J Mater Sci (2009) 44:3943–3947
DOI 10.1007/s10853-009-3533-5

Studies on band-gap energy and valence-band splitting from photocurrent response of photoconductive $CdGa_2Se_4$ layers

K. J. Hong · T. S. Jeong · C. J. Youn

Received: 9 February 2009 / Accepted: 29 April 2009 / Published online: 19 May 2009

Abstract The photoconductive cadmium gallium selenide ($CdGa_2Se_4$) layer was grown through the hot wall epitaxy method. From the photocurrent (PC) measurements, the three peaks in the PC spectra were associated with the band-to-band transitions. The PC intensities were observed to decrease with decreasing temperature. The valence-band splitting on $CdGa_2Se_4$ was also observed by means of the PC spectroscopy. The crystal field splitting and the spin orbit splitting turned out to be 0.1604 and 0.4179 eV at 10 K, respectively. The temperature dependence of the optical band gap on the $CdGa_2Se_4$ was estimated using the PC. The band-gap energy of $CdGa_2Se_4$ at room temperature was 2.5446 eV.

Introduction

Cadmium gallium selenide ($CdGa_2Se_4$), which has a defect chalcopyrite structure with space group S_4^2–I4-, is an attractive material because of its applicability to electro-optical devices [1]. The material can be applied to field photodetectors and non-linear harmonic generators [2, 3]. Optical absorption and reflection experiments have been studied to determine their applications [4–6]. Through this research, the fundamental material parameters of the band gap and its temperature dependence were found out. The band-gap energy obtained from these methods is known to be inaccurate because of the difficulty in defining the position of the absorption edge. Therefore, the early optical studies reported that the direct band-gap energy for $CdGa_2Se_4$ ranges between 2.1 and 2.57 eV at room temperature [1, 5, 7, 8]. But, the photocurrent (PC) measurement is used as an alternative method to overcome the difficulty in analyzing the data after the absorption experiments are completed. PC measurement on $CdGa_2Se_4$ had been studied for the applications in photodetection and radiation measurements [8]. It is important to investigate the conductivity change of photoconductive $CdGa_2Se_4$ caused by incident radiation. In PC measurement, the absorbed photons with higher energy than the band-gap energy create electron and hole carriers. These carriers instantly flow out through the electrodes. Thereby, the obtained PC peak corresponds to the direct band-gap energy. 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 in the Brillouin zone [9]. Consequently, the photoresponse measurement offer valuable data about the valence band splitting and the band-gap energies toward the higher energy stages. Despite the abundance of information obtained from the PC results, PC studies on $CdGa_2Se_4$ have been limited [7, 10].

In this study, photoconductive $CdGa_2Se_4$ layers were grown by the hot wall epitaxy (HWE) method. The temperature dependence of the band-gap energy was observed through the PC spectroscopic measurements. Thus, the valence-band splitting for electronic transitions restricted by a selection rule is also discussed.

K. J. Hong (✉)
Department of Physics, Chosun University, Gwangju 501-759, South Korea
e-mail: kjhong@chosun.ac.kr

T. S. Jeong · C. J. Youn
Semiconductor Physics Research Center (SPRC), School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju 561-756, South Korea

