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Size- and temperature-control optical direct/indirect band tuning in layered compounds: band gap engineering

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Abstract: The X-ray diffraction (XRD) is studied in thermally evaporated cadmium iodide (CdI₂) thin films with various thicknesses. The grain size, calculated from the XRD, is found to increase with increasing the thickness of the film, while the reflectivity and refractive index decrease with increasing the wavelength of the exciting light. The optical absorption spectra show both allowed direct and indirect interband transitions across a fundamental gap in CdI₂. It is found that both indirect and direct band gap (E_g) decrease with increasing the thickness of the film and that the indirect E_g is lower than the direct E_g by an amount of about 0.7 eV. The direct E_g is also decreased with increasing both the grain size and temperature. However, the temperature dependence of E_g follows the Varshni relation. Our results highlight the possibility of engineering or tuning the E_g of CdI₂ by controlling the thickness of the film, grain size as well as temperature.

Keywords: Layered compounds; Band gap engineering; E_g

1. Introduction

Cadmium iodide (CdI₂) is one of the group IIB iodides and typically dihalides as MX₂. This is an important compound having a layered structure with an infinite hexagonal

sheet of Cd atoms sandwiched between two similar sheets of I atoms. The Cd atoms are octahedrally coordinated to constitute the basic layer by a strong covalent bonding within *ab*-plane forming a sheet like structure and these sheets are arranged along the third direction *c* to form a three-dimensional solid. A weak van der Waals bonding between these sheets leads to polytype structures having a number of polytypes, as many as 200 [1].

CdI₂ is a wide-band gap semiconductor having optical band gap (E_g) near a weak insulator and with highly anisotropic chemical bonds. [2]. Band structure calculations for CdI₂ have shown [3-5] large anisotropy of the space charge density distribution causing high anisotropy of optical spectra and the presence of a direct E_g and a slightly smaller indirect E_g . CdI₂ is central symmetric or centrosymmetric in the bulk. However, the anisotropic behaviour of CdI₂ makes it polar, so a strong electron-phonon interaction is expected. This favours the local noncentrosymmetry for the observation of the second harmonic generation (SHG) in CdI₂ nanostructures [6-8]. The role of photo-induced electron-phonon anharmonic interactions in SHG was explored [9].

The thermoluminescence and photoluminescence studies revealed that this material processes higher order optical nonlinearity [10-14]. Materials exhibiting higher order optical nonlinearities have received much attention due to their potential in applications such as optical switching, amplification and limiting [15]. The ferroelectric was studied by Kityk et al. [16]. This is most probably the first extensive study on CdI₂ thin films.

These interesting structural and nonlinear optical properties of CdI₂ make it a better candidate for the intensive studies [17]. The various aspects of the layered compounds have thus been investigated for the better understanding and advancing new device ideas. Band gap engineering is a powerful technique for the design of new semiconductor materials and devices [18,19]. In this process, the transport properties of electrons and holes could be independently and continuously tuned for a given application or device (e.g. photomultiplier). The experimental demonstration on the band gap engineering of layered hexagonal SnSe₂ nanostructured thin films by varying the thickness was first

given by Mukhokosi et al. [20]. They showed that for a 50-nm thick film, the band gap E_g is about 2.04 eV, whereas E_g is approximately 1.2 eV for the bulk or 1200-nm thick film. Their study highlights the possibility of engineering the band gap of layered CdI₂ by controlling the thickness of the films. In a recent study, CdI₂ thin films were grown by chemical bath deposition and their crystalline structure and linear optical properties including optical band gap were controlled by changing the pH of the chemical bath at room temperature [21]. Dependence of E_g on residual stress in ZnI₂, CdI₂ and HgI₂ films was also studied [22]. However, studies focusing on the optical band gap and its related properties are quite limited for CdI₂ thin films. As the new generation of devices with unique capabilities is emerging from this approach, it would be worthy to carry out a systematic and intensive study on this issue in CdI₂ thin films. Here, in the present investigation, we study the dependence of the direct and indirect E_g on grain size, film thickness and temperature. In addition, we also study the reflectivity and refractive index of the films as function of wavelength of the exciting light.

2. Experimental

One of the convenient methods to grow group IIB iodides is thermal evaporation. Thin films CdI₂ were grown on glass substrates at room temperature by evaporation using a molybdenum boat. The typical glass substrates were 2.5 cm × 5 cm sizes. The starting material was high purity (99.99%) analar grade powder that was palletized for evaporation. All the CdI₂ films used in this study were grown at the vacuum of 10⁻⁶ Torr. The film thickness was monitored by a quartz crystal thickness monitor during evaporation and subsequently confirmed by DEKTAK IIA surface profiler measurements. The structural study was carried out by X-ray-diffraction (XRD) analysis (PHILIPS, Model PW-1830). The film composition of the as grown films was found to be stoichiometric. However, no significant deviation from stoichiometric film composition was observed for heat-treated films or films grown at substrate temperatures up to a couple hundred °C. The optical absorption measurements were carried out in the UV-Visible region using a Shimadzu UV-260 spectrophotometer. For the low temperature measures the samples were mounted in a liquid nitrogen temperature-regulated cryostat. The temperature of the sample may be varied between 80 and 300 K.

