

Growth and electrical/optical properties of the photoconductive ZnAl_2Se_4 layers grown by hot wall epitaxy method

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The photoconductive $\text{ZnAl}_2\text{Se}_4(112)/\text{GaAs}(100)$ layers were successfully grown by using the hot wall epitaxy method. From the Hall effect measurement, scattering at the high-temperature range ($T > 150$ K) was mainly related to the acoustic phonon mode of lattice vibration and scattering at the low-temperature range ($T < 77$ K) was superior to the dislocation scattering. In the photocurrent (PC) spectroscopy, we observed the A, B, and C peaks corresponding to 351.6(3.5263 eV), 343(3.6147 eV), and 333.5 nm(3.7177 eV) at 10 K, respectively. Three peaks of A, B, and C were caused by the band-to-band transitions from the valence band state of $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$ to the conduction band state of $\Gamma_1(s)$, respectively. Thus, a characteristic splitting of the valence band governed by the selection rule was first extracted through the method of PC spectroscopy. We noted that the crystal field splitting and spin orbit splitting were 0.088 and 0.103 eV, respectively. PACS numbers: 78.20.-e, 78.56.-a.

Key words: A1. Characterization, A1. Photocurrent, A3. Hot wall epitaxy, B1. ZnAl_2Se_4 , B2. Semiconducting ternary compounds.

Introduction

Zinc aluminum selenide (ZnAl_2Se_4), which crystallized with the defect chalcopyrite structure in the I-4 space group, is an attractive photoconduction material because of its applicability to photovoltaic devices [1-3]. Thus, they have high photosensitivity and strong luminescent properties. For these applications, it is of primary importance to grow high quality crystals and to find out the fundamental material parameters. It has been reported that the bulk of ZnAl_2Se_4 crystals grew through the chemical transport reaction method, and its characterization investigated through absorption, photoluminescence, and Raman experiments, etc [3, 4]. It is also important to measure the change in photoconductivity of ZnAl_2Se_4 caused by incident radiation. Photoconductivity is complex process involving thermal and hot carrier relaxation processes, charge carrier statistics, effects of electrodes, and several mechanisms of recombination. So, the photocurrent (PC) exploring in ZnAl_2Se_4 can enforce the applications in photo detection and radiation measurements [5]. However, the information on ZnAl_2Se_4 is still very limited and, no PC spectroscopy analysis has been reported yet. In PC measurements, the absorption of photons with higher energy than the bandgap energy creates electron

and hole carriers in ZnAl_2Se_4 . These carriers instantly flow out through the electrodes, and then the PC peak corresponding to the bandgap can be obtained. Therefore, it is possible to obtain the direct bandgap energy as a direct reading of the PC-peak position. Moreover, the electronic transitions from the levels of the valence band to the levels of the conduction band on these generated carriers are restricted by a selection rule based on the symmetry in the Brillouin zone [6]. Therefore, the transitions between these states are polarized because of the effects of the crystal field and the spin orbit splitting.

In this work, we grew the photoconductive ZnAl_2Se_4 layers by using hot wall epitaxy (HWE) method. The grown ZnAl_2Se_4 layers were investigated by the double crystal X-ray diffraction (DCXD), atomic force microscopy (AFM), Hall effect, and PC spectroscopy. Based on these results, we discussed the growth and electrical/optical properties of the photoconductive ZnAl_2Se_4 layers. The valence band splitting restricted by a selection rule was also discussed.

Experimental Procedures

Prior to the ZnAl_2Se_4 layer, ZnAl_2Se_4 polycrystalline was formed. The starting materials were the 6N purity shot-types of Zn, Al, and Se. After the materials were weighed in stoichiometric proportions, they were sealed in a quartz tube to maintain the vacuum atmosphere. Then the sealed ampoule was placed in the horizontal synthesis furnace for the formation of the

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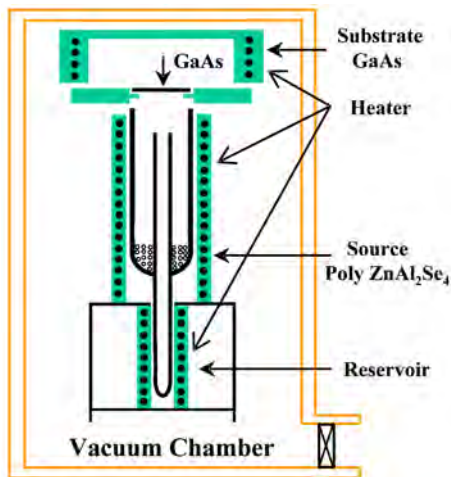


Fig. 1. Schematic diagram of the HWE apparatus used for the ZnAl_2Se_4 layers.