Experiment

Prior to the layer growth, a $CdGa_2Se_4$ polycrystalline was formed. The starting materials were the 6N purity shot-types of Cd, Ga, and Se. After the materials were weighed in the mole fraction of each element, they were sealed in a quartz tube to maintain the vacuum atmosphere. The sealed ampoule was placed in the synthesis furnace. In order to avoid the explosion of the ampoule due to the Se vapor pressure, the temperature of the ampoule was gradually increased to 1323 K and maintained for 48 h. To grow the $CdGa_2Se_4$ layers, the ingot of $CdGa_2Se_4$ polycrystalline was used as a HWE source. The $CdGa_2Se_4$ layers were grown on semi-insulating GaAs (100) by the HWE method. To find optimum growth conditions, the layers were estimated by measuring the double crystal X-ray diffraction. At this time, the optimum temperatures of the substrate and the source turned out to be 693 and 903 K, respectively. The thickness of the grown $CdGa_2Se_4$ layer was confirmed to be 2.4 μm. Thus, the stoichiometric composition on the $CdGa_2Se_4$ layers was measured using an energy dispersive X-ray spectrometer (EDS). Table 1 presents the composition ratios of each element on the synthesized polycrystalline and the layer analyzed through the EDS measurement. As shown in Table 1, the rate of the Cd components increased a little bit, while that of the Se components decreased. But, it suggests that the component rate of the starting material is continuously maintained during the layer growth. The result of EDS indicates that the grown $CdGa_2Se_4$ layers are formed into the stoichiometric composition. By measuring the Hall effect, the $CdGa_2Se_4$ layers were found to be n-type. The carrier density and the Hall mobility of the $CdGa_2Se_4$ layers were 8.27×10^{17} cm^{-3} and 3.45×10^2 cm^2/V s at 293 K, respectively. Figure 1 shows a schematic diagram of the photoconductive cell prepared to measure the PC spectra. As Fig. 1 shows, the two Au electrodes with a coplanar geometry on the photoconductive $CdGa_2Se_4$ layer were fabricated by an e-beam evaporator, and the ohmic contact of electrodes was confirmed by a current-voltage measurement. After the electrodes were connected to a wire, the sample was mounted on the holder of a low-temperature cryostat. The PC spectroscopic measurements were taken while the monochromatic light emitted from a halogen lamp illuminated the sample. The measurement temperature varied from 10 to 293 K. To find the optical band gap of the $CdGa_2Se_4$ layer, an optical absorption experiment was performed with a UV–VIS–NIR spectrophotometer from a range of 400–500 nm with the temperature varying from 10 to 293 K.

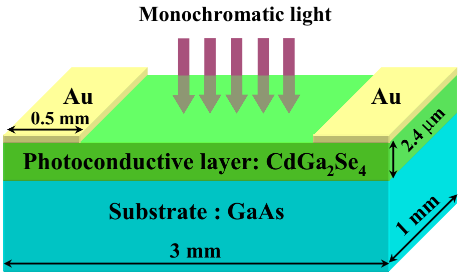

Fig. 1 A schematic diagram of the photoconductive cell prepared to measure the PC spectra

Table 1 Composition ratios of each element on the synthesized polycrystalline and the layer analyzed through the EDS measurement (Units: %)

Element	Synthesized polycrystalline		Layer growth
	Before	After	
Cd	14.29	14.18	14.71
Ga	28.57	28.97	28.86
Se	57.14	56.85	56.43

Results and discussion

Photocurrent spectra

Figure 2 shows the PC spectra of the photoconductive $CdGa_2Se_4$ layer at the temperatures ranging from 10 to 293 K. As shown in Fig. 2, the PC spectrum shows a steep slope at the short wavelength region below the PC apex. This suggests that the electrons and holes generated by the incident light disappear as a result of recombination [11]. Also, the smooth slope at the long wavelength side of the spectra shown in Fig. 2 is evidentiary of the homogeneity of the composition in the crystal. On the other hand, the PC spectra with three peaks were observed at each temperature. These peak positions at 293 K were located at 487.3 (2.5443 eV),

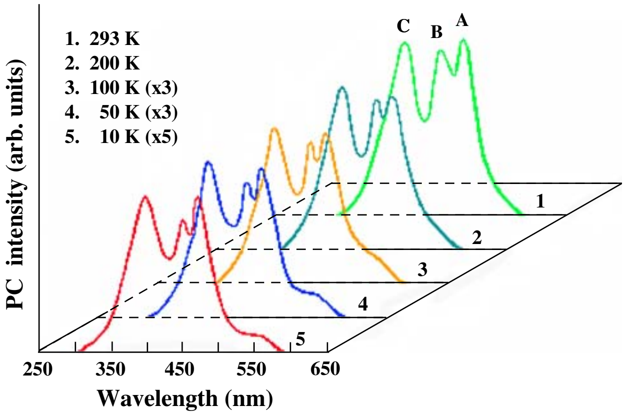

Fig. 2 PC spectra of the photoconductive $CdGa_2Se_4$ layer at the temperatures ranging from 10 to 293 K

