A STUDY ON POINT DEFECTS OF ZnSe/Ga As EPILAYER OBTAINED FROM PHOTOLUMINESCENCE MEASUREMENT

K. J. Hong 1, S.H. You 1, J. W. Jeong 1, H.W. Baek 1, C.S. Park 2, K.H. Im 3, Fumio S. Ohuchi 4

1 Department of Physics, Chosun University, Kwangju 501-759, South Korea
2 Division of Metallurgical and Material Science Engineering, Chosun University, Kwangju 501-759, South Korea
3 Department of Automotive Engineering, Woosuk University, Wanju-kun Chonbuk 565-701, South Korea
4 Department of Materials Science & Engineering, University of Washington, Seattle, WA., 98195-2120, USA

ABSTRACT. The ZnSe epilayers were grown on the GaAs substrate by hot wall epitaxy. After the ZnSe epilayers treated in the vacuum-, Zn-, and Se-atmosphere, respectively, the defects of the epilayer were investigated by means of the low-temperature photoluminescence measurement. The dominant peaks at 2.7988 eV and 2.7937 eV obtained from the PL spectrum of the as-grown ZnSe epilayer were found to be consistent with the upper and the lower polariton peak of the exciton, I₁(D⁺, X), bounded to the neutral donor associated with the Se-vacancy. This donor-impurity binding energy was calculated to be 25.3 meV. The exciton peak, I₁, at 2.7812 eV was confirmed to be bound to the neutral acceptor corresponded with the Zn-vacancy. The I₁ peak was dominantly observed in the ZnSe/GaAs:Se epilayer treated in the Se-atmosphere. This Se-atmosphere treatment may convert the ZnSe/GaAs:Se epilayer into the p-type. The SA peak was found to be related to a complex donor like a (V₁-Se - V₁ - V₁).

INTRODUCTION

ZnSe has been recently tried to grow the p-type ZnSe for fabricating blue laser diode and light emitting diode [1-8]. Generally, the grown ZnSe epilayer is known to be n-type. Therefore, a major problem for obtaining better device performance is to grow the p-type ZnSe layer with low electrical resistivity. The difficulty in the p-type growth and the conductivity control for ZnSe are well known to be strongly related to the native defects and self-compensation of the ZnSe due to the stoichiometric deviation generated during the growth or the additional thermal treatment [9,10]. The stoichiometric deviation is mainly
caused by the reason that the partial vapor pressure of selenium is higher than that of the zinc during the growth. These native defects are consisted of Se-vacancy (V_{Se}), Zn-vacancy (V_{Zn}), Se-interstitial (Se^*), Zn-interstitial (Zn^*) and complex of these single defects. Among the defects, the V_{Se} and Zn^* acted as a donor. Other defects such as V_{Zn} and Se^* could work as deep levels and/or acceptor. The low-temperature crystal growth method for ZnSe has been preferred to reduce native defects. Hot wall epitaxy (HWE) [11] is one of the low-temperature crystal growth technologies so that this method can grow a high-purity ZnSe epilayer at the low-temperature. HWE has been especially designed to grow epilayers under the condition of the near thermodynamics equilibrium [12].

In this paper, the ZnSe epilayer was grown using HWE and its crystal quality was investigated by means of the double crystal x-ray diffraction technique. The ZnSe epilayers treated in the various atmospheres were investigated using the PL spectra. Based on these results, we will discuss the origin of point defects formed in the ZnSe epilayer.

EXPERIMENTAL PROCEDURE

A HWE apparatus used for growing the ZnSe epilayers (ZnSe/GaAs) on the semi-insulating (100) GaAs was shown in Fig. 1. Prior to growth, the GaAs 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 H_2SO_4 : H_2O : H_2O (5:1:1). The substrate was degreased in organic solvents, and rinsed with deionized water (18.2 MΩ). 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. The grown ZnSe/GaAs epilayers were analyzed by the double crystal x-ray diffraction (Bede Scientific Co. FR 590) to obtain the optimum growth

![FIGURE 1. Schematic diagram of the hot wall epitaxy apparatus.](image)
FIGURE 2. The x-ray rocking curves of the as-grown ZnSe/GaAs epilayer.

