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The temperature-dependent behavior of the photocurrent spectra of $CdIn_2S_4$ films

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$CdIn_2S_4$ (110) films were grown on semi-insulating GaAs (100) by a hot wall epitaxy method. Using photocurrent (PC) measurements, the PC spectra in the temperature range of 30 to 10 K appeared as three peaks in the short wavelength region. It was found that three peaks, A-, B-, and C-excitons, correspond to the intrinsic transition from the valence band states of Γ_4(z), Γ_5(x), and Γ_5(y) to the exciton below the conduction band state of Γ_1(s), respectively. A 0.122 eV crystal field splitting and the 0.017 eV spin orbit splitting were obtained. Thus, the temperature dependence of the optical band gap obtained from the PC measurements was well described by $E_g(T)=2.7116\ eV-(7.65\times10^{-4}\ eV/K)T^2/(425+T)$. However, the behavior of the PC was different from that generally observed in other semiconductors. The PC intensities decreased with decreasing temperature. This phenomenon had ever been reported in a PC experiment on bulk crystals grown by the Bridgman method. From the relation of log J_{ph} vs 1/T, where J_{ph} is the PC density, two dominant levels were observed, one at high temperatures and the other at low temperatures. Consequently, the trapping centers due to native defects in the $CdIn_2S_4$ film were suggested to be the cause of the decrease in the PC signal with decreasing temperature.

Key words: Photocurrent, Band gap, Valence band splitting, Hot wall epitaxy, Ternary compounds.

Introduction

Cadmium indium sulfide ($CdIn_2S_4$) is a semiconducting ternary chalcogenide of the type A^{II}-B_2^{III}-C_4^{VI}. The band gap of $CdIn_2S_4$ with a direct transition is 2.62 eV at room temperature. Therefore, it is an attractive material for its application in electro-optical devices [1-3]. To grow high quality crystals required for practical applications, it is important to understand the fundamental material parameters such as the band gap and its structure. However, the growth of high quality $CdIn_2S_4$ film is very difficult because of the stoichiometric deviation generated during growth or additional thermal treatment. Consequently, the fundamental physical properties on the $CdIn_2S_4$ films have rarely been investigated since it is hard to obtain high quality films. This has only been achieved in poly films of $CdIn_2S_4$ deposited by using vacuum evaporation [4-6]. On the other hand, the band-gap energy can be obtained by measuring the absorption, reflectance, or photoluminescence (PL) spectra [7-9]. In particular, absorption experiments are frequently used to obtain the band-gap energy. However, this method is vulnerable to frequent errors because of the difficulty in defining the position of the absorption edge. Therefore, photocurrent (PC) measurements were used to overcome this difficulty in analyzing the data obtained from the absorption experiment. In PC measurements, the PC peak position obtained corresponds to the direct band energy. However, PC measurements give us information on the valence band splitting together with the band-gap energy. 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 [10]. Therefore, the valence band is split according to the symmetry of the crystal. The energy states of the split valence band have a certain symmetry. Both p and d orbitals of this compound are known to be partially lifted due to degeneracy. Therefore, the photoresponse is enhanced on the higher energy side of the photoconduction process. These photoresponse techniques, including photovoltage and photoconductivity, have been reported to be a powerful means of investigation. Despite the abundance of information obtained from the PC results, however, PC studies have been limited except for a few researchers [11, 12].

In this paper, the $CdIn_2S_4$ films were grown by a hot wall epitaxy (HWE) method. From the PC measurements, we present the valence band splitting for electronic transitions restricted by a selection rule. In addition, PC generation in the $CdIn_2S_4$ films will be also discussed, as well as the temperature dependences of the band-gap energy and the PC intensity.

