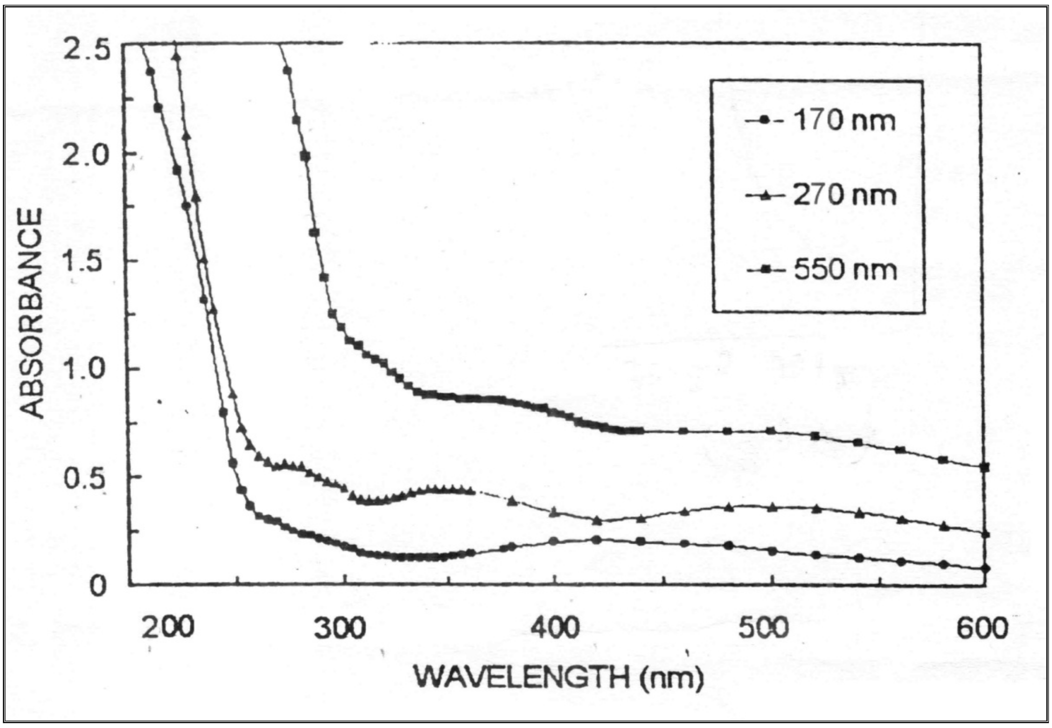

Fig. 1: The optical absorption spectra of CdI_2 films of different thickness.

It can be seen the figures that these fringes smoothen out as films thickness increases. The fringe pattern is much more pronounced in transmission spectra [12]. The step rise in the absorbance near the absorption edge hints a direct type of transition. The absorption coefficient α was calculated by

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

Where A is the absorbance and t is the film thickness, neglecting the reflection coefficient, which is insignificant near the absorption edge. Dependence of α on $h\nu$ near the absorption edge is shown in figure 2 for a 170 nm thick film.