FIGURE 3. The photographs of SEM for the as-grown ZnSe/GaAs epilayer: (a) the surface morphology and (b) the cross section of epilayer.

condition. However, to grow the undoped ZnSe/GaAs epilayers, the most suitable temperatures of the substrate and the source containing ZnSe powder tuned out to be 400 °C and 670 °C, respectively.

Figure 3 showed the surface morphology and the cross section of the ZnSe/GaAs epilayer observed by scanning electron microscopy (SEM). The ZnSe/GaAs epilayer grew to the very smooth surface like a mirror, as shown in Fig. 3(a). Also, the thickness and the growth rate of epilayer were 1.8 μm and 0.03 μm/min, respectively.

After growing, the as-grown ZnSe/GaAs epilayers were prepared in the following conditions: (1) after the epilayer and the powder of Zn were sealed in a quartz ampoule at \( \sim 10^{-5} \) torr, the ampoule was annealed for 1 h at 600 °C, ZnSe/GaAs:Zn. (2) after the epilayer and the powder of Se were sealed in a quartz ampoule at \( \sim 10^{-5} \) torr, the ampoule was
annealed for 1 h at 230 °C, ZnSe/GaAs:Se. (3) the as-grown epilayer was annealed in the vacuum for 1 h at 600 °C, ZnSe/GaAs:vac.

The PL measurements at 10 K were carried out using a cryogenic helium refrigerator (AP, CSA-202B). The samples mounted on the cold finger of a cryostat were focused using the 325 nm line of He-Cd laser (1K 545IR, Kimmon Electric Co) with power of 10 mW and the emitted light was detected by a photomultiplier tube (RCA, C3 1034) through the monochromator. The detected signal was amplified by a lock-in amplifier (EG&G, 5208) and recorded in a x-y plotter.

RESULTS AND DISCUSSION

As-Grown ZnSe/GaAs Epilayer

Figure 4 shows the typical PL spectra of the as-grown ZnSe/GaAs epilayer measured at 10 K. The free exciton peak, Ex, at 442.4 nm appears on the shoulder toward the short-wavelength region. The energy of the Ex is 2.802 eV, which is equal to the values obtained from the undoped ZnSe/GaAs epilayers grown with MOMBE by Migita et al. [14] and with MBE by Akimoto et al. [15], respectively. As shown in the sub-figure of Fig. 4, the very strong intensity peaks, I2 (D°, X), were observed to be at 443 nm (2.7988 eV) and 443.8 nm (2.7937 eV), which are believed to be the peaks bounded to the neutral donor. Each of the peaks represents the upper polariton, I2 U, and the lower polariton, I2 L, respectively [16,17]. The splitting energy between the upper and the lower polariton was 5.1 meV. This polariton is known to be caused by the strain due to the lattice mismatch between substrate and epilayer in the heteroepilayer growth. The FWHM value of the I2 L peak was 5.7 meV. This value has been reported to be the 6.35 meV by Hingerl et al. [18], which was obtained from the 17 K cathodoluminescence spectrum. Also, the bound exciton peak, I, was observed at 443.4 nm (2.7963 eV) in the 4.2 K PL of sample grown with MBE by Yao [19]. The observance of the I2 L suggests that the undoped ZnSe epilayers grown in this experiment have a very high optical quality. And the I2 L is generally known to be the bound exciton, I2 [20,21]. Therefore, the binding energy [22] of the donor-impurity, E_D, can be calculated using the eq. (1)

