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Band gap energy and valance band splitting of photocurrent behaviour for $AgInS_2$ epilayers grown by hot wall epitaxy

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A silver indium sulfide ($AgInS_2$) epilayer was grown by the hot wall epitaxy method, which has not been reported previously in the literature. The grown $AgInS_2$ epilayer was found to have the chalcopyrite structure and evaluated to be a high quality crystal. From the photocurrent(pc) measurements in the temperature range from 30 K to 300 K, only two peaks A and B were observed, whereas three peaks A, B, and C were seen in the PC spectrum at 10 K. These peaks are ascribed to band-to-band transitions. The valence band splitting of $AgInS_2$ was investigated by means of the photocurrent measurements. Crystal field splitting, Δ_{cr}, and spin orbit splitting, Δ_{so}, have been obtained to be 0.150 eV and 0.009 eV at 10 K, respectively. Also, the band gap energy at room temperature has been determined to be 1.868 eV. Further, the temperature dependence of the energy band gap, $E_g(T)$, was determined.

Key words: $AgInS_2$, hot wall epitaxy, photocurrent, valence band splitting, energy band gap.

Introduction

$AgInS_2$ has been known to be a ternary compound semiconductor, with a wide band gap in the visible region of the spectrum. Ordinary, ternary chalcopyrite crystals are currently of technological interest since they show promise for application in the areas of visible and infrared light-emitting diodes, infrared detectors, optical parametric oscillators, upconverters, and far infrared generators. In order to realize these applications, it is of primary importance to grow high quality epilayers and to characterize the fundamental material parameters such as band gap energy. However, the fundamental physical properties of these compounds have rarely been investigated since it is hard to obtain a large ternary chalcopyrite crystal. Also, studies of the temperature dependence of the band gap for only a limited number of ternary chalcopyrite crystals have been reported in the literature [1-3]. Generally, absorption experiments are used to measure the band gap energy. However, this method is known to be in accurate to obtain the band gap energy due to the difficulty in defining the position of the absorption edge.

In the chalcopyrite structure of $AgInS_2$, the splitting of the valence band is known to be dominated by the uniaxial lattice compression. Therefore, the uppermost valence bands of $AgInS_2$ are profoundly influenced by the proximity of the d levels of the valence band of the noble-metal [4-6]. Then, both p and d orbitals of $AgInS_2$ are known to be partially elevated due to this degeneracy. These states participate in the photoconduction process, resulting in extending the photo-response on the higher energy side. Such studies were carried out for a single crystal of chalcopyrite $AgInS_2$ that was grown by chemical transport and for others grown by the Bridgman method [7]. The band structure of chalcopyrite $AgInS_2$ has been generally investigated by absorption spectroscopy, reflectivity, and electroreflectivity data [8]. However, optical properties and the epitaxial growth of $AgInS_2$ have not been well understood. Only a few researchers [9, 10] have investigated the electrical properties and the growth of polycrystalline $AgInS_2$ films.

In this paper, we first attempted to grow $AgInS_2$ epilayers using hot wall epitaxy (HWE) which is designed specifically to grow epilayers under the conditions of close thermodynamic equilibrium [11]. Electrical and optical measurements of the grown $AgInS_2$ epilayer have been carried out in the temperature range from 10 to 300 K. Also, the valence band splitting and the temperature dependence of the band gap energy have been determined using the photocurrent (PC) spectra.

