

Optoelectrical properties of CuInSe₂ thin films grown using hot wall epitaxy

Hyuk Jung^a and Kwangjoon Hong^{b*}

^aDepartment of Obstetrics and Gynecology, Chosun University, Kwangju 501-759, Korea

^bDepartment of Physics, Chosun University, Kwangju 501-759, Korea

In this study, the photocurrent (PC) spectroscopy of undoped p-type CIS layers has been investigated at temperatures ranging from 10 to 293 K. Three peaks, A, B, and C, corresponded 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 at 0.0059 and 0.2301 eV, respectively, and the temperature dependence of the optical band gap could be expressed using the empirical equation $E_g(T) = E_g(0) - (8.57 \times 10^{-4})T^2/(T+129)$. But the behavior of the PC was different from that generally observed in other semiconductors: the PC intensities decreased with decreasing temperature. From the relation of $\log J_{ph}$ vs $1/T$, where J_{ph} is the PC density, the dominant level was observed at the higher temperatures. We suggest that in undoped p-type CIS layers, the trapping center limits the PC signal due to native defects and impurities with decreasing temperature.

Key words: copper indium diselenide, photocurrent spectroscopy, crystal field splitting, spin orbit splitting, optical band gap, trapping center.

Introduction

Copper indium diselenide (CuInSe₂, CIS) has received considerable attention in recent years because of its applications in photovoltaic devices [1-3]. Moreover, it is one of the most environmentally-friendly materials for Cd-free buffer layers because of its high absorbance in solar cells in the UV visible range [4]. Structurally, the chalcopyrite CIS is analogous to the structure of the uppermost valence bands of the ZnSe binary compound. These valence bands are 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, Δ_{cr} , and the spin orbit splitting, Δ_{so} . It can be seen that the degeneracy of both p and d orbitals is partially lifted. These states participate in the photoconduction process, extending the photoresponse to the higher energy side. Therefore, photoresponse measurements, including photovoltage and photoconductivity, provide valuable information about physical properties of materials and offers applications in photodetection and radiation measurements, even if it is a complex process involving thermal and hot carrier relaxation processes, charge carrier statistics, effects of electrodes, and several mechanisms of recombination [5]. Despite the abundance of information obtained from photocurrent (PC) measurements, PC studies on CIS have been limited with a few exceptions [6, 7].

In this paper, undoped p-type CIS layers grown using a hot wall epitaxy (HWE) technique were investigated by measuring their PC spectra at different temperatures. From the PC measurements, the valence band splitting on undoped p-type CIS are discussed along with the temperature dependencies of the band-gap energy and the PC intensity.

Experimental Procedure

Prior to the layer growth, a CIS polycrystalline was formed. The starting materials were 6 N purity shot-types of Cu, In, and Se. After the materials were weighed in the mole fraction of each element, they were sealed in a quartz tube to maintain a vacuum atmosphere. The sealed ampoule was placed in the synthesis furnace. In order to avoid the explosion of the ampoule, the temperature of the ampoule was increased gradually to 1050 °C and maintained for 48 h. To grow the CIS layers, an ingot of CIS polycrystalline was used as a HWE source. The CIS layers were grown on semi-insulating GaAs (100) by a HWE method. The optimum temperatures of the substrate and the source turned out to be 410 and 620 °C, respectively. The grown CIS layers, which were labeled as samples R06-1 and R06-2, were found to be p-type by measuring the Hall effect. Also the carrier densities of these samples were 9.62×10^{16} and $4.85 \times 10^{16} \text{ cm}^{-3}$ at 293 K, respectively. The detailed growth procedures have been published elsewhere [8]. In order to record the PC measurements, two Au electrodes with a coplanar geometry on the CIS layer were fabricated by an e-beam evaporator, and the ohmic contact of electrodes was confirmed by a current-

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

voltage measurement. After the electrodes were connected to a wire, the sample was mounted on the holder of a low-temperature cryostat. The PC spectral measurements were taken while monochromatic light emitted from a halogen lamp passed through a chopper to illuminate the sample. The measurement temperature varied from 10 to 293 K. The photoluminescence (PL) was measured at 10 K. The surface of the CIS layer was illuminated by 632.8 nm light emitted from a He-Ne laser (Nippon, 50 mW) and the light coming from the sample was dispersed with a monochromator. The dispersed light was detected with a photomultiplier tube (RCA, C3-1034) and then converted into a current. This current was recorded on an x-y recorder after it was amplified by a lock-in amplifier (EG&G 5210). To find the optical band gap of the CIS layer, an optical absorption experiment was performed with a UV-VIS-NIR spectrophotometer in the range of 1040 to 1240 nm with the temperature varying from 10 to 293 K.