$$E(D^0, X) = E_g - E_{ex} - 0.15 E_D$$

where Eex is the binding energy of the free exciton. E_D was determined to be 25.3 meV. This value is close to the ionization energies of donors such as Al, Cl, and Li, which have been reported to be 25.3 meV, 25.9 meV, and 26 meV, respectively [23]. A neutral acceptor bound exciton, I A (A°, X), of the sharp intensity peak at 445.8 nm (2.7812 eV) and its LO phonon replicas at 451 nm (2.7491 eV) and 456.3 nm (2.7172 eV) appear on the right region of the wavelength. A I0 emission and its LO phonon replicas were observed at 447 nm (2.7737 eV) and 452.5 nm (2.7400 eV), respectively. The thermal stability of the binding force of the I0 emission could be characterized by observing a regular peak position irrespective of the epilayer growth condition. The origin of the I0 emission is related to the dislocation or the complex defects acted as the dislocation [24]. The peaks at 476.5 nm (2.6020 eV) and 482.2 nm (2.5712 eV) are coincident with Y0 emission [25] and its LO phonon replica associated with the dislocation generated due to the lattice-mismatch. The observance of the Y0 emission in the epilayer indicates that the grown sample is a high quality crystal [26]. A 566 nm (2.1906 eV) peak of flat slope with a low intensity at the
long wavelength region corresponds with a self-activated (SA) emission.

**Annealing Effect of the ZnSe/GaAs Epilayers**

In order to know the origins of the several peaks of the as-grown ZnSe/GaAs, we measured the PL spectra for samples annealed in vacuum, Zn-, and Se-atmosphere. The obtained PL spectra are shown in the Figs. 5 and 6. First, when the ZnSe/GaAs epilayer annealed in the vacuum for 1 h at 600 °C (the ZnSe/GaAs:vac epilayer), the epilayer became non-stoichiometry because the Zn and the Se atoms vaporized out, leaving the vacancies such as $V_{Zn}$ and $V_{Se}$. Therefore, we can observe all peaks related to the $V_{Zn}$ and $V_{Se}$. Figure 5 shows that the $I_x$ emission at 443.4 nm (2.7962 eV) and the $I_y$-like emission at 446.5 nm (2.7768 eV) dominantly appeared in the PL spectrum of ZnSe/GaAs:vac epilayer. The $I_x$ is consistent with the donor and the $I_y$-like emission corresponds to the acceptor. Also the peaks related to LO phonon replicas of the $I_y$-like are seen at the wavelength range from 451.5 nm (2.7461 eV) to 462.1 nm (2.6831 eV). On the other hand, the $I_x$ and the $Y_o$ peaks observed in the as-grown epilayer disappeared and the intensity of the SA spectrum at 620 nm (1.9998 eV) increased. The new peak associated with the Cu-green emission was observed to be at 535.4 nm (2.3158 eV). This Cu-green emission is known to be associated with the residual Cu impurities in ZnSe powder.

Second, to know a role of Zn, we prepared ZnSe/GaAs samples annealed in Zn-atmosphere for 1 h at 600 °C (ZnSe/GaAs:Zn epilayer). The Zn-atmosphere annealing could diffuse the additional Zn into the ZnSe/GaAs epilayer. Consequently, the Zn-vacancies in the ZnSe/GaAs epilayer are filled with the diffused Zn. By comparing the peaks in Fig. 4 with those in Fig. 5, we found that the peaks related to the $I_x$ and the SA emission completely disappeared in the ZnSe/GaAs:Zn epilayer and the $I_y$ emission at 443.4 nm (2.7962 eV) became the dominant peak. This $I_y$ peak was generally observed in the typical n-type. The FWHM value of the $I_y$ peak was taken to be 7.5 meV. The disappearance of the $I_x$ and the SA emission indicates that these peaks are certainly associated with $V_{Zn}$. This disappearance also implies that the $I_y$ peak is not related to Zn-vacancy, $V_{Zn}$, because the sites of $V_{Zn}$ should be substituted with the diffused Zn. As the intensity of the $I_y$ peak increase, the intensity of the SA emission decrease. This may mean that the ZnSe/GaAs:Zn epilayers are purified by annealing in Zn-atmosphere. Among the samples prepared in this experiment, the donor-acceptor pair (DAP) emission and its LO phonon
replicas were observed only in the sample annealed in the Zn-atmosphere. Such DAP emission is caused by an interaction between donors (such as Al and Cl) and shallow acceptors.