3. Results and discussion

We studied XRD and determined grain size (D) and film thickness (L). We carried out measurements on a large number of samples. As there existed a number of XRD and TEM/SEM based structural, compositional and morphological studies on this material in the literature [19,20], we are not interested to report them here. We only focus on the XRD data which are relevant to the objectives of the present study. The grain size D of the material was calculated using the well-known Debye-Scherrer formula [23]

$$D = \frac{0.9\lambda}{H \cos \theta}, \quad (1)$$

where H is the half width of XRD lines, λ is its wavelength and θ is the half diffraction angle (i.e. Bragg angle) of 2θ . Film thickness was obtained from the relation $L = D^3 N$, where N is the number of crystallites per unit area. Grain size D as a function of film thickness L is shown in Fig. 2. As can be seen, D increases with increasing film thickness. As can be seen the grain size varies from 110 nm to 160 nm for the film thickness 50 nm to 550 nm. The dislocation density (S) can also be obtained from the relation $S = 1/D^2$.

We performed optical absorption and reflectance measurements on a large number of samples with different thicknesses. Figure 3 insert shows the reflectance (r) as a function of λ for a film of thickness $L = 360$ nm. As can be seen, r decreases with increasing λ and a maximum value of about 20% is obtained for the higher frequency. The refractive index (μ) was calculated using the relation [24]

$$\mu = \frac{1+r}{1-r} + \sqrt{\frac{4r}{(1-r)^2} - \left(\frac{\alpha\lambda}{4\pi}\right)^2}, \quad (2)$$

where α is the absorption coefficient and is related to the extinction coefficient (β) as $\beta = \alpha\lambda / (4\pi)$. The refractive index as a function of wavelength is shown in Fig. 1, where

μ decreases with λ . The refractive index varies from 2.1 to 2.6 for wavelength $\lambda=700$ nm to 250 nm.

For the direct type of transition, the conduction band (CB) minimum and the valance band (VB) maximum is in line on the energy (E) scale in the E - k diagram, where $k = 2\pi / \lambda$ is the wave vector (Fig. 3). However, it deviates for the phonon-assisted indirect transition, as there are phonons involved in the process. Therefore, the band gap E_g is the energy difference between the CB minimum and VB maximum, or the energy difference between the CB and VB at $k = 0$.

The absorption coefficient α was calculated from $\alpha = 2.303A / L$, where A is the absorbance, neglecting the reflection which is insignificant near the absorption edge. The optical absorption shows both allowed direct and indirect interband transitions across a fundamental gap confirming the results of the earlier band structure calculations for the optical direct and indirect band gap E_g in CdI₂ thin films. Figure 4 shows a typical absorption spectrum of the material, where the dependence of α on E_λ is plotted near the absorption edge. Here $E_\lambda = h\nu = hc / \lambda$ is the of excited photon energy. In crystalline materials and for parabolic bands, as shown in Fig. 3, the optical transitions (either direct or indirect) can be evaluated by the relation between α and E_g . For the direct transition

$$\alpha E_\lambda = C_1 (E_\lambda - E_g)^p \quad (3)$$

and the indirect transition [25,26]

$$\alpha E_\lambda = \frac{C_2 (E_\lambda - E_g + E_{ph})^p}{\exp(\Theta_D / T) - 1} + \frac{C_3 (E_\lambda - E_g - E_{ph})^p}{1 - \exp(-\Theta_D / T)} \quad (4)$$

where C_1 , C_1 and C_1 are fitting constants, Θ_D is the Debye temperature, E_{ph} is the phonon energy assisting the indirect transition, and for a direct (indirect) type of transition $p = 1/2$