Results and Discussion

Photocurrent spectra

Figure 1 shows the PC spectra measured from the undoped p-type CIS layer of R06-1 at temperatures ranging from 10 to 293 K. Three peaks appeared in each PC spectrum for a given temperature, as shown in Fig. 1. These peak positions at 293 K were located at 1224.9 (1.0121 eV), 1217.8 (1.0180 eV), and 993.4 nm (1.2481 eV). These PC peaks represent intrinsic transitions caused by the band-to-band transitions [9, 10]. The electrons excited from the valence band to the conduction band by the absorbed photons flow immediately through the electrodes. Then, only the PC peaks corresponding to the band gap are detected. Therefore, the peak at 1.0121 eV, peak "A", is ascribed to the electronic transition from the $\Gamma_7(A)$ valence band to the Γ_6 conduction band. The peak at 1.0180 eV, peak "B", is associated with the electronic transition from the

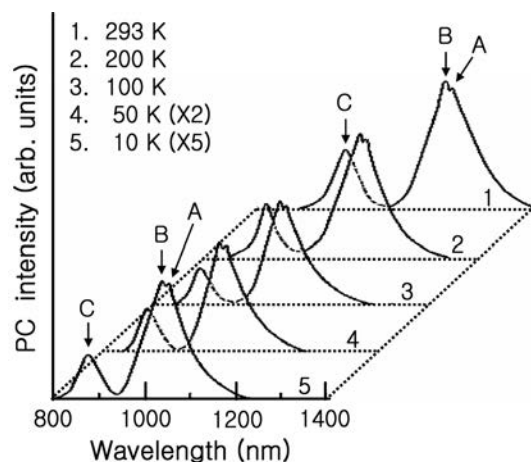


Fig. 1. PC spectra measured from undoped p-type CIS layer of R06-1 at temperatures ranging from 10 to 293 K.

$\Gamma_6(B)$ valence band to the Γ_6 conduction band, and the peak at 1.2481 eV, peak "C", is ascribed to the electronic transition from the $\Gamma_7(C)$ valence band to the Γ_6 conduction band. In spite of the decrease of the measurement temperature, these three peaks were continuously observed until the lowest temperature. At 10 K, it is suggested that three peaks at 1047.2 (1.1839 eV), 1041.4 (1.1898 eV), and 873.2 nm (1.4199 eV) correspond to the peaks A, B, and C, respectively.

Valence band splitting

Figure 2 shows the energy band structure of the chalcopyrite CIS layer at the Γ point due to the selection rule [1]. 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 at $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$. The $\Gamma_7(A)$ is the uppermost valence band. The effective mass in the $\Gamma_7(A)$ depends significantly on the direction of k . The $\Gamma_6(B)$ is the middle band and the $\Gamma_7(C)$ is the lowest valence band. Generally, the crystal field of the ternary compound has been investigated by reflectance and photoconductivity measurement [11, 12], but in this study, the valence band splitting of CIS was observed using the PC measurements. The Δ_{cr} is the energy difference between $\Gamma_7(A)$ and $\Gamma_6(B)$. The energy obtained of Δ_{cr} is 0.0059 eV. The value is the energy difference between the peak A, 1.1839 eV, and the peak B, 1.1898 eV, at 10 K. This value is almost an order of magnitude smaller than those of II-VI analogues [13]. The Δ_{so} is the energy difference between $\Gamma_6(B)$ and $\Gamma_7(C)$. This value is 0.2301 eV due to the energy difference between the B peak, 1.1898 eV, and the C peak, 1.4199 eV, at 10 K. The Δ_{cr} and Δ_{so} values between the three peaks at several temperatures are coincident to the values of 0.0059 and 0.2301 eV, respectively. Basically, the splitting and the symmetry properties of the valence