Experimental Procedure

The starting materials used were high purity Ag, In, and S to grow $AgInS_2$ epilayers and the purity of these materials is 6 N. After weighing in stoichiometric proportions, these materials were sealed in a quartz tube whose lining was coated with carbon. The sealed

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ampoule was placed in a synthesis furnace and continuously rotated at a rate of 1 revolution per minute. In order to avoid the explosion of the ampoule due to the high sulfur vapor pressure, the temperature of the ampoule was gradually increased to 1050 °C. This temperature was then maintained for 48 hours. After the growth of the polycrystalline $AgInS_2$ ingot, $AgInS_2$ epilayers were grown on semi-insulating (100) GaAs by the HWE method using the polycrystalline $AgInS_2$ ingot as source material [12]. The grown $AgInS_2$/GaAs was analyzed by double crystal x-ray diffraction (Bede Scientific Co. FR 590) to obtain the optimum growth conditions. The most suitable substrate and source temperatures to grow the $AgInS_2$/GaAs layes was found to be 410 °C and 680 °C, respectively. The thickness of the as-grown $AgInS_2$/GaAs layes was measured with an α-step profilometer (Tenco, α-step 200) and was 2.6 μm. Furthermore, the chalcopyrite structure was confirmed by an x-ray diffraction (XRD) study.

Hall effect measurements on the $AgInS_2$ epilayer were carried out using the van der Pauw method in the temperature range from 10 K to 300 K. Electrodes were made on both ends of the sample to measure the PC spectra. After the sample was mounted on a holder in a low-temperature cryostat, the PC spectrum measurements were made whilst monochromatic light emitted from a halogen lamp passed through a chopper to illuminate the sample and the temperature was controlled from 10 K to 300 K.

Results and Discussion

Structural and Electrical Properties

Figure 1 shows the XRD pattern of the $AgInS_2$ epilayer grown on the GaAs substrate. This pattern contains the diffraction peaks of GaAs (400) and $AgInS_2$ (200). The observation of only the (200) peak indicates that the $AgInS_2$ has grown epitaxially onto the GaAs (100) substrate and its structure is chalcopyrite. From the results of the x-ray double crystal rocking curve (DCRC) to evaluate the crystallographic quality of the epilayer, the minimum value of the full width at half maximum (FWHM) for the grown $AgInS_2$ was obtained to be 121 arcsec, as shown in Fig. 2. The electrical properties of the grown $AgInS_2$ epilayer were obtained from the Hall effect measurements using the van der Pauw technique. The carrier density and Hall mobility of the epilayer at 300 K were determined to be 9.35×10^{17} cm^{-3} and 294 $cm^2/V{\cdot}s$, respectively, and the crystal was confirmed to be n-type. As the temperature was decreased, the carrier density gradually diminished since the carriers existed in a frozen state. Therefore, the value measured at 10 K was 1.68×10^{16} cm^{-3} and the Hall mobility in the same temperature was also 164 $cm^2/V{\cdot}s$.

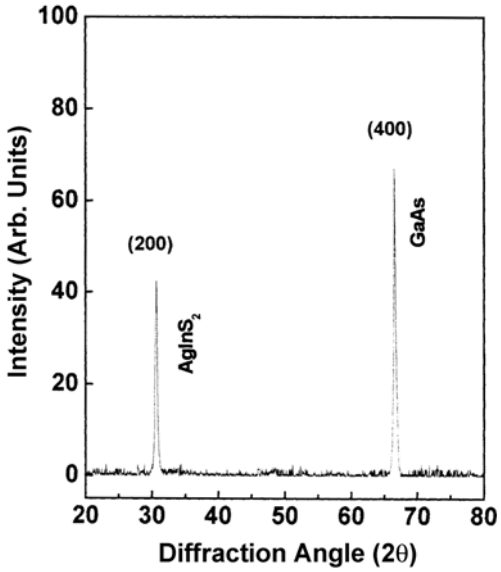

Fig. 1. X-ray diffraction pattern of the $AgInS_2$ epilayer grown on the GaAs substrate.

