

Temperature dependence of photocurrent and optical band gap in CdIn₂Te₄ single crystals

Kwangjoon Hong*

Department of Physics, Chosun University, Kwangju 501-759, Korea

Single crystals of p-CdIn₂Te₄ were grown by the Bridgman method without using seed crystals. From photocurrent measurements, it was found that three peaks, A, B, and C, correspond to the intrinsic transition from the valence band states of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$ to the conduction band state of Γ_6 , respectively. Crystal field splitting and spin orbit splitting were found to be at 0.2360 and 0.1119 eV, respectively, from photocurrent spectroscopy. The temperature dependence of the CdIn₂Te₄ band gap energy was given by the equation $E_g(T) = E_g(0) - (9.43 \times 10^{-3})T^2/(2676 + T)$. $E_g(0)$ was estimated to be 1.4750, 1.7110, and 1.8229 eV at the valence band states of A, B, and C, respectively. The band gap energy of p-CdIn₂Te₄ at room temperature was determined to be 1.2023 eV.

Key words: CdIn₂Te₄ single crystal, Photocurrent spectroscopy, Crystal field splitting, Spin orbit splitting, Band gap energy.

Introduction

Cadmium indium telluride (CdIn₂Te₄), which has the chalcopyrite structure¹ with space group $S^2_4-I4_2$, is an attractive material because it is practically applicable to electro-optical devices.²⁻⁵ For these applications, it is of primary importance to grow high quality crystals and to characterize the fundamental material parameters such as the band gap and its temperature dependence. However, so far few studies of the temperature dependence of the band gap of CdIn₂Te₄ have been published.^{6,7} Generally, absorption experiments are used to measure the band gap energy.⁶ However, the band gap energy obtained from this method is known to be inaccurate because of the difficulty in defining the position of the absorption edge. Therefore, photocurrent (PC) measurements are frequently used to overcome these difficulties in controlling the data after the absorption experiments are completed. In these PC measurements, the PC peak position obtained corresponds to the direct band energy. Here, the absorbed photons with higher energy than the band gap energy create the electron and hole carriers. Consequently, the PC peak corresponding to the band gap energy flows out through the electrodes. Moreover, the electronic transitions from the levels of the valence band to the levels of the conduction band are restricted by a selection rule based on the symmetry point in the Brillouin zone.⁸ For this reason, the curve of the spectral peak corresponding to the principal absorption edge shows a steep slope.

Also, the PC measurement gives us information on the valence band splitting together with the band gap energy. The valence band is split according to the symmetry of the crystal. The energy states of the split valence band have a certain symmetry. The transitions between these states are polarized because of the effects of the crystal field and the spin orbit splitting. Therefore, it can be seen that the degeneracy of both the p and d orbitals is partially lifted. These states participate in the PC process, extending the photo-response to a higher energy side. Such an effect has been predominantly observed in copper-based ternary semiconducting compounds, which are analogs of II-VI or III-V compounds.

In this study, single crystals of p-CdIn₂Te₄ were grown by the Bridgman method without seed crystals. We also present the results of the temperature dependence of the p-CdIn₂Te₄ band gap energy obtained through PC spectroscopy. The valence band splitting for electronic transitions restricted by a selection rule is also discussed.

Experimental Procedure

Single crystals of p-CdIn₂Te₄ were grown in a three-stage vertical electric furnace by applying the Bridgman method. Prior to the growth of a p-CdIn₂Te₄ single crystal, polycrystalline CdIn₂Te₄ was used as a source material. A sealed ampoule filled with polycrystalline CdIn₂Te₄ without a seed crystal was placed in the middle position of the three-stage vertical electric furnace. The top, middle, and bottom temperatures of the furnace were gradually increased to 700, 900, and 350 °C, respectively, these temperatures were maintained

*Corresponding author:
Tel : +82-62-230-6637
Fax: +82-62-234-4326
E-mail: kjhong@mail.chosun.ac.kr

for 48 hours to keep the CdIn_2Te_4 in a uniformly molten state. This ampoule with a spire tip was then pulled down at a speed of 0.75 mm/h using a speed-control motor, and the growth temperature at the spire position was 715 °C. The detailed growth procedures have been published elsewhere.⁹ From Hall effect measurements, the carrier density and the Hall mobility of the p- CdIn_2Te_4 single crystal were obtained, and they were $8.61 \times 10^{17} \text{ cm}^{-3}$ and $2.42 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{s}$ at 300 K, respectively, but these values were found to be $1.01 \times 10^{15} \text{ cm}^{-3}$ and $2.64 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{s}$, at 10 K, respectively.

For the PC spectroscopic measurements, CdIn_2Te_4 cleaved off along the (110) plane was used. After electrodes on both ends of the sample were made, wires were connected to these electrodes. Then, the sample was mounted on a holder in a low-temperature cryostat. The PC spectral measurements were carried out when the samples were illuminated by monochromatic light emitted from the light source of a halogen lamp passed through a chopper. The monochromatic light was polarized parallel to the c-axis of the (110) plane. The measurement temperature was varied from 10 to 300 K.