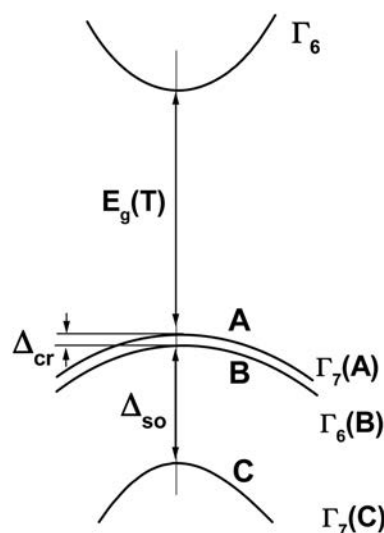


Fig. 2. Energy band structure of the chalcopyrite CIS layer at Γ point according to the selection rule.

bands at the Brillouin-zone center can be satisfactorily explained by the Hopfield quasicubic model [13]:

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

where E_1 and E_2 are the difference of $E_G^C - E_G^A$ and $E_G^C - E_G^B$, respectively. Also, E_G^A , E_G^B , and E_G^C mean the energy band gaps to the conduction band at each state of the valence band. By extraction from Eq. (1), the Δ_{cr} and Δ_{so} were reported at 0.006 and 0.230 eV, respectively [1]. Consequently, the Δ_{cr} and Δ_{so} directly obtained from the PC experiment are equivalent in the reported values. We have not found a published value for the valence band splitting of CIS observed by a PC measurement yet, except for the values obtained from a the reflectivity experiment [14, 15].

Temperature dependence of peak position and intensity

Figure 3 shows the optical absorption spectra of R06-1 obtained in the temperature range from 10 K to 293 K. To identify the band-gap energy for the CIS layer, 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. 3. The relation for a direct band gap between $h\nu$ and α is given by

$$(\alpha h\nu)^2 \sim (h\nu - E_g). \quad (2)$$

According to Eq. (2), $(\alpha h\nu)^2$ linearly depends upon the photon energy. From the 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 $(\alpha h\nu)^2 = 0$. Figure 4 displays the variation of the energy band gap as a function of temperature on the CIS layer obtained from PC and absorption measurements. We have found that the PC peak positions are consistent with the absorption calculated using Eq. (2) at the same temperature. Therefore, this figure shows that the variation of the energy band gap as a function of temperature on the CIS layer

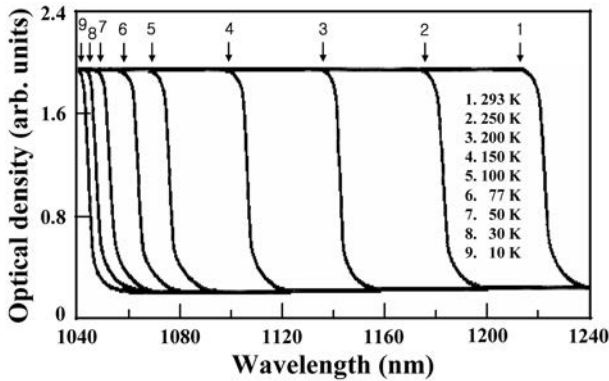


Fig. 3. Optical absorption spectra of R06-1 obtained in the temperature range from 10 K to 293 K.

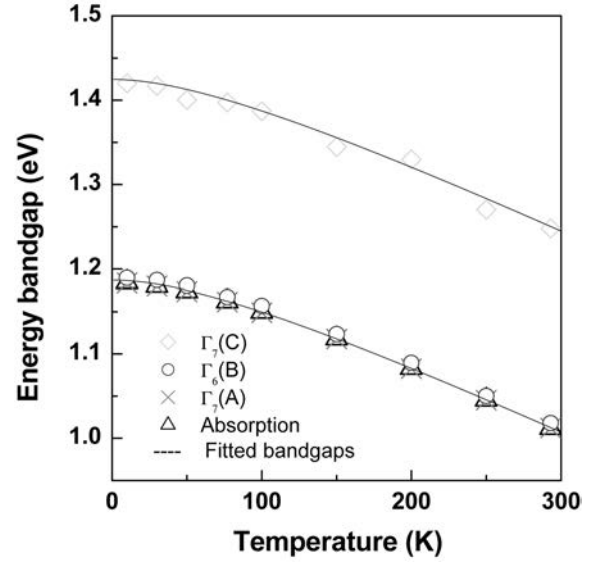


Fig. 4. Variation of the energy band gap as a function of temperature on the CIS layer obtained from PC and absorption measurements.