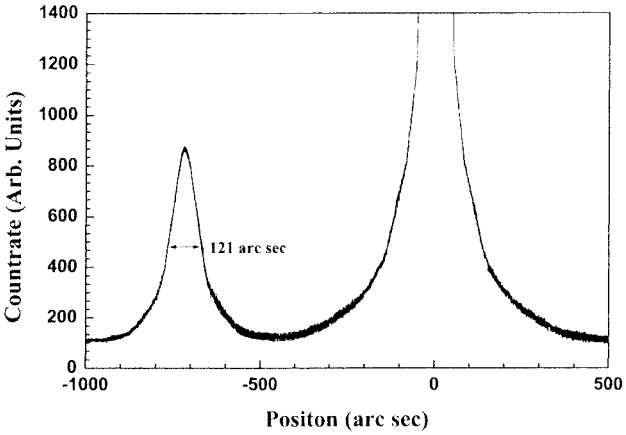

Fig. 2. X-ray double crystal rocking curve of the $AgInS_2$ epilayer.

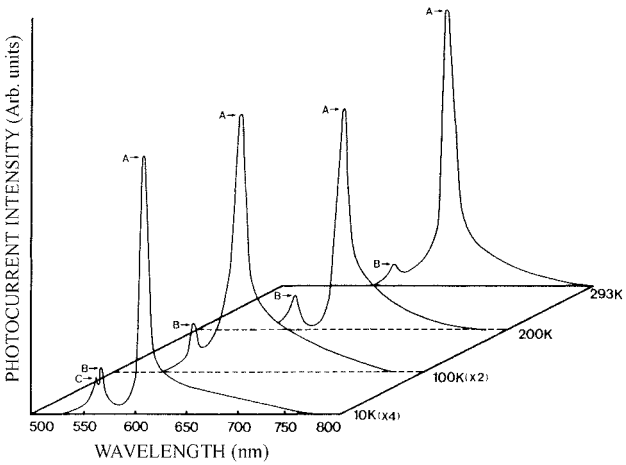

Fig. 3. Photocurrent spectra of the $AgInS_2$ epilayer measured at different temperatures.

Photocurrent Spectra

Figure 3 shows the PC spectra of the $AgInS_2$ epilayer measured in the temperature range from 10 K to 300 K. The left part of the peak in the PC spectra steeply decreased. When the light illuminates the sample, most of the incident light is absorbed at the surface of the sample and the electrons and holes generated by the absorbed light disappear as result of mutual recombination [13]. However, PC peaks were observed only when the electrons transited from the valence band to the conduction band by the absorbed light. Therefore, the PC peaks flowed out through the electrodes. At 300 K, the PC peaks were observed at 663.6 nm (1.868 eV) and 614.3 nm (2.018 eV). The peak at 1.868 eV has a very sharp and strong intensity, which is consistent with the A peak due to the band-to-band transition. Here, the band-to-band transition means that electrons are transited from $\Gamma_4(z)$ of the valence band to $\Gamma_1(s)$ of the conduction band. This peak has been reported to be 1.87 eV by Shay *et al*. [14], and this value was taken from electro-reflectance measurements. Also, this peak has been determined to be 1.88 eV by Okamoto and Kinoshita [15], which was obtained from the optical transmittance. Our observation is in good agreement with the value measured at 300 K by Shay *et al*. [19]. The peak observed at 2.018 eV, which appears on the left shoulder of the 1.868 eV peak in the shorter wavelength region, corresponds to the B peak due to the transition from $\Gamma_5(x)$ of the valence band to $\Gamma_1(s)$ of the conduction band. The B peak has been reported to be 2.02 eV [14]. However three peaks appeared in the PC spectrum at 10 K. These peaks were observed at 609 nm (2.036 eV), 567.3 nm (2.186 eV), and 564.9 nm (2.195 eV). Here, the peaks at 2.036 eV and 2.186 eV correspond to the A and B peak of the valence band, respectively. The peak at 2.195 eV corresponds to the C peak of the valence band due to the transition from $\Gamma_5(y)$ of the valence band to $\Gamma_1(s)$ of the conduction band. For the temperature range from 30 K to 300 K, we only observed two peaks A and B. The C peak was not observed in the PC spectra measured in the same temperature range. It is known that it is associated with the electrons scattered in the valence band due to the mutual interaction between electrons when the carrier concentration is high [16]. From the Hall effect result measured to be of the order of 10^{17} cm^{-3} at high temperature, our sample could existed with a higher scattering probability, therefore, the electrons could excite between the split valence band levels such as $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$. Whereas, the scattering probability of the carriers at 10 K is low since the carriers in the valence band are in a frozen state and the carrier density obtained from the Hall effect measurement at 10 K is low. Consequently, the spectra containing the A, B, and C peaks was expected to be seen only at 10 K. Also, a PC peak due to the imperfections in the long wavelength region was not observed. This means that the $AgInS_2$ epilayer grown is a high quality crystal.