470.4 (2.6357 eV), and 409.1 nm (3.0307 eV). The information suggests that these PC peaks are the intrinsic transition caused by the band-to-band transition [12]. Thus, the peak at 2.5443 eV, A peak, is ascribed to the electronic transition from the $\Gamma_6(\Gamma_7)$(A) valence band to the $\Gamma_5(\Gamma_8)$ conduction band. The peak at 2.6357 eV, B peak, is associated with the electronic transition from the $\Gamma_5(\Gamma_8)$(B) valence band to the $\Gamma_5(\Gamma_8)$ conduction band, and the peak at 3.0307 eV, C peak, is ascribed to the electronic transition from the $\Gamma_6(\Gamma_7)$(C) valence band to the $\Gamma_5(\Gamma_8)$ conduction band. While decreasing the measurement temperature, three peaks were continuously observed until the lowest temperature. At 10 K, the three peaks at 469.8 (2.6391 eV), 454.0 (2.7310 eV), and 396.7 nm (3.1254 eV) correspond to the peaks A, B, and C, respectively.

As Fig. 2 shows, the PC intensities decrease with decreasing temperature. During the crystal growth, the photoconductive layers include many trapping centers in the band gap. The centers generated by native defects and impurities, do not play an important role in the actual recombination process. However, the PC density, J_{ph}, on n-type semiconductor can be described by

$$J_{\mathrm{ph}} = \mathrm{e}G\mu_{\mathrm{n}}\tau_{\mathrm{n}}E = \sigma_{\mathrm{ph}}E, \quad (1)$$

where μ_{n}, τ_{n}, and G are the electron mobility, the lifetime of the electrons, and the generation rate, respectively, and σ_{ph} is the photoconductivity induced by the photon energy [11]. Here, the PC strength relates to τ. Therefore, if the electron carrier lifetime of Eq. 1 is long enough, we can collect the charge and observe a strong PC signal. Otherwise, carriers are readily trapped and cannot be collected, so the PC signal is reduced. The carrier trapping persists until the defects are thermally activated by a proper increase in temperature or until they are saturated by a substantial increase of the exciting photon. The facts, it suggests a decrease in the PC intensities with decreasing temperature.

Valence-band splitting

Figure 3 shows the energy band structure and selection rules for the transitions in chalcopyrite $CdGa_2Se_4$. This notation had ever been introduced by Kerimova et al. [10] and Guseinova et al. [13] on the basis of the experimental polarization dependences and of the group-theoretic analysis. The figure shows that the conduction band of *s*-like state has a $\Gamma_5(\Gamma_8)$ symmetry, and the valence band of *p*-like state is split into three double degenerate states such as $\Gamma_6(\Gamma_7)$(A), $\Gamma_5(\Gamma_8)$(B), and $\Gamma_6(\Gamma_7)$(C). The $\Gamma_6(\Gamma_7)$(A) is the uppermost valence band. The effective mass in the $\Gamma_6(\Gamma_7)$(A) is strongly dependant on the direction of *k*. The $\Gamma_5(\Gamma_8)$(B) is the middle band. The $\Gamma_6(\Gamma_7)$(C) is the lowest valence band. Generally, the crystal field of the ternary compound has been investigated by reflectance and photoconductivity measurement [14–17]. The Hamiltonian matrix eigenvalues for the quasicubic model are given by