obtained from PC and absorption measurements is in good agreement. This fact shows that this PC measurement is one of the useful methods for the band-gap determination of the CIS layer. In fact, the absorption experiment has been known to be inaccurate for obtaining the energy band gap because of the difficulty in defining the position of the absorption edge, but the PC measurement can directly give the energy corresponding to the band gap by measuring the PC peak position. The temperature dependence of the optical band-gap energy in our experiment is well fitted numerically by the following formula [16, 17]:

$$E_g(T) = E_g(0) - aT^2/(T+b), \quad (3)$$

where a is a constant and b is approximately the Debye temperature. Also, $E_g(0)$ is the band-gap energy at 0 K, which is estimated to be 1.187 eV. When a and b are taken to be 8.57×10^{-4} eV/K and 129 K, respectively, the curve plotted by Eq. (3) closely fits the experimental values.

To understand the PC generation on the temperature dependence, we consider the total current density in a p-type semiconductor [18]. The current density of a p-type semiconductor in the dark is given by $J = e\mu_p E$ since the electron contribution can generally be neglected. Here, p and μ_p are the hole carriers and the hole mobility, respectively. Also, E and σ are the electric field and the conductivity, respectively. Therefore, the PC density, J_{ph} , is described by

$$J_{ph} = eG\mu_p\tau_p E = \sigma_{ph} E, \quad (4)$$

where τ_p and G are the lifetime of holes and the generation rate, respectively, and σ_{ph} is the photoconductivity induced by the photon energy. Figure 5 presents a plot of $\log J_{ph}$ vs $1/T$ for the PC response of the A

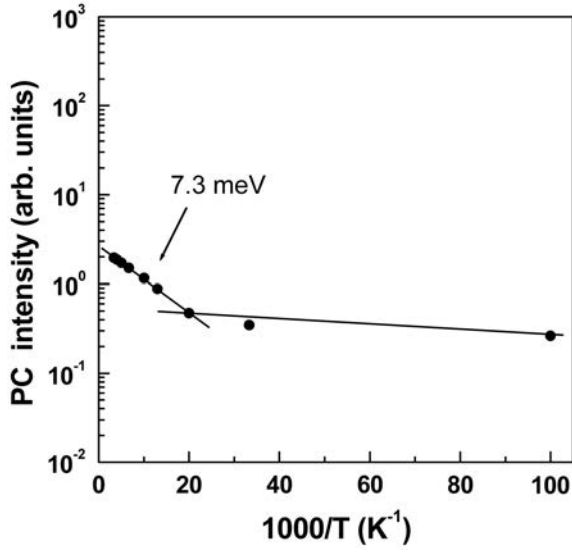


Fig. 5. A plot of $\log J_{ph}$ vs $1/T$ for the PC response of the A peaks related to the two samples of R06-1 and R06-2 as a function of temperature.

peaks related to the two samples of R06-1 and R06-2 as a function of temperature. As shown in Fig. 5, the PC intensities of undoped p-type CIS layers decrease with decreasing temperature. Also the slope on these samples shows the same tendencies as the temperature varies. However, the $\mu_p\tau_p$ of Eq. (4) is generally known to have a tendency to increase with decreasing temperature. Therefore, Eq. (4) does not explain our result. This situation is similar to the result obtained from the PC experiment on CdTe grown by the gradient freezing Bridgman method including many trapping centers in the band gap [19]. For the explanation of this phenomenon, Simmons and Taylor proposed a theory for the temperature dependence of J_{ph} for p-type amorphous chalcogenide semiconductors [20]. They divided the temperature range into three different photoexcitations as follows: (i) In the high-temperature region where photoexcitation is low ($\sigma_{ph} < \sigma_{dark}$; dark conductivity), σ_{ph} increases and reaches a peak value with decreasing temperature. (ii) In the moderate-temperature region ($\sigma_{ph} > \sigma_{dark}$), σ_{ph} decreases with decreasing temperature. (iii) Finally, in the low-temperature region ($\sigma_{ph} > \sigma_{dark}$), σ_{ph} is independent of temperature. As shown in Fig. 5, our results obtained from the PC measurements are similar to temperature region (ii). In the high-temperature region, the dominant level should be observed, but it does not show any temperature dependence at the low-temperature region. From the hypothesis of Simmons and Taylor, σ_{ph} for the region (ii) is expressed by