Third, to know a role of Se, the ZnSe/GaAs samples were annealed in Se-atmosphere for 1 h at 230 °C (ZnSe/GaAs:Se). This Se-atmosphere annealing makes the Se-vacancies in the ZnSe/GaAs epilayer filled with the diffused Se. As shown in Fig. 6, the $I_{1}$ peak at 445.8 nm is very sharp and its PL intensity is high. However, the $Ex_{1}$, $I_{1}^{U}$ and $I_{1}^{L}$ are observed to be a relatively very weak emission at 442.4 nm, 443 nm and 443.5 nm, respectively. With a comparison of the peaks in Fig. 4, the dominant $I_{1}$ emission significantly decreases and the intensity of the $I_{1}^{U}$ peak increases. The FWHM value of the $I_{1}$ peak was 2.5 meV and very sharp. The LO phonon replicas of the $I_{1}$ are the dominant peaks in the PL spectra of the ZnSe/GaAs:Se. The $I_{1}$ has been known to be associated with a deep acceptor level originated from the $V_{Zn}$ due to stoichiometric deviation [27]. The origin of the $I_{1}^{U}$ also reported by other authors [28,29]. Additionally, the as-grown ZnSe epilayers were annealed at 400 °C and 600 °C in the Se-atmosphere, respectively, to study the heat-treatment effect of Se. However, only the SA emission was seen and the emission peaks on the short-wavelength region could not be observed in these samples. This can be caused by the absorption of light emitted from the sample due to the recrystallized Se on the sample conversion of the p-surface. The dominant $I_{1}$ peak and its replicas could be observed in the sample annealed in the Se-atmosphere at 230 °C. This suggests that the only the Se-atmosphere annealing at 230 °C could convert the as-grown ZnSe into p-type. The type ZnSe crystal is well known to be difficult due to the self-compensation, although the ZnSe crystal is intentionally doped with impurities such as Li and P.

From results of the $I_{1}$ emission, the binding energy [22] of the acceptor-impurity, $E_{A}$, is obtained using the eq. (2)

$$E(A^+, X) = E_g - E_{X} - 0.08 E_{A},$$

(2)
where $E_a$ was calculated to be 268 meV. This value is larger than 200 meV reported by Yao et al. [30]. The origin of acceptor-impurity has been reported to be the Cu-related by Bhargava [31]. This indicates that the origin of the $I_e^a$ emission is related to $V_{Zn}$. The SA emission disappeared after the Se-atmosphere annealing. This means that the origin of the SA emission is related to $V_w$. And the ZnSe/GaAs epilayer after the Se-atmosphere annealing is also purified like a Zn-atmosphere annealing. The S-band [32] at 516.4 nm (2.4010 eV) was seen, even this peak was not known to the origin and, and the $Y_o$ emission at 476.5 nm was also observed in the Se-atmosphere treated samples.

CONCLUSIONS

The ZnSe/GaAs epilayers were grown on the semi-insulating (100) GaAs by HWE method. The optimum growth temperatures of the substrate and the source containing ZnSe powder were found to be 400 °C and 670 °C, respectively. FWHM from the x-ray rocking curves and thickness were obtained to be 195 arcsec and 1.8 μm, respectively. The PL measurement showed that the dominant peaks at 2.7988 eV and 2.7937 eV obtained from the as-grown ZnSe epilayer corresponded to the upper and the lower polariton peak of the exciton, $I_2^e$ ($D^e, X$). This polariton peak is associated with the strain due to the lattice mismatch between substrate and epilayer. When the samples were treated in the vaccum, Zn, and Se-atmosphere, respectively, the $I_2^e$ peak was observed and its origin was not related to $V_{Zn}$ but $V_{Se}$. The donor-impurity binding energy was calculated to be 25.3 meV. The exciton bounded to a neutral acceptor, $I_e^a$, was also seen. However, the $I_e^a$ emission and its LO phonon replicas were dominate peak in the spectrum of ZnSe/GaAs:Se. The PL measurement showed that the ZnSe/GaAs:Se epilayer was obviously converted into the p-type and its origin of the $I_e^a$ is related to $V_{Se}$. The acceptor-impurity binding energy of the $I_e^a$ was estimated to be 268 meV. The $I_e^a$ was related to the Zn-site replaced by the residual Cu-impurity. The origin of the SA emission may be associated with a complex donor like a ($V_{Se}$ - $V_{Zn}$) - $V_{Zn'}$.

REFERENCES