ZnAl_2Se_4 polycrystalline. It was continually rotated at a rate of 1 revolution per minute. In order to avoid an explosion of the ampoule due to the selenium vapor pressure, the temperature of the ampoule was increased gradually to 1050°C , which was then maintained for 48 hrs. Fig. 1 presents a schematic diagram of the HWE apparatus used for the ZnAl_2Se_4 layer. To grow the ZnAl_2Se_4 layer, the ingot of ZnAl_2Se_4 polycrystalline was used as a HWE source. The ZnAl_2Se_4 layers were grown on semi-insulating GaAs (100). Here, the substrate was cleaned ultrasonically for 1 min in successive baths of trichloroethylene, acetone, methanol, and 2-propanol and etched for 1 min in a solution of $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O}$ (5 : 1 : 1). The substrate was degreased in organic solvents and rinsed with deionized water (18.2 MW). After the substrate was dried off, the substrate was immediately loaded onto the substrate holder in Fig. 1 and was annealed at 580°C for 20 min to remove the residual oxide on the surface of the substrate.

However, DCXD measurement was conducted for the optimum growth condition and the analysis of the structural characterization of the grown ZnAl_2Se_4 layers. At this time, the thickness and stoichiometric composition of the ZnAl_2Se_4 layers were measured by using an α -step profilometer and an energy dispersive X-ray spectrometer (EDS), respectively. In order to measure the surface morphology, the atomic force microscopy (AFM) was used. Also, the electrical property was achieved by Hall effect measurement of the van der Pauw method with various temperatures. In order to take PC measurements, two Au electrodes with a coplanar geometry on ZnAl_2Se_4 were fabricated by an e-beam evaporator and an Ohmic contact of electrodes was confirmed by the 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 spectrum measurement was done while monochromatic light emitted from a

xenon lamp illuminated the sample. At this time, the PC experiment was measured while varying the temperature from 10 to 293 K.

Results and Discussion

ZnAl_2Se_4 layer growth and electrical property

As shown in Fig. 1, the source material of HWE was used to the ingot of synthesized ZnAl_2Se_4 polycrystalline. Also, the temperature of this source material was fixed at 620°C throughout experimental repetition process and the substrate temperature was varied from 380 to 420°C . In order to find the optimum growth conditions, DCXD rocking curve was measured. Here, the optimum growth condition was determined when the full width at half maximum (FWHM) of the grown layers was a minimum.

Fig. 2 shows the DCXD rocking curves on the ZnAl_2Se_4 layers grown as a function of the substrate

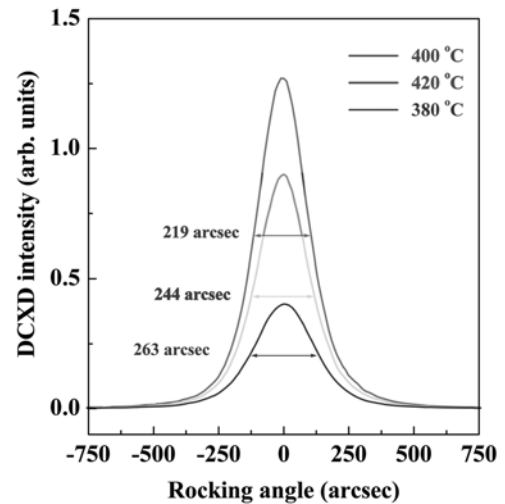


Fig. 2. DC-XRD rocking curves on the ZnAl_2Se_4 layers grown as a function of the substrate temperature.

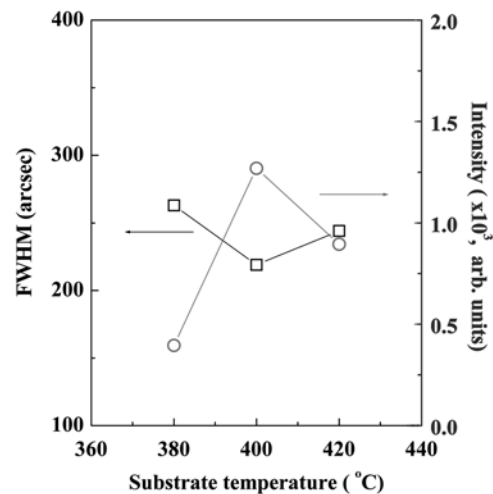


Fig. 3. Intensity and FWHM value of the DC-XRD rocking curves on the ZnAl_2Se_4 layers grown as a function of the substrate temperature.

temperature. The DCXD observation measured along the diffraction angle of the (112) phase indicates that these layers were grown epitaxially along the (112) direction on to the GaAs (100) substrate. As Fig. 2 shows, the layer grown at 400 °C has the highest DCXD intensity among several growth temperatures.