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Experimental Procedure

$CdIn_2S_4$ films were grown on semi-insulating GaAs (100) by the HWE method. The source materials for the $CdIn_2S_4$ growth were a polycrystalline $CdIn_2S_4$ ingot. To synthesize the polycrystalline $CdIn_2S_4$ ingot, 6N purity shot-types of Cd, In, and S were weighed with stoichiometric proportions, and were synthesized in a horizontal polycrystalline-synthesis furnace. Prior to growing the $CdIn_2S_4$ films, the substrate was cleaned ultrasonically for 1 minute in successive baths of trichloroethylene, acetone, methanol, and 2-propanol. The substrate was etched for 1 minute in a solution of H_2SO_4:H_2O_2:H_2O (5:1:1). The substrate was immediately loaded onto the substrate holder as shown in Fig. 1, and it was annealed at 580 ℃ for 20 minutes to remove the residual oxide on the surface of the substrate. The optimum temperatures of the substrate and the source for the $CdIn_2S_4$ growth turned out to be 420 and 630 ℃, respectively. The detailed growth procedures have been published elsewhere [13].

The thickness and the growth rate of grown film were 2.4 μm and 0.5 μm/h, respectively. The $CdIn_2S_4$ was grown epitaxially along the <110> direction onto a GaAs (100) substrate. The Hall effect measurement on the $CdIn_2S_4$ film was carried out using the van der Pauw method for temperatures ranging from 293 to 30 K. In addition, the carrier densities tended to decrease from 9.01×10^{16} to 4.72×10^{15} cm^{-3} with decreasing temperature.

To measure the PC spectra, two electrodes were made on both ends of the sample and ohmic contact of the electrodes was confirmed by a current-voltage measurement. After the sample was mounted on a holder in a low-temperature cryostat, the PC spectrum measurement was done while monochromatic light, emitted from a halogen lamp, illuminated the sample. The measurement temperature was varied from 10 to 293 K.

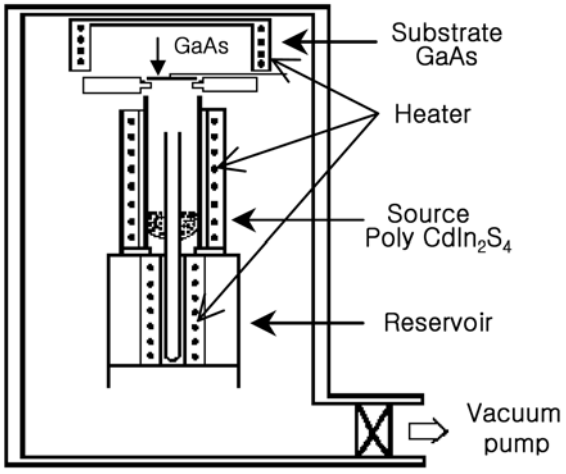

Fig. 1. Schematic diagram of the HWE apparatus.

Results and Discussion

A. Photocurrent measurement

Figure 2 shows the PC spectra of the $CdIn_2S_4$ film for temperatures ranging from 10 to 293 K. In the PC measurements, the absorbed photons with energies higher than the band-gap energy create electron and hole carriers. Therefore, the electrons in the valence band, excited by the absorbed light, transited from the $\Gamma_4(z)$, $\Gamma_5(x)$, or $\Gamma_5(y)$ of the valence band to the exciton below the conduction band of $\Gamma_1(s)$. Immediately, the transited electrons flowed out to both sides of the electrodes. Consequently, the PC peaks corresponding to the exciton in the short wavelength region were guided to the electrodes. Here, the A-, B-, and C-excitons, caused by the intrinsic transition from the $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$ valence band to the exciton below the conduction band, are labeled as Ex(A), Ex(B), and Ex(C), respectively. Also, most of the incident light was absorbed on the surface of the sample when the light illuminated it. In the short wavelength region, the observed PC is small except near the peaks since the electrons and holes generated by the incident light disappear as a result of recombination [14]. As shown in Fig. 2, the two peaks with strong intensities at temperatures between 293 to 50 K revealed themselves in the short wavelength region. Two peaks of 473.5 (2.6185 eV) and 452.7 (2.7388 eV) nm at a temperature of 293 K corresponded to Ex(A) and Ex(B), respectively. Also, in the long wavelength region, a peak of low intensity originating from the native defects in the film appeared at 521.4 nm (2.3779 eV). However, the PC spectra in the temperature range of 30 to 10 K appeared as three peaks in the short wavelength region. The three peaks are the A-, B-, and C-excitons as labeled in Fig. 2, and they correspond to Ex(A), Ex(B), and Ex(C), respectively. The low intensity peak caused by the native defects was observed as well, at all temperatures in the long wavelength region. Generally, the excitons are generated by the attraction between holes