$$\sigma_{ph} = e\mu_p [GN_o / (\nu\sigma_t N_t)]^{1/2} \exp[-(E - E_v)/2kT], \quad (5)$$

where σ is the thermal velocity of holes, σ_t the capture cross section of E, and k the Boltzmann constant. Here, N_c and N_v , which means the effective density of states

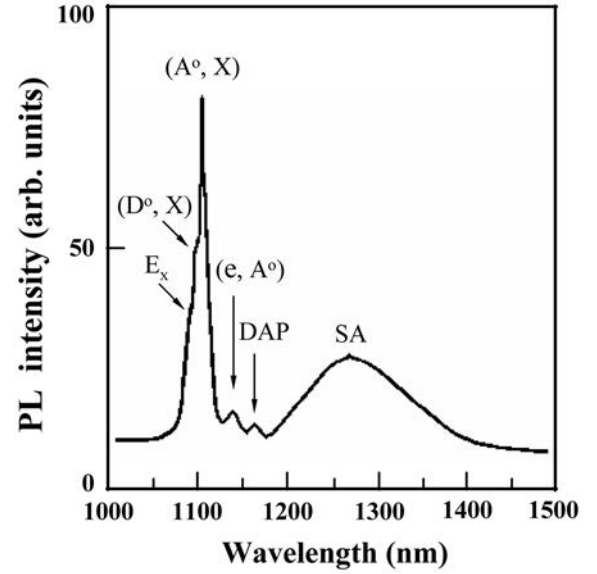


Fig. 6. A typical PL spectrum of R06-1 measured at 10 K.

of the conduction and the valence bands, respectively, are assumed to be equal to N_o . N_t is the density of E. Thus, E is a trap level energy in the forbidden gap of a photoconductor. Therefore, Eq. (4) and (5) can be concisely expressed as

$$J_{ph} \propto A \exp(-\Delta E_{ph}/2kT), \quad (6)$$

where ΔE_{ph} is the activation energy and A is substituted for $e\mu_p [GN_o / (\nu\sigma_t N_t)]^{1/2}$. As Fig. 5 shows, the PC intensities rapidly decrease at high-temperature between 293 and 50 K. Also, at low-temperature between 50 and 10 K, the PC intensities show a zero slope. Thus, ΔE_{ph} obtained from the plots of $\log J_{ph}$ vs $1/T$ is estimated to be 7.3 meV. Therefore, to find the role of the activation energy, we compare the PC results with those of the PL experiment. Figure 6 shows a typical PL spectrum of R06-1 measured at 10 K. The two peaks on the shoulder appear at 1098.7 (1.1284 eV) and 1100 nm (1.1247 eV) toward the shorter-wavelength region. These peaks are associated with the free exciton (E_x) and the neutral donor bound exciton (D^0, X) caused by the recombination from free exciton to neutral donor, respectively. The strong peak of the neutral acceptor bound exciton (A^0, X) appears at 1104.5 nm (1.1225 eV) as shown in Fig. 6. This belongs to the typical p-type configuration of the PL spectrum observed in the CIS layer. This exciton has been known to be related to the recombination from free exciton to neutral acceptor. The binding energy, E_{bx}^b , for the (A^0, X) emission is

$$E_{bx}^b = E(E_x) - E(A^0, X) \text{ or } E(D^0, X). \quad (7)$$

Here E_{bx}^b was calculated to be 5.9 meV ($=1.1284 - 1.1225$). By comparing the PC results with those of the PL experiment, we find that the activation energy of 7.3 meV is close to the binding energy, 5.9 meV, of the (A^0, X) emission. This fact indicates that the activation

energy is the dissociation energy of the neutral acceptor bound exciton. We suggest that trapping centers, due to native defects and impurities, limit the PC signal with decreasing temperature. However, the PC signal in the low-temperature region below 50 K remains constant with varying temperature. This situation implies that trapping centers are saturated at low-temperatures.