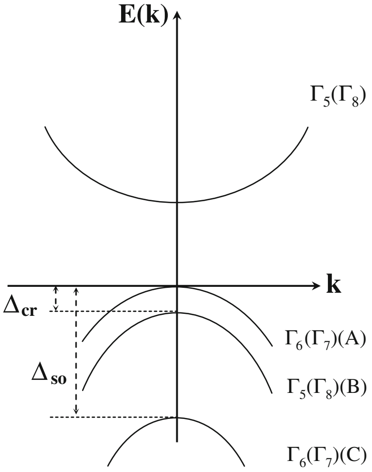

Fig. 3 Energy-band structure and selection rules for the transitions in chalcopyrite $CdGa_2Se_4$

$$\Delta_{1\{2\}} = (1/2)(\Delta_{\mathrm{so}} + \Delta_{\mathrm{cr}}) - \{+\}\left[(1/4)(\Delta_{\mathrm{so}} + \Delta_{\mathrm{cr}})^2 - (2/3)(\Delta_{\mathrm{so}} \cdot \Delta_{\mathrm{cr}})^{1/2}\right], \quad (2)$$

where the Δ_{cr} and the Δ_{so} represent the crystal field splitting and the spin orbit splitting, respectively [18]. The Δ_1 and the Δ_2 are the difference between $\{\Gamma_5(\Gamma_8)(\mathrm{B})\}-\{\Gamma_6(\Gamma_7)(\mathrm{A})\}$, and $\{\Gamma_6(\Gamma_7)(\mathrm{C})\}-\{\Gamma_6(\Gamma_7)(\mathrm{A})\}$, respectively. From the PC spectra measured at 10 K, the Δ_1 value is 0.0919 eV. This value is the energy difference between the peak A, 2.6391 eV, and the peak B, 2.7310 eV. The Δ_2 value is 0.4863 eV due to the energy difference between the A peak, 2.6391 eV, and the C peak, 3.1254 eV. Therefore, the Δ_{cr} and the Δ_{so} can be calculated by inserting the Δ_1 and the Δ_2 into Eq. 2. The Δ_{cr} and Δ_{so} were estimated to be 0.1604 and 0.4179 eV, respectively. The obtained values are in excellent agreement with 0.13 and 0.42 eV obtained from the absorption measurement (at 90 K) by Bacewicz et al. [14], respectively. But, the Δ_{cr} and Δ_{so} values of 0.20 and 0.17 eV obtained by using quasicubic model from the photoconductivity measurement (at 300 and 77 K) by Kerimova et al. [10] are large difference in comparison to our results, respectively. Thereby, to overcome the large difference-values, Kerimova et al. [10] deduced the new values of 0.33 and 0.48 eV by introducing the tetragonal compression on $CdGa_2Se_4$, respectively. Thus, they reported that the splitting of this valence band is due to the presence of two types of atom in the cation sublattice and also due to the tetragonal compression [10].

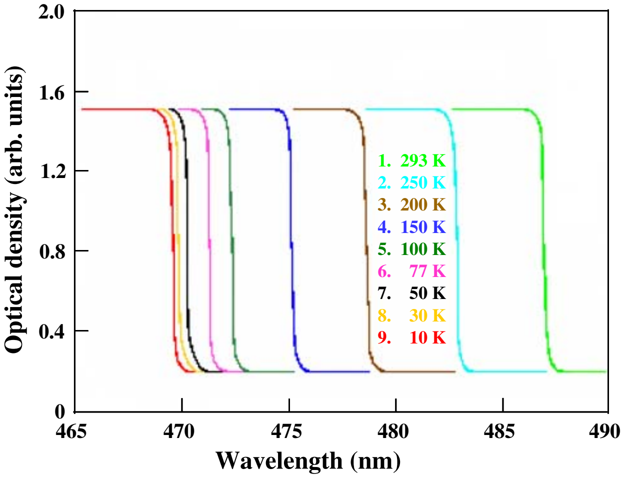

Fig. 4 Optical absorption spectra of $CdGa_2Se_4$ obtained in a temperature range of 10–293 K