Fig. 3 displays the intensity and FWHM values of the DC-XRD rocking curve as a function of the substrate temperature. At the substrate temperature of 400 °C, the intensity of DC-XRD showed the highest peak and its FWHM was a minimum value of 219 arcsec. This FWHM value is nearly equal to that obtained from the ZnSe/GaAs epilayer grown by HWE method by Hong *et al.* [7]. These results indicate that the most suitable substrate temperature is 400 °C. The optimum temperatures of the substrate and the source turned out to be 400 and 620 °C, respectively. Thus, the ZnAl₂Se₄ layers grown under these optimum conditions were obtained with a thickness of 2.5 μm and a growth rate of 1.25 Å/sec.

On the other hand, the direction of the ZnAl₂Se₄ layers grown on the GaAs (100) substrate was the (112) plane. This converted phenomenon had ever been observed for the case of the CdTe epilayer grown on the GaAs (100). Faurie *et al.* [8] reported that the growth of the CdTe (100) or (111) planes on GaAs (100) was possible by controlling the annealing temperatures and times of the substrate. Therefore, we suggest that the growth of the disparately direction between layer and substrate relates to the pre-annealing process used to remove the residual oxide on the surface of the substrate.

Fig. 4 shows the AFM surface-morphology of the layer grown below optimum growth conditions. As shown in Fig. 4, the surface morphology of the grown layer was smooth. The root-mean-square value roughness, R_{ms} , of the surface was 0.57 nm. It suggests that the smooth surface and the low R_{ms} value are attributed to low growth rate of 1.25 Å/sec. Such low growth rate is one of the many benefits of having the HWE method. Thus, the stoichiometric composition on the ZnAl₂Se₄ layer was analyzed through the EDS measurement. 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 Zn components increased a little bit, while that of the Se components decreased. However, the component ratios of initial mole fraction were continuously maintained during the layer growth. The EDS result indicates that the grown ZnAl₂Se₄ layers were formed into the stoichiometric composition.

Fig. 5 shows the electron mobility as a function of the temperature T . As shown in Fig. 5, the mobility increased as a function of T^1 at the low-temperature range ($T < 77$ K). And its increase rate saturated at the intermediate temperature range due to the dominant

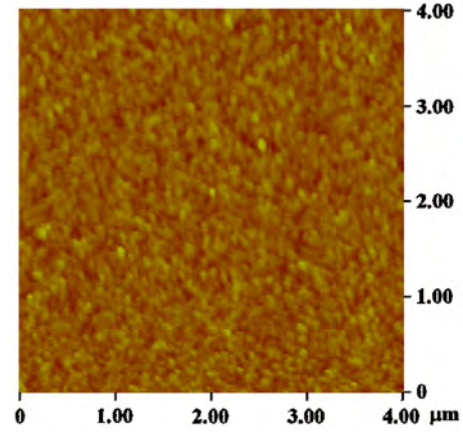


Fig. 4. AFM surface-morphology of the ZnAl₂Se₄ layers grown below optimum growth conditions.

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	
Zn	14.29	14.43	14.58
Al	28.57	28.46	28.45
Se	57.14	57.11	56.97

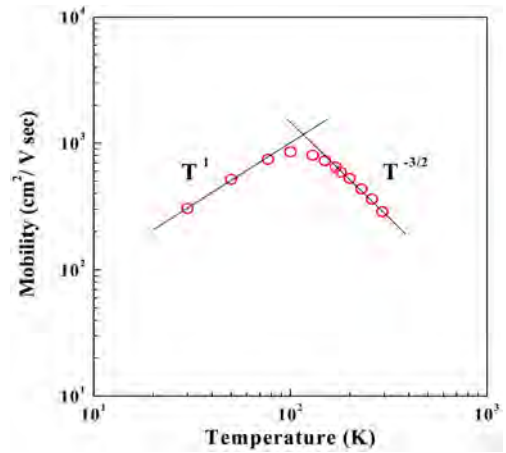


Fig. 5. Temperature dependence of the Hall mobility on the ZnAl₂Se₄ layers.