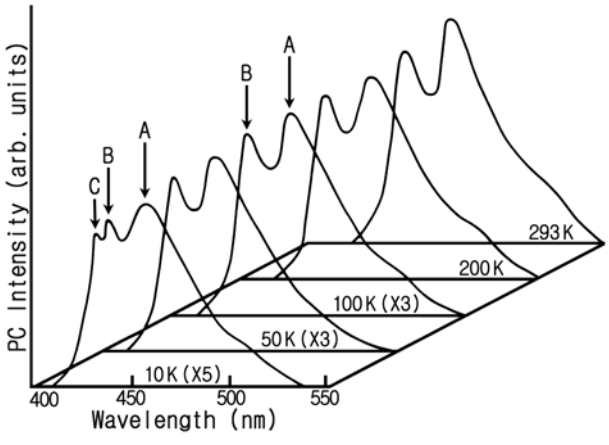

Fig. 2. PC spectra of the $CdIn_2S_4$ film for temperatures ranging from 10 to 293 K.

and electrons when the carrier concentration is low. By contrast the contrary, electrons are scattered due to the mutual interaction between electrons when the carrier concentration is high [15]. Therefore, the scattering probability between carriers and the exciton electrons excited from the split valence band levels such as $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$ increased at high temperatures. Consequently, the scattering probability of carriers at temperatures from 293 to 50 K increased owing to a high carrier concentration obtained from the Hall measurement. Therefore, only the Ex(A) and Ex(B) peaks are seen. However, the carrier densities at temperatures below 30 K were low since the carriers were in a frozen state. For these reasons, the Ex(A), Ex(B), and Ex(C) peaks could be observed simultaneously at a low temperature.

B. Valence band splitting

Figure 3 shows the energy band structure and selection rules for transitions in chalcopyrite $CdIn_2S_4$. According to the selection rules [16], at the Γ point, the conduction band has an s-like state and $\Gamma_1(s)$ symmetry. The valence band has a p-like state which is split into the three doubly degenerate levels such as $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$. The uppermost $\Gamma_4(z)$ has an effective mass that strongly depends on the k-direction. Generally, the crystal field of the ternary compound has been investigated by reflectance and photoconductivity measurements [17-20].

In this study, the valence band splitting of $CdIn_2S_4$ caused by the crystal field was observed using the PC measurements. The crystal field splitting, Δ_{cr}, is the energy spacing between $\Gamma_4(z)$ and $\Gamma_5(x)$ bands. The energy obtained of Δ_{cr} is 0.1218 eV. This value is the energy difference between the peak Ex(A), 457.8 nm (2.7083 eV), and the peak Ex(B), 438.1 nm (2.8301 eV), at 10 K. This value is about five times larger than those of CdS [21]. The spin orbit splitting, Δ_{so}, is the energy difference between $\Gamma_5(x)$ and $\Gamma_5(y)$ bands. This value is 0.0175 eV due to the energy difference between the peak Ex(B), 2.8301 eV, and the peak Ex(C), 2.8476 eV, at 10 K. The split gap energies between the three peaks at several temperatures are coincident to the values of 0.122 and 0.017 eV, respectively. For the chalcopyrite structure, the splitting of the valence band is generated by deviation of the lattice constants. However, the process of the valence band splitting on $CdIn_2S_4$ is not yet known.

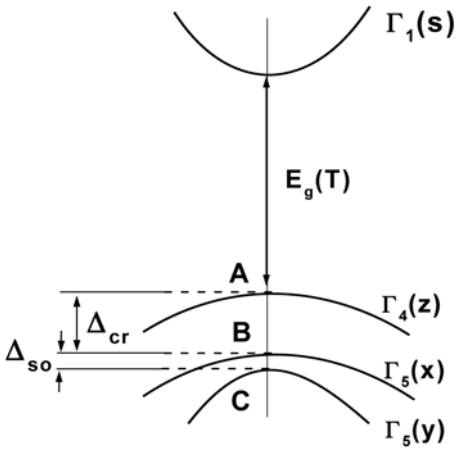

Fig. 3. Energy band structure of the chalcopyrite $CdIn_2S_4$ at Γ point according to the selection rule.

