Temperature dependences of the band-gap energy and the PC intensity for CuInSe$_2$ thin films

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Abstract : 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. The crystal field splitting and the 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 by 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.

1. INTRODUCTION

Copper indium diselenide (CuInSe$_2$, 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 of solar cells in the UV visible range.[4]

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

2. RESULTS AND DISCUSSION

2.1 Photocurrent spectra

Figure 1 shows the PC spectra measured from undoped p-type CIS layer of R06-1 at the 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 the intrinsic transition caused by the band-to-band transition.[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 $\Gamma_6(B)$ 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 suggests 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.
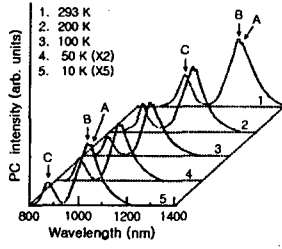
FIG. 1. PC spectra measured from undoped p-type CIS layer of R06-1 at temperatures ranging from 10 to 293 K.

2.2 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] The Δ_{cr} is the energy difference between $\Gamma_7(A)$ and $\Gamma_6(B)$. The obtained energy 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 bands at the Brillouin-zone center can be satisfactorily explained by the Hopfield quasicubic model:[13]

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

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 extracting 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 the value published on the valence band splitting of CIS observed by the PC measurement yet, except the values obtained from the reflectivity experiment.[14,15]
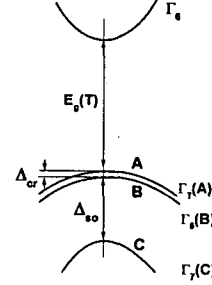

FIG. 2. Energy band structure of the chalcopyrite CIS layer at Γ point according to the selection rule.

3. CONCLUSIONS

The PC response on undoped p-type CIS layers grown by using the HWE method was performed at temperatures ranging from 10 to 293 K. The Δ_{cr} and Δ_{so} of CIS obtained the PC experiment were 0.0059 and 0.2301eV, respectively. The temperature dependence of the optical band gap could be well expressed by 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.

REFERENCES

[1] J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*, (Pergamon, Oxford, 1975).