phonon scattering. At this time, the mobility reached a maximum of 856 cm²/V · sec at 100 K. Thereafter, the mobility decreases as a function of $T^{-3/2}$ by increasing the temperature at the high temperature range ($T > 150$ K). This indicates that scattering at the high-temperature range is mainly due to the acoustic phonon mode of lattice vibrations through a deformation potential [9]. At the low-temperature range having the temperature dependence of $\propto T^1$, it suggests that scattering can be explained by the dislocation scattering model [10]. The grown sample was always *n*-type owing to slight stoichiometric deviations originating from the native defects including an excess of selenium vacancies. Therefore, from the relation between the

reciprocal temperature and the carrier concentration, the activation energy caused by these native defects was observed to be 79.6 at high-temperature range and 15.5 meV at low-temperature range. It suggests that these parameters correspond to the shallow donor levels caused by the native defects below the edge of the conduction band.

PC characteristic of photoconductive ZnAl_2Se_4 layers

For photoconductive material, the volume lifetime is much larger than the surface lifetime; therefore, a maximum in the spectral PC response occurs when a transition is made from surface excitation (exciting photon energy greater than the band gap) to volume excitation (exciting photon energy less than the band gap) with increasing wavelength [11]. This maximum spectrum represents the intrinsic transition caused by the band-to-band transition [12]. Therefore, the bandgap energy can be directly extracted from the PC-peak position. Figure 6 shows the PC spectra of the photoconductive ZnAl_2Se_4 layers obtained at temperatures ranging from 10 to 293 K.

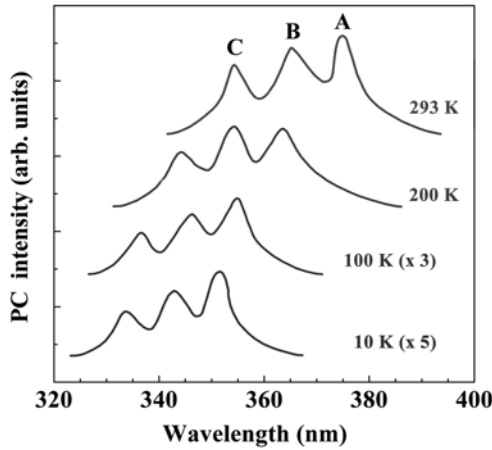


Fig. 6. PC response of the photoconductive ZnAl_2Se_4 layers obtained at temperatures ranging from 10 to 293 K.

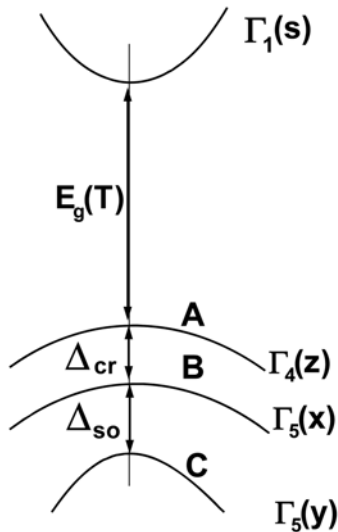


Fig. 7. Energy band structure of ZnAl_2Se_4 at the Γ point due to the selection rule.

photoconductive ZnAl_2Se_4 layers obtained at temperatures ranging from 10 to 293 K. Three peaks, suggesting the band-to-band transition caused by the intrinsic transition, appeared in the whole temperature range as shown in Fig. 6. These three peaks at 10 K were posited at 351.6(3.5263 eV), 343(3.6147 eV), and 333.5 nm(3.7177 eV) in the PC spectrum and were labeled as peaks A, B, and C, respectively. Moreover, three peaks even at the highest temperature of 293 K were continuously observed at 374.8(3.3080 eV), 365.1(3.3959 eV), and 354.3 nm(3.4994 eV) in the PC spectrum corresponding to the peaks A, B, and C, respectively. Room-temperature observation of these peaks caused by the band-to-band transition is uneasy, owing to the electrons scattering in the valence band. When the temperature is low, the scattering probability of the carriers is lower since the carriers in the valence band are in a frozen state. Therefore, the three peaks are easily observed at the low temperatures. However, the electrons in the valence band are scattered, owing to the mutual interaction between electrons when the carrier concentration in the semiconductor is high [13]. So, it is difficult to observe all three peaks when the temperature is high. Nevertheless, three peaks were observed at the high temperatures as well. This suggests that it is caused by the low carrier concentration in the semiconductor. In this study, the carrier concentration at 293 K is $8.53 \times 10^{16} \text{ cm}^{-3}$, which is sufficiently low. Also, one can assume that the defects must be lowly formed, meaning there was a high crystal quality of the grown ZnAl_2Se_4 layer. Therefore, these facts lead to a small scattering in the layer, so it suggests that all of these peaks were yielded at a high temperature of 293 K.