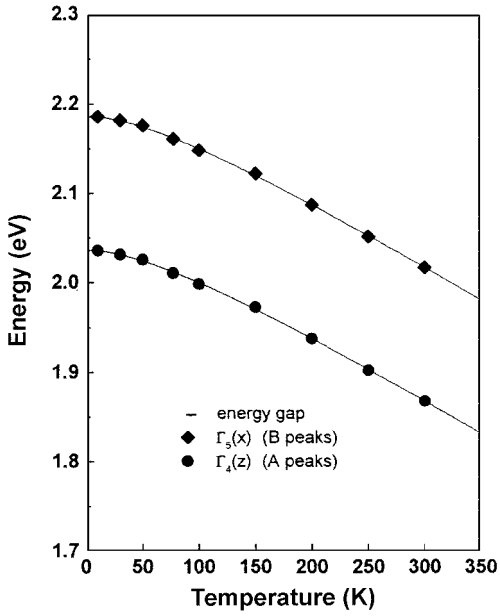

Fig. 4. Experimental values of the photocurrent peak energies and the band gap energy as a function of temperature.

Temperature Dependence of the Energy Band Gap

Figure 4 displays the variation of the band gap energy of $AgInS_2$ and the energy gap of the A and B peak obtained from the PC peaks as a function of temperature. As shown in Fig. 4, the energy gap variation of the A and B peaks corresponding to the split-levels of the $\Gamma_4(z)$ and $\Gamma_5(x)$ valence band shows a nonlinear relationship. Generally, the energy gap of these peaks varies proportionately to the square of the temperature when the measurement temperatures is much lower than the Debye temperature, whereas the energy gap varies linearly with the temperature when the measurement temperature is much higher than the Debye temperature. The energy band variation of these peaks as a function of temperature fits well numerically with the following formula: [17]

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

where α is a constant and β is approximately the Debye temperature. When α and β are taken to be 7.78×10^{-4} eV/K and 116 K, respectively, the curve plotted by eq. (1) closely fits the experimental values, as shown in Fig. 4. The Debye characteristic temperature $\theta_\perp$ [18] of $AgInS_2$ was found to be 117 K at 300 K and is in reasonable agreement with our results. Also, Eg(0) is the energy band gap at 0 K, which is estimated to be 2.036 eV at the valence band state A and 2.186 eV at the valence band state B. The energy band gap at 300 K fitted by eq. (1) was 1.868 eV. This band gap energy shows a slightly smaller value than that obtained from

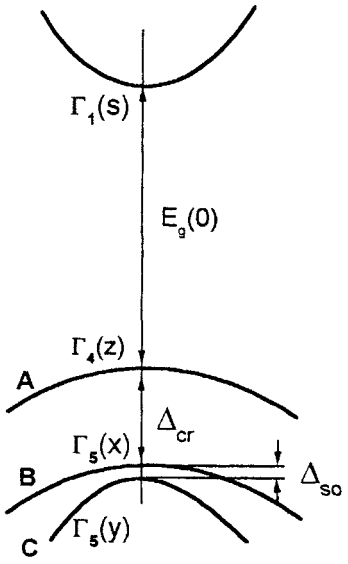

Fig. 5. Energy band structure of chalcopyrite $AgInS_2$ at the Γ point according to the selection rule.

photoconductivity by Joshi *et al*. [7], which was 1.91 eV at 300 K. But our observation is in good agreement with the value measured at 300 K by Shay *et al*. [14], which was found from electro-reflectance measurements. Generally, the band gap energy of $AgInS_2$ at room temperature is known to be 1.87 eV.