Conclusions

The PC response on undoped p-type CIS layers grown using an HWE method was performed at temperatures ranging from 10 to 293 K. In the PC experiment, three peaks due to band-to-band transitions were observed over the total temperature range. From that, the A, B, and C peaks obtained were associated with the intrinsic transitions from the valence band state of $\Gamma_7(A)$, $\Gamma_6(B)$, and $\Gamma_7(C)$ to the conduction band state of Γ_6 , respectively. The Δ_{cr} and Δ_{so} of CIS obtained from the PC experiments were 0.0059 and 0.2301 eV, respectively. The temperature dependence of the optical band gap could be well expressed using Varshni's formula: $E_g(T) = E_g(0) - aT^2/(b+T)$, where a and b were 8.57×10^{-4} eV/K and 129 K, respectively. Also, contrary to our expectation, the PC intensities decreased with decreasing temperature. In the $\log J_{ph}$ vs $1/T$ plot, the dominant level was observed in the high-temperature region. This level corresponding to 7.3 meV was associated with the binding energy of the neutral acceptor bound exciton. The trapping centers, due to native defects and impurities in CIS, are suggested to be the causes of the decrease in the PC signal with decreasing temperature.

Acknowledgement

This study was supported in part by research grants from Chosun University, 2004.

References

1. J.L. Shay and J.H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, (Pergamon, Oxford, 1975).
2. A. Rockett and R.W. Birkmire, *J. Appl. Phys.* 70 (1991) R81-R84.
3. K.H. Lam, J. Close, and W. Durisch, *Solar Energy* 77 (2004) 121-125.
4. M. Yamaguchi, *J. Appl. Phys.* 78 (1995) 1476-1481.
5. N.V. Joshi, *Photoconductivity: Art, Science, and Technology*, (Marcel Dekker, New York, 1990), Chap. 1.
6. G.A. Medvedkin and M.A. Vagomedov, *J. Appl. Phys.* 82 (1997) 4013-4015.
7. M.E. Boiko and G.A. Medvedkin, *Sol. Energy Mater. Sol. Cells* 41/42 (1996) 307-311.
8. S.H. You, K.J. Hong, J.W. Jeong, T.S. Jeong, C.J. Youn, J.D. Moon, and H.S. Kim, *Cryst. Res. Technol.* (submitted paper).
9. S.H. You, K.J. Hong, T.S. Jeong, C.J. Youn, J.S. Park, D.C. Shin, and J.D. Moon, *J. Cryst. Growth* 256 (2003) 116-119.
10. C.C. Klick, *Phys. Rev.* 89 (1953) 274-281.
11. R. Bacewicz, R. Trykozko, A. Borghesi, M. Cambiaghi, and E. Reguzzoni, *Phys. Lett. A* 75 (1979) 121-125.
12. S. Charbonneau, E. Fortin, and A. Anedda, *Phys. Rev. B* 31 (1985) 2326-2330.
13. B. Segall and D.T.F. Marple, in: M. Aven and J.S. Prenerin (Eds), *Physics and Chemistry of II-VI Compounds*, (North-Holland, Amsterdam, 1967), Ch. 7.
14. K.S. Ramaiah, V.S. Raja, A.K. Bhatnaar, F.S. Juang, S.J. Chang, and Y.K. Su, *Mater. Lett.* 45 (2000) 251-256.
15. M.I. Alonso, K. Wakita, J. Pascual, M. Garriga, and N. Yamamoto, *Phys. Rev.* 63 (2001) 5203-5207.
16. Y.P. Varshni, *Physica* 34 (1967) 149-154.
17. K.J. Hong, T.S. Jeong, C.J. Yoon, and Y.J. Shin, *J. Cryst. Growth* 218 (2000) 19-23.
18. R.H. Bube, *Photoconductivity of Solids*, (Wiley, New York, 1969).
19. S. Yamanaka, S. Tsushima, H. Shimizu, and Y. Tokumaru, *Jpn. J. Appl. Phys.* 41 (2002). 5538-5541.
20. J.C. Simmons and G. W. Taylor, *J. Phys. C* 7 (1974) 3051-3055.