Results and Discussion

Photocurrent spectra

Figure 1 shows the PC spectra of a p- CdIn_2Te_4 single crystal at temperatures ranging from 10 to 300 K. The electrons excited from the valence band to the conduction band by the absorbed photons flowed immediately out of the electrodes. Consequently, only the PC peaks corresponding to the band gap are detected. This band-to-band transition PC peak has been known as the intrinsic transition.^{10,11} As shown in Fig. 1, the PC spectrum at 300 K shows two peaks: one at 1033.4 nm (1.1998 eV) and the other at 863.4 nm (1.4360 eV). The peak at 1.1998 eV is the A peak. This peak is

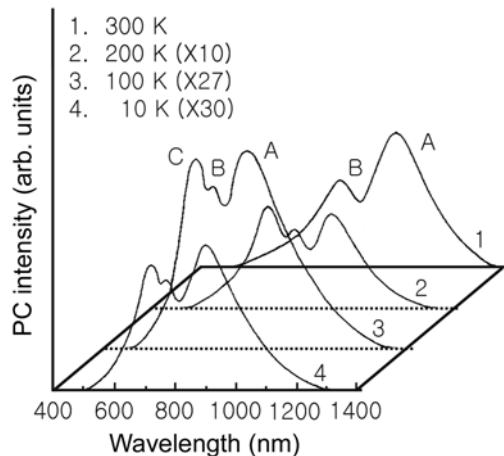


Figure 1. PC spectra of p- CdIn_2Te_4 single crystals obtained at temperatures ranging from 10 to 300 K.

ascribed to the electronic transition from the $\Gamma_7(\text{A})$ of the valence band to the Γ_6 of the conduction band. Likewise, the peak at 1.4360 eV is the B peak. This peak is associated with the electronic transition from the $\Gamma_6(\text{B})$ of the valence band to the Γ_6 of the conduction band. The PC spectra obtained from temperatures ranging from 10 to 250 K show three peaks. The peaks at 10 K, especially, are located at 842.8 nm (1.4711 eV), 726.3 nm (1.7071 eV), and 681.6 nm (1.8190 eV). The two peaks at 1.4711 and 1.7071 eV correspond to peaks A and B, respectively. The peak at 1.8190 eV is labeled the C peak. This peak is ascribed to the electronic transition from the $\Gamma_7(\text{C})$ of the valence band to the Γ_6 of the conduction band. However, only two peaks are observed in the PC spectrum at 300 K. This is related to the scattered electrons in the valence band. It has been known that electrons in the conduction band are scattered owing to the mutual interaction between electrons when the carrier concentration of the sample is high.¹² The carrier concentration of a p- CdIn_2Te_4 single crystal obtained from the Hall effect measurement was 10^{17} cm^{-3} at 300 K. This concentration is not high enough to be compared with other semiconductors. But, there is some scattering probability in our sample between the split valence band levels such as $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$. When the temperature is low, the scattering probability of the carriers is lower than that at 300 K since the carriers in the valence band are in a frozen state. Consequently, the spectra containing peaks A, B, and C are seen only at the low temperature. Also, the smooth slope at the long wavelength side of the spectra shown in Fig. 1 seems to be an evidence of the homogeneity of the composition in the crystal.

Valence band splitting

Figure 2 shows the energy band structure of CdIn_2Te_4 at the Γ point based on the selection rule.¹³ This figure shows that the conduction band of the s-like state has a Γ_6 symmetry, and that the valence band of the p-like state is split into three double degenerate states such as $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$. The $\Gamma_7(\text{A})$ is the uppermost valence band. The effective mass in the $\Gamma_7(\text{A})$ depends considerably on the direction of k . The $\Gamma_6(\text{B})$ is the middle band. The $\Gamma_7(\text{C})$ is the lowest valence band. Generally, the crystal field of the ternary compound has been observed by reflectance and photoconductivity measurements.¹⁴⁻¹⁷ In this study, the valence band splitting of CdIn_2Te_4 owing to the crystal field was observed by using PC measurements. The crystal field splitting, Δ_{cr} , is the energy difference between $\Gamma_7(\text{A})$ and $\Gamma_6(\text{B})$. The value obtained is 0.2360 eV from the energy difference between peak A, 842.8 nm (1.4711 eV), and peak B, 726.3 nm (1.7071 eV), at 10 K. This is almost an order of magnitude larger than those of II-VI analogues.¹⁸ The spin orbit splitting, Δ_{so} , is the energy difference between $\Gamma_6(\text{B})$ and $\Gamma_7(\text{C})$. This value