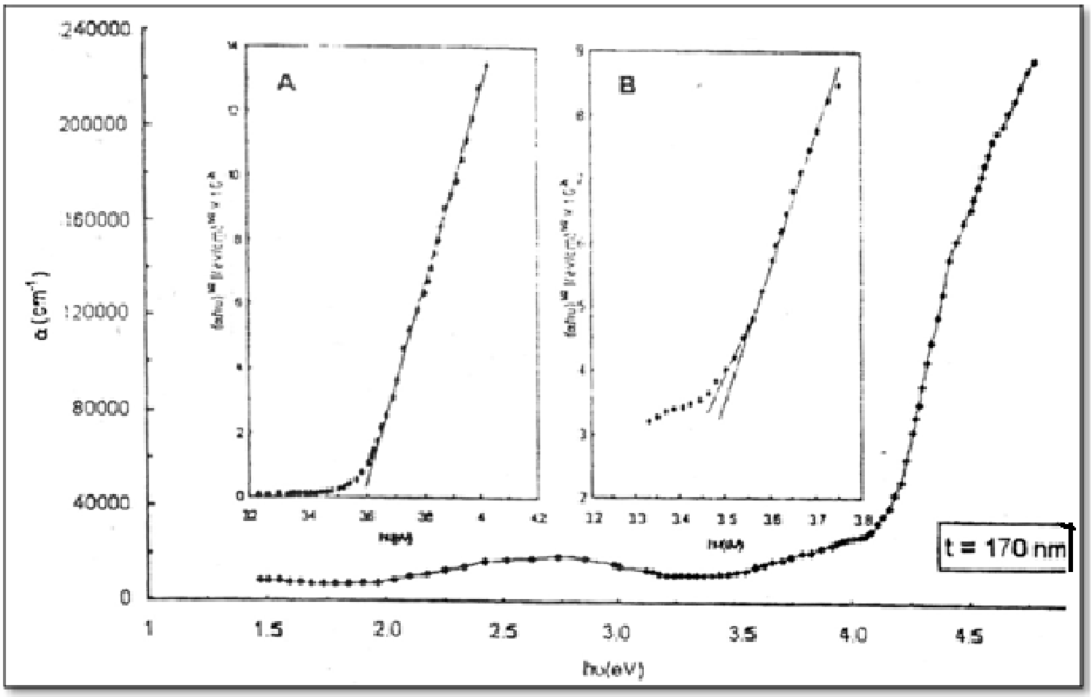

Figure 2: The absorption coefficient α as a function of *hv.* The inset A shows $(\alpha_{\mathrm{hv}})^2$ versus *hv* plot for the determination of E_s (direct) white inset B shows $(\alpha_{\mathrm{hv}})^2$ versus *hv* plot for the determination of E_g (Indirect).

We have plotted $(\alpha_{\mathrm{hv}})^{1/n}$ versus *hv* for CdI_2 films of various thickness and the best fit was obtained for *n* = ½ indication a direct type of allowed transition as shown in the inset A of Figure 2.

Since indirect gap is just less than the direct gap, it lies near the onset of direct gap and can hardly be noticed in $(\alpha_{\mathrm{hv}})^2$ versus *hv* plot of much dominated direct transition. Therefore, part of the optical absorption data near the knee or tail of the direct absorption edge have to be re-plotted as $(\alpha_{\mathrm{hv}})^2$ versus *hv* to determine indirect gap as shown in the inset B of Figure 2. We have plotted $(\alpha_{\mathrm{hv}})^2$ versus *hv* for the sake of comparison with the reported values of E_g (indirect) in the literature. However, we still believe that the optical absorption data reveal clearly a direct energy gap showing the best fit to *n* = ½. Thus determined valus of E_g (indirect) agrees well with earlier experimental results as well as band structure calculations. Our values of E_g (direct) of 3.7 eV determined for films of thickness ≤ 260 nm agree well with the predicted value of 4.0 eV from band structure calculation [13]. The thickness dependence of E_g (eV) is shown in Figure 3.

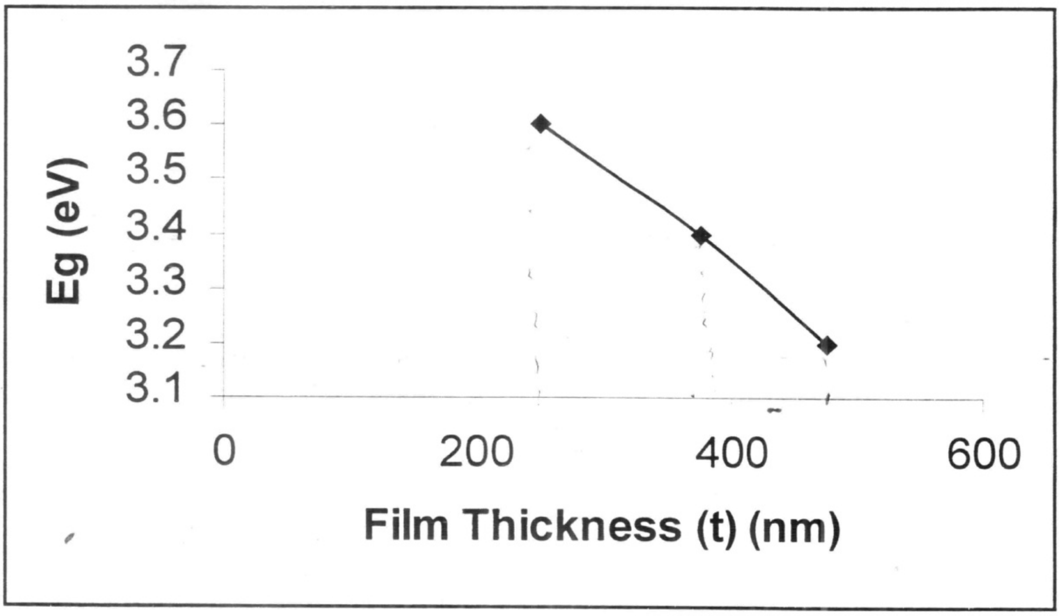

Fig. 3: The thickness dependence of E_g of CdI_2 Films.

CONCLUSION

The CdI_2 films grown by thermal evaporation, show both direct and indirect nature of band gap in confirmation with the existing theoretically calculated band structure in literature. The thickness dependence of Eg as observed in the present study needs to be explored further for better understanding.

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