Temperature dependence of the band-gap energy

Figure 4 shows the optical absorption spectra obtained in a temperature range of 10 to 293 K. In order to identify the band-gap energy for $CdGa_2Se_4$, we carefully examined the relation between the optical absorption coefficient (α) and the incident photon energy ($h\nu$) from the optical absorption measurements in Fig. 4. The relation for a direct band gap between $h\nu$ and α is follows:

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right), \tag{3}$$

where A is a function of refractive index and hole/electron effective masses, and $h\nu$ is the energy of the incident photon. According to Eq. 3, $(\alpha h\nu)^2$ linearly depends upon the photon energy. From plots of $(\alpha h\nu)^2$ versus photon energy for different temperatures, the band gaps were determined by extrapolating the linear portions of the respective curves to $(\alpha h\nu)^2$.

Figure 5 presents the band-gap variation as a function of temperature on $CdGa_2Se_4$ obtained from PC and absorption measurements. The band gap on $CdGa_2Se_4$ obtained from both methods was nearly equal. The PC peak positions are consistent with the absorption calculated by using Eq. 3 at the same temperature, which suggests PC measurement is a useful methods for determining the band gap of $CdGa_2Se_4$. The band-gap variation as a function of temperature can be well fitted numerically by the following formula:

$$E_g(T) = E_g(0) - aT^2/(T + b), \tag{4}$$

where a is a constant and b is approximately the Debye temperature [19, 20]. $E_g(0)$ is the band-gap energy at 0 K. When a and b are set at 7.721×10^{-4} eV/K and 392 K, respectively, the curve plotted in Eq. 4 closely fits the experimental values. Furthermore, the value of $E_g(0)$ is 2.6414, 2.7318, and 3.1262 eV at the valence-band states of $\Gamma_6(\Gamma_7)$(A), $\Gamma_5(\Gamma_8)$(B), and $\Gamma_6(\Gamma_7)$(C), respectively. Our result on the a value is in very close agreement with the value of 5×10^{-4} eV/K obtained from photoconductivity measurement by Kerimova et al. [10]. However, the obtained b value is slightly smaller than the value of 544 K at pure single crystal [21]. Using Eq. 4, the band-gap energy was estimated to be 2.5446 eV at 293 K. The data fits with the value of 2.55 eV measured at room temperature by Abdullaev et al. [22], which was found from the reflection spectra.

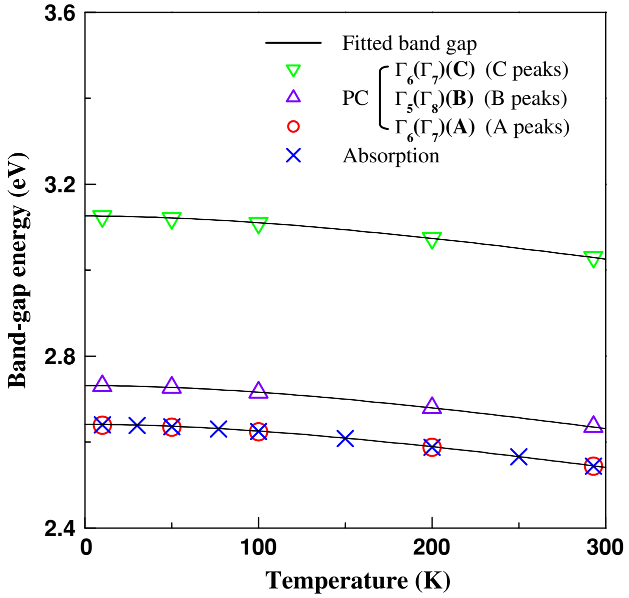

Fig. 5 Band-gap variation as a function of temperature on $CdGa_2Se_4$ obtained from PC and absorption measurements. The solid line is fitted by Eq. 4