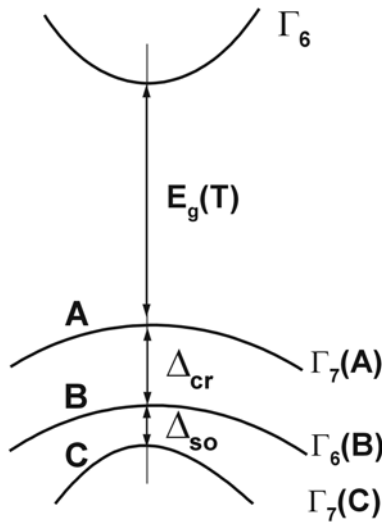


Figure 2. Energy band structure of the chalcopyrite CdIn_2Te_4 at Γ point according to the selection rule.

is determined to be 0.1119 eV from the energy difference between the B peak, 1.7071 eV, and the C peak, 1.8190 eV, at 10 K. The split gap energies between the three peaks at several temperatures are coincident to the values of 0.2360 and 0.1119 eV, respectively. However, we have not found information published on the valence band splitting of CdIn_2Te_4 yet except the information¹⁹ on peaks A and B by measuring the photoconductivity for $\text{Cd}_{0.83}\text{In}_{0.34}\text{Te}_{1.34}$.

Temperature dependence of the band gap energy

Figure 3 displays the band gap energies of the $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$ as a function of temperature. As shown in Fig. 3, the variation of the $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$ valence band shows a nonlinear relationship. The temperature dependence of these band gap energies fits

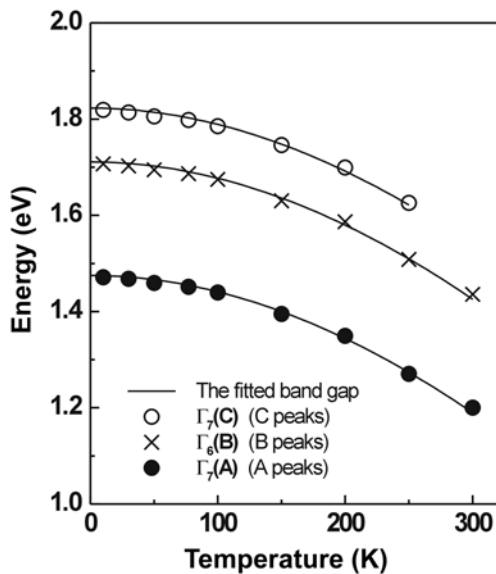


Figure 3. Experimental values of the PC peak energies and the energy band gaps as a function of temperature.

well with the following formula:²⁰

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T), \quad (1)$$

where α and β are constants. When α and β are taken to be 9.43×10^{-3} eV/K and 2676 K, respectively, the curve plotted by Eq. (1) closely fits the experimental values. Also, $E_g(0)$ is the band gap energy at 0 K. Therefore, it is estimated to be 1.4750, 1.7110, and 1.8229 eV, for A, Band C respectively. However, a $E_g(0)$ larger than our value of 1.475 eV has not yet been reported in the literature. Only Couturier *et al.*²¹ and Quintero *et al.*⁶ have reported that their $E_g(0)$ value were 1.26 and 1.312 eV, respectively. The band gap energy at 293 K fitted by Eq. (1) was 1.2023 eV. This band gap energy is slightly smaller than the value of 1.25 eV at 293 K obtained from absorption by Koval *et al.*²² But our result is in good agreement with the value taken from the photoconductivity measurement at 293 K by Paulavicius *et al.*²³ Recently, the direct band gap energy obtained by several researchers has been reported to be 1.22 eV at room temperature.^{19,24,25}

Conclusions

$\text{p-CdIn}_2\text{Te}_4$ single crystals were grown in a three-stage vertical electric furnace using the Bridgman method without seed crystals. The carrier density and the Hall mobility of a $\text{p-CdIn}_2\text{Te}_4$ single crystal obtained at 300 K were $8.61 \times 10^{17} \text{ cm}^{-3}$ and $2.42 \times 10^2 \text{ cm}^2/\text{V}\cdot\text{sec}$, respectively. From the PC measurements, three peaks in the PC spectra were observed in the temperature range of 10 to 250 K. However, only two peaks at 300 K were obtained. This indicates that the electrons in the valence band are scattered because of the mutual interaction of electrons caused by carrier concentration. The peaks A, B, and C obtained are the intrinsic transitions from the valence band state of $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$ to the conduction band state of Γ_6 , respectively. The Δ_{cr} and Δ_{so} of $\text{p-CdIn}_2\text{Te}_4$ obtained are 0.2360 eV and 0.1119 eV, respectively. The temperature dependence of the band gap energy is well described by the equation $E_g(T) = E_g(0) - (9.43 \times 10^{-3}) T^2 / (2676 + T)$. The $E_g(0)$ is estimated at 1.4750, 1.7110, and 1.8229 eV at the valence band states of $\Gamma_7(\text{A})$, $\Gamma_6(\text{B})$, and $\Gamma_7(\text{C})$ respectively. The band gap energy of $\text{p-CdIn}_2\text{Te}_4$ obtained at room temperature is 1.2023 eV.

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