Figure 5 displays the point of the chalcopyrite $AgInS_2$ according to the selection rule [8]. This figure shows that the conduction band of the s-like state has a $\Gamma_1(s)$ symmetry and the valence band of the p-like state has been split into three double degenerate states such as $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$. In three valence bands, the uppermost one is the $\Gamma_{v4}(z)$ valence band with an effective mass that strongly depends on the direction of k, and the middle one is the $\Gamma_5(x)$ valence band. The lower one is the $\Gamma_5(y)$ valence. The crystal field of the I-III-IV_2 compound family has been examined by measuring the electroreflectance [4, 14, 19] and the photoconductivity [7]. In this work, the valence band splitting of the $AgInS_2$ epilayer arising from the crystal field could be observed in the PC measurements. The valence band energies of $\Gamma_4(z)$, $\Gamma_5(x)$ and $\Gamma_5(y)$ corresponded to the A, B, and C peak energies, respectively. The crystal field splitting, Δ_{cr}, indicates the energy difference between $\Gamma_4(z)$ and $\Gamma_5(x)$, and the spin orbit splitting, Δ_{so}, is the energy difference between $\Gamma_5(x)$ and $\Gamma_5(y)$. The Δ_{cr} was 0.150 eV, as calculated from the energy difference between the A peak, 2.036 eV, and the B peak, 2.186 eV, at 10 K. The Δ_{cr} has been previously reported by Shay *et al*. [14] to be 0.15 eV based on electro-reflectance measurements, and also, 0.16 eV was obtained from photoconductivity measurements by Joshi *et al*. [7]. This value is almost an order of magnitude larger than those of II-VI analogues [20]. Also, the Δ_{so} reported by Shay *et al*. [14] was less than 0.01 eV, which is small enough to be negligible. However our result of the Δ_{so} was 0.009 eV. This value was determined from the energy difference between the B peak, 2.186 eV, and the C peak, 2.195 eV, at 10 K. Therefore, unlike the conclusion mentioned by Shay *et al*., it has been shown here that the gap between $\Gamma_5(x)$ and $\Gamma_5(y)$ in the valence band is not the degenerate band but the split band.

Conclusions

$AgInS_2$ epilayers on a GaAs substrate have been grown for the first time using the HWE method. From the results of the XRD and DCRC measurements, the grown $AgInS_2$ epilayers were evaluated to be high quality crystal and with the chalcopyrite structure. The carrier density and Hall mobility of the $AgInS_2$ epilayer at 300 K were estimated to be 9.35×10^{17} cm^{-3}, 294 $cm^2/V{\cdot}s$, respectively. From the photocurrent measurement, we only observed two peaks A and B in the temperature range from 30 K to 300 K, whereas three peaks A, B, and C corresponding to the band-to-band transition appeared in the PC spectrum at 10 K. The temperature dependence of the energy band gap for $AgInS_2$ was also first obtained from PC measurements. The variation of the band gap energy with temperature was well described by the equation of $E_g(T) = Eg(0) - (7.78 \times 10^{-4})T^2/(116+T)$. Also, Eg(0) is estimated to be 2.036 eV at the valence band state A and 2.186 eV at the valence band state B. Further the band gap energy of $AgInS_2$ at room temperature turned out to be 1.868 eV. The Δ_{cr} and Δ_{so}, which is the valence band splitting of $AgInS_2$, were obtained to be 0.150 eV and 0.009 eV at 10 K, respectively. We confirmed that the gap between $\Gamma_5(x)$ and $\Gamma_5(y)$ in the valence band is not the degenerate band but the split band.

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