Conclusion

The photoconductive $CdGa_2Se_4$ layer, which has the carrier density of 8.27×10^{17} cm^{-3} and the Hall mobility of 3.45×10^2 cm^2/V s at 293 K, was grown by using the HWE method. From the PC measurements, three peaks of A, B, and C were observed, indicating the intrinsic transitions from the valence-band states of $\Gamma_6(\Gamma_7)$(A), $\Gamma_5(\Gamma_8)$(B), and $\Gamma_6(\Gamma_7)$(C) to the conduction band state of $\Gamma_5(\Gamma_8)$. The intensities of the PC spectra decreased with decreasing temperature. The valence-band splitting on $CdGa_2Se_4$ was also observed using PC measurement. The Δ_{cr} and Δ_{so} were 0.1604 and 0.4179 eV at 10 K, respectively. By conducting the PC and absorption experiments, the band-gap energy on $CdGa_2Se_4$ was extracted out. Thus, the temperature dependence of the band-gap energy was described by $E_g(T) = E_g(0) - (7.721 \times 10^{-4})T^2/(392 + T)$. The $E_g(0)$ was estimated to be 2.6414, 2.7318, and 3.1262 eV at the valence-band states of $\Gamma_6(\Gamma_7)$(A), $\Gamma_5(\Gamma_8)$(B), and $\Gamma_6(\Gamma_7)$ (C), respectively. Furthermore, the band-gap energy of $CdGa_2Se_4$ at room temperature was 2.5446 eV.

Acknowledgement This study was supported by the Chosun University Research Fund of 2008.

References

1. Madelung O (1996) Numerical semiconductors-basic data, 2nd edn. Springer, Berlin
2. Abdullaev GB, Agaev VG, Antonov VB, Nani RKh, Salaev EYu (1972) Sov Phys Semicond 6:1492
3. Levine CG, Bethea HM, Kasper HM (1974) IEEE J Quantum Electron 10:904
4. Soliman HS, Hindia T, Dorra HA, Hashem E (1994) J Mater Sci Mater Electron 5:248
5. El-Sayad EA, Sakr GB (2004) Phys Status Solidi A 201:3060
6. Syrbu NN, Tezlevan VE (1995) Physica B 210:43
7. Kshirsagar ST, Sinha APB (1977) J Mater Sci 12:1614. doi: 10.1007/BF00542812
8. Joshi NV (1990) Photoconductivity: art, science, and technology. Marcel Dekker, New York
9. Greenaway KL, Harbeke G (1968) Optical properties and band structure of semiconductors. Pergamon, Oxford
10. Kerimova TG, Mamedov ShS, Mekhtiev NM, Nani RKh, Salaev EYu (1979) Sov Phys Semicond 13:291
11. Bube RH (1969) Photoconductivity of Solids. Wiley, New York
12. You SH, Hong KJ, Jeong TS, Youn CJ, Park JS, Shin DC, Moon JD (2003) J Cryst Growth 256:116
13. Guseinova DA, Kerimova TG, Nani RKh (1977) Sov Phys Semicond 11:670
14. Bacewicz R, Trykozko R, Borghesi A, Cambiaghi M, Reguzzoni E (1979) Phys Lett A 75:121
15. Shay JL, Tell B, Schiavone LM, Kasper HM, Thiel F (1974) Phys Rev B 9:1719
16. Joshi NV, Martinez L, Echeverria R (1981) J Phys Chem Solids 42:281
17. Charbonneau S, Fortin E, Anedda A (1985) Phys Rev B 31:2326
18. Aven M, Prenerin JS (1967) Physics and chemistry of II–VI compounds, chap 7. North-Holland Publishing Company, Amsterdam
19. Varshni YP (1967) Physica 34:149
20. Hong KJ, Jeong TS, Yoon CJ, Shin YJ (2000) J Cryst Growth 218:19
21. Madelung O, Rössler U, Schulz M (2000) Landolt-Börnstein: numerical data and functional relationships in science and technology, Group III condensed matter, vol 41E. Springer, Berlin
22. Abdullaev GB, Guseinova DA, Kerimova TG, Nani RKh (1973) Sov Phys Semicond 7:575