C. Temperature dependence of the band-gap energy and the PC intensity

Figure 4 displays the variation of the band-gap energy obtained from the PC spectra as a function of temperature. The A band of $\Gamma_4(z)$ means the band-gap energy of the $CdIn_2S_4$ film, and it was obtained by adding the Ex(A) to the exciton binding energy. Generally, the exciton binding energy is a value independent of the temperature variation. Also it is known to be 3.2 meV which was experimentally obtained through PL spectroscopy [22]. In addition, the fitted band gap was previously obtained from the optical absorption measurement [13]. The line curve of the fitted band gap may be described by Varshni's equation [23]:

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

where α is a constant and β is approximately the Debye temperature. Also, $E_g(0)$ is the optical energy gap at absolute zero. From the results of the optical absorption measurements, $E_g(0)$, α, and β were determined to be 2.7116 eV, 7.65×10^{-4} eV/K, and 425 K, respectively. As shown in Fig. 4, the A band obtained from the PC measurement is in good agreement with the curvature plotted by Eq. (1). As such, the band-gap energy at 300 K induced by the PC peaks was measured as 2.6166 eV, which is in good agreement with the value, 2.62 eV, measured at 300 K by Ref. [1].

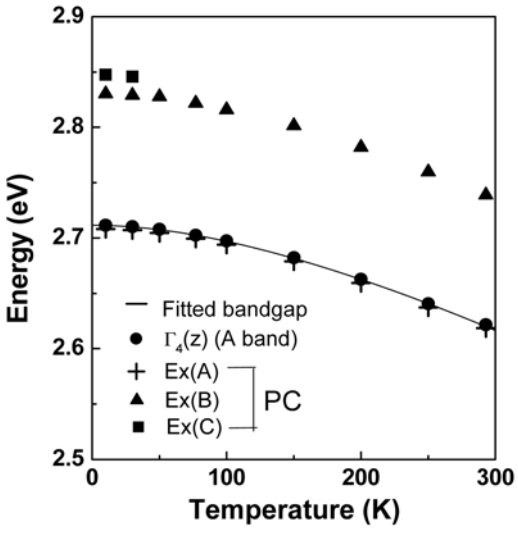

Fig. 4. Experimental values of the peak energies and the band-gap energy obtained from the PC spectra as a function of temperature.

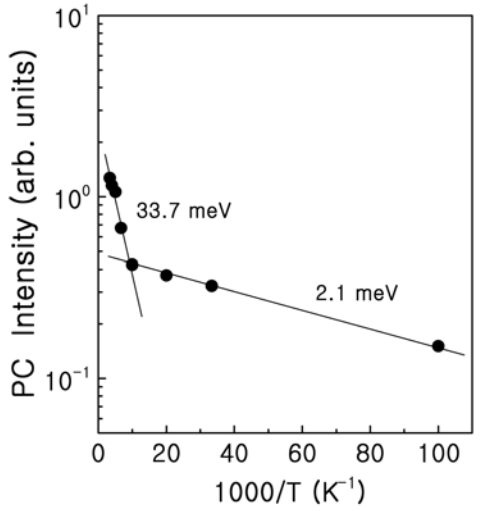

Fig. 5. Plot of log J_{ph} vs 1/T for the PC response of the PC peaks corresponding to Ex(A) as a function of temperature.

However, room temperature values of the direct gap ranging from 2.2 to 2.7 eV have been reported [1, 2, 24].

To understand the PC generation, we consider the total current density in an n-type semiconductor [14]. The current density of an n-type semiconductor in the dark is given by $J \approx en\mu_n E=\sigma E$ since the hole contribution can generally be neglected. Here, n and μ_n, are the electron carriers and the electron mobility, respectively. Also, E and σ are the electric field and the conductivity, respectively. Therefore, the PC density, J_{ph}, is described by:

$$J_{ph}=eG\mu_n\tau_n E=\sigma_{ph}E, \quad (2)$$

where τ_n and G are the lifetime of the electrons 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 PC peaks corresponding to Ex(A) as a function of temperature. As Fig. 5 shows, the PC intensities decrease with decreasing temperature. However, the $\mu_n\tau_n$ of Eq. (2) is generally known to have a tendency to increase with decreasing temperature. Therefore, Eq. (2) doesn't explain our result. However, this situation is similar to the result obtained from the PC experiment on a CdTe crystal grown by the Bridgman method [25]. Fundamentally, the crystal grown using the gradient freezing Bridgman method includes many trapping centers in the band gap. The trapping centers are generated due to native defects and impurities. These centers, which capture the released carriers, do not play an important role in the actual recombination process. The strength of the excitonic PC, thus, is related to τ. Therefore, if the electron carrier lifetime of Eq. (2) is long enough, we can collect the charge and observe a strong PC signal. Otherwise, in the presence of traps or defects, carriers are readily trapped and cannot be collected, so the PC signal is reduced. Under this condition, the PC is limited by carrier trapping. The condition of trapping-limited PC 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. Simmons and Taylor proposed a theory for the temperature dependence of J_{ph} for p-type amorphous chalcogenide semiconductors [26]. They divided the temperature range into three different photoexcitations as follows.

(i) 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. Our results obtained in this PC measurement are similar to temperature region (ii). In the high- and the low-temperature regions, two dominant levels should be observed. From the hypothesis of Simmons and Taylor, σ_{ph} for the region (ii) can be expressed by:

$$\sigma_{ph}=e\mu_n[GN_o/(\upsilon\sigma_t N_t)^{1/2}\exp[-(E_c-E)/2kT], \quad (3)$$

where υ is the thermal velocity of electrons, σ_t, the capture cross section of E, and k, the Boltzmann constant. Here, N_c and N_v, which are the effective density of states 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. (3) can be concisely expressed as $J_{ph} \propto A\exp(-\Delta E_{ph}/2kT)$, where ΔE_{ph} is the activation energy and A is substituted for $e\mu_n[GN_o/(\upsilon\sigma_t N_t)^{1/2}$. As Fig. 5 shows, the PC intensity rapidly decreases at high-temperatures between 300 and 100 K. Also, at low-temperatures between 100 and 10 K, the PC intensity shows a moderate slope. Thus, ΔE_{ph} obtained from the plots of log J_{ph} vs 1/T in these two temperature regions are estimated to be 33.7 and 2.1 meV, respectively. Let us compare the PC results with these of the PL experiment on the $CdIn_2S_4$ film [22]. We find that the activation energy of 2.1 meV is close to the binding energy, 3.2 meV, of the free exciton. Also, the activation energy of 33.7 meV is similar to the binding energy, 39 meV, of the neutral donor bound exciton (D^o, X) due to the sulfur vacancy. Therefore, we suggest that trapping centers caused by native defects limit the PC signal with decreasing temperature.

Conclusions

$CdIn_2S_4$ films were grown on a semi-insulator substrate of GaAs using the HWE method. From the PC measurement, three peaks appeared in the short wavelength region in the PC spectra at a temperature range of 30 to 10 K while only two peaks with strong inten-

sities at temperatures from 293 to 50 K were observed. This reduction was influenced by the scattering probability between carriers since the carriers at low temperatures below 30 K are in a frozen state. As such, the three peaks were observed at low temperature. In addition, these three peaks caused by the transition from the $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$ valence band to the exciton below the conduction band were associated with the Ex(A), Ex(B), and Ex(C) excitons, respectively. Also, from the split gap energies between the three peaks, we found that the Δ_{cr} and the Δ_{so} values were taken to be the values of 0.122 and 0.017 eV, respectively. Thus, the optical band gap obtained from the PC measurement was well described by the Varshni's equation, $E_g(T)=2.7116\ eV-(7.65\times10^{-4}\ eV/K)T^2/(425+T)$. It has now become clear that the band-gap energy can be easily extracted through PC spectroscopy. Also, contrary to our expectation, the PC intensities decreased with decreasing temperature. In the log J_{ph} vs 1/T plot, two dominant levels were observed, one at high temperatures and the other at low temperatures. These levels, corresponding to 2.1 and 33.7 meV were associated with the binding energies of the free exciton and the neutral donor bound exciton, respectively. Consequently, we suggest that in the $CdIn_2S_4$ film, the trapping centers due to native defects limit the PC signal with decreasing temperature.

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