or $3/2$ ($p = 2$ or 3) depending on whether the transition is allowed or forbidden. The optical band gap E_g of CdI₂ thin films was estimated from Tauc plot. The Tauc technique of determining E_g is to plot a $(\alpha E_\lambda)^{1/p}$ versus E_λ graph and look for that value of p which gives the best linear fit in the absorption. For an allowed transition $p = 1/2$ ($p = 2$) for a direct (indirect) type. As can be seen from Eqs. (3) and (4), there will be one (two) linear region(s) for the direct (indirect) transition. We plotted $(\alpha E_\lambda)^{1/p}$ versus E_λ for the films of various thicknesses and discovered both type of allowed transitions. Figures 5 and 6 show the results. A linear fit to the data of the higher wavelength region of the graph gives a direct E_g as an intercept of the vertical axis (Fig. 5). Similarly, two lines fitted to the data of the low and high wavelength regions of the graph gives the indirect type E_g (Fig. 6). Figure 7 shows the dependence of E_g on L for the direct and indirect transitions. As can be seen, the optical band gap E_g for both direct and indirect types varies with the thickness of the film. This variation looks like quadratic in nature. The direct (indirect) E_g is found to vary from about 3.05 to 3.65 eV (2.50 to 3.20 eV) for the variation of film thickness from 400 nm to 5.5 μ m. This variation consists well with that for the other layered hexagonal SnSe₂ nanostructured thin films [20]. The increase of E_g with L may be attributed to the formation of crystal defects, which can produce localized states that change the effective Fermi level due to an increase in carrier concentrations [14,26]. Tyagi et al. [22] studied the variation of E_g of CdI₂ thin films, grown on glass substrate, with residual stress parameter and showed that there exists a threshold tensile stress above which E_g decreases linearly. They found a direct E_g of 3.60 eV for the film. The possible optical transition in these films was found to be allowed direct transition with the E_g decreasing from 3.76 to 3.57 eV with increasing the film thickness [27]. Our values agree well with these. A slight decrease of our values might be responsible for the growth conditions which affect the formation of the defects. This could reduce the concentration of localized states in band structure. However, the band gap E_g for the indirect transition is lower than that of the direct transition by an amount of ~ 0.7 eV, which is due to the phonon assisted transition. The dependence of E_g on D for the direct transition is shown in Fig. 8. For the higher D , the dependence is seen to be linearly decreasing with increasing D . The observed variation, almost similar to the thickness dependence, might be due to the defect densities either line defects (e.g. dislocation) or planar defects [28].

Figure 9 shows the dependence of E_g on the temperature T for the direct transition. The dependence is modeled by the Varshani relation [29]

$$E_g(T) = E_g(0) - \frac{aT^2}{b+T}, \quad (5)$$

where $E_g(0)$ is the band gap at $T = 0$ K, and a and b are temperature independent constants. In Fig. 9, we also plot Eq. (3) using the parameters' values for the material. The plot shows the experimental data agrees well with the Varshani relation and E_g decreases with increasing T . This is because of band-shifting effect at higher temperature, supporting earlier investigations [30]. This study shows a way of tuning the band gap in layered structured cadmium iodide compounds by controlling the temperature and film thickness/grain size.

4. Conclusions

CdI₂ thin films with various thicknesses were grown by thermal evaporation and studied by XRD. Optical band gap E_g and its related properties were determined. The grain size was found to increase with increasing the thickness of the film, while the reflectivity and refractive index decreased with increasing the wavelength. The optical absorption spectra showed both allowed direct and indirect interband transitions across a fundamental gap. It was found that both indirect and direct E_g decrease with increasing thickness of the film and that the indirect E_g was lower than the direct E_g , confirming the results of the earlier band structure calculations. The direct E_g was also decreased with increasing both grain size and temperature. The temperature dependence of E_g , however, followed the Varshni relation. The findings resulting from this investigation suggest the possibility of tuning and engineering the E_g of CdI₂ by controlling the thickness of the film, grain size as well as temperature. The results are discussed in comparison with those in the literature.

Conflicts of interest

The author declares no conflicts of interest.

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Figure 1. Grain size as a function of film thickness measured from XRD. Calculation details are given in the text.

Figure 2. Refractive index as function of wavelength of the exciting light λ for a film of thickness $L = 360$ nm. Insert show the dependence of reflectivity on λ .

Figure 3. Direct (left) and phonon-assisted or indirect (right) band gap E_g as a function of the wave vector k . E_g is the energy difference between the conduction band (CB) minimum and the valance band (VB) maximum, or the energy difference between the CB and VB at $k = 0$. In indirect E_g , the phonon involvement is indicated by a wave.

Figure 4: A typical absorption spectra. The absorption coefficient α was calculated from the absorbance and the film thickness.

Figure 5: A plot of $(\alpha E_\lambda)^2$ versus E_λ with $E_\lambda = h\nu = hc / \lambda$. Line is a linear fit to the data of the higher wavelength region of the absorbed photon energy curve.

Figure 6: A plot of $(\alpha E_\lambda)^{1/2}$ versus E_λ . Lines are linear fits to the data of the low (solid) and high (dashed) wavelength regions of the curve.

Figure 7: Dependence of E_g on L for the direct and indirect transitions between parabolic bands.

Figure 8: Dependence of E_g on D for the direct transition. For the higher D , the dependence is linear.

Figure 9: Dependence of E_g on T for the direct transition. The solid line is a fit to the data by the Varshni relation.