Fig. 7 shows the energy band structure of ZnAl_2Se_4 at the Γ point due to the selection rule [14]. This figure shows that the conduction band of the s -like state has a $\Gamma_1(s)$ symmetry, and that the valence band of the p -like state is split into three double degenerate states such as $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$. The $\Gamma_4(z)$ is the uppermost valence band. The effective mass in the $\Gamma_4(z)$ depends significantly on the direction of k . The $\Gamma_5(x)$ is the middle band, and the $\Gamma_5(y)$ is the lowest valence band. Therefore, peak A is ascribed to the electronic transition from the $\Gamma_4(z)$ valence band to the $\Gamma_1(s)$ conduction band. Peak B is associated with the electronic transition from the $\Gamma_5(x)$ valence band to the $\Gamma_1(s)$ conduction band, and peak C is ascribed to the electronic transition from the $\Gamma_5(y)$ valence band to the $\Gamma_1(s)$ conduction band. Generally, the crystal field of the ternary compound has been investigated by reflectance and photoconductivity measurements [15–17]. However, the valence band splitting of ZnAl_2Se_4 caused by the crystal field was directly extracted through the PC measurements. As shown in Fig. 7, the crystal field splitting, Δ_{cr} , is the energy spacing between $\Gamma_4(z)$ and $\Gamma_5(x)$ bands. The Δ_{cr} value is 0.0884 eV.

The value is the energy difference between peak A, 3.5263 eV, and peak B, 3.6147 eV, at 10 K. The spin orbit splitting, Δ_{so} , is the energy difference between $\Gamma_5(x)$ and $\Gamma_5(y)$ bands. This value is 0.1030 eV due to the energy difference between B peak, 3.6147 eV, and C peak, 3.7177 eV, at 10 K. At several temperatures, the split gap energies between the three peaks in the PC spectrum are coincident to the values of 0.088 and 0.103 eV, respectively. At this time, for the ZnAl_2Se_4 layer having chalcopyrite structure, it suggests that the splitting of the valence band is caused by the deviation of the lattice constants. However, we have yet to find any information on the valence band splitting of ZnAl_2Se_4 .

Conclusions

The photoconductive ZnAl_2Se_4 layers were successfully grown on GaAs substrates through the HWE method. The optimum temperatures for the growth turned out to be 400 °C for the substrate and 620 °C for the source. Under these optimum conditions, the grown ZnAl_2Se_4 layers showed a thickness of 2.5 μm , a growth rate of 1.25 Å/sec, and FWHM on DCXD of 215 arcsec. Also, they were epitaxially accumulated along the $\langle 112 \rangle$ direction onto the GaAs (100) and formed into the stoichiometric composition. From the Hall effect measurement, the mobility showed a maximum of 856 $\text{cm}^2/\text{V}\cdot\text{sec}$ at 100 K. At a high temperature range ($T > 150$ K), it tended to decrease as a function of $T^{-3/2}$ by increasing the temperature, and increase as a function of T^1 at the low-temperature range ($T < 77$ K). The former was dominant in the scattering of the acoustic phonon mode due to lattice vibrations and the latter was the scattering having a superior to the dislocation scattering. Also, from the relationship between the reciprocal temperature and the carrier concentration we extracted out the shallow donor levels located at 76.9 and 15.5 meV below the edge of the conduction band. In the PC measurement, we observed the A, B, and C peaks corresponding to 351.6 (3.5263), 343 (3.6147), and 333.5 nm (3.7177 eV) at 10 K, respectively. These three peaks of A, B, and C were caused by the band-to-band transitions from the valence band state of $\Gamma_4(z)$, $\Gamma_5(x)$, and $\Gamma_5(y)$ to the conduction band state of $\Gamma_1(s)$, respectively.

According to the selection rule, the Δ_{cr} and Δ_{so} were extracted to be 0.088 and 0.103 eV through PC measurement, respectively.

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