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A Study point defect for thermal annealed ZnSe/GaAs epilayer

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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, I_2 (D^o, 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, I_1^d, at 2.7812 eV was confirmed to be bound to the neutral acceptor corresponded with the Zn-vacancy. The I_1^d 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 (V_{Se} - V_{Zn}) - V_{Zn}.

Key Words: ZnSe; hot wall epitaxy; annealing treatment; defect; photoluminescence

1. 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_{int}), Zn-interstitial (Zn_{int}) and complex of these single defects. Among the defects, the V_{Se} and Zn_{int} acted as a donor. Other defects such as V_{Zn} and Se_{int} 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.

2. Growth and 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_2 : H_2O (5:1:1). The substrate was degreased in organic solvents, and rinsed with deionized water (18.2 M). After the substrate was dried off, the substrate was immediately loaded onto the substrate holder in Fig. 1 and was annealed at 580 ℃ 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 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 ℃ and 670 ℃, respectively. The minimum value of a full width at half maximum (FWHM) of the ZnSe/GaAs epilayer obtained from the x-ray rocking curves was 195 arcsec as shown in Fig. 2., This value is better than the value obtained from the ZnSe/GaAs epilayer grown with MOVPE by Fujita *et al.* [13]. 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 m and 0.03 m/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 ℃, 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 ℃, ZnSe/GaAs:Se. (3) the as-grown epilayer was annealed in the vacuum for 1 h at 600 ℃, ZnSe/GaAs:vac..The PL measurements at 10 K were carried out using a cryogenic helium refrigerator (AP, CSA-202B).

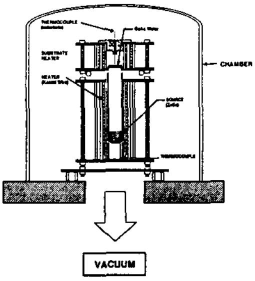

Fig. 1. Schematic diagram of the hot wall epitaxy apparatus

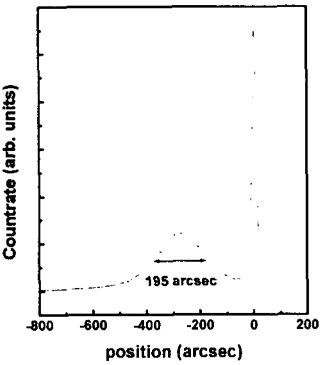

Fig. 2. The x-ray rocking curves of the as-grown ZnSe/GaAs epilayer.

3. Result and discussion

3.1 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

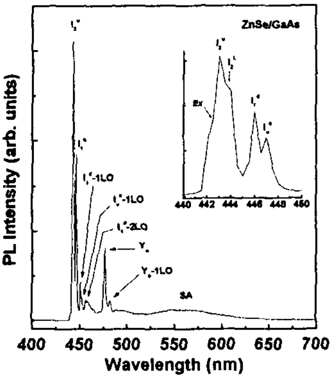

Fig. 4. Photoluminescence spectrum at 10 K for the as-grown ZnSe/GaAs epilayer.

in the sub-figure of Fig. 4, the very strong intensity peaks, I_2 (D^o, 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, I_2^U, and the lower polariton, I_2^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 I_2^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_2, 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 I_2^L suggests that the undoped ZnSe epilayers grown in this experiment have a very high optical quality. And the I_2^L is generally known to be the bound exciton, I_2 [20,21]. Therefore, the binding energy [22] of the donor-impurity, E_D, can be calculated using the eq. (1)

$$E\ (D^o,\ X) = E_g - E_{ex}^b - 0.15\ E_D, \quad (1).$$

where E_{ex}^b 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_{int}, which have been reported to be 25.3 meV, 25.9 meV, and 26 meV, respectively [23]. A neutral acceptor bound exciton, I_1^d (A^o, 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 I_v^o 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 I_v^o emission could be characterized by observing a regular peak position irrespective of the epilayer growth condition. The origin of the I_v^o 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 Y_o emission [25] and its LO phonon replica associated with the dislocation generated due to the lattice-mismatch. The observance of the Y_o 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.

3.2. 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 ℃ (the ZnSe/GaAs:vac epilayer), the epilayer became non-stoichiometry because the Zn and the Se atoms vapored 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_2 emission at 443.4 nm (2.7962 eV) and the I_1-like emission at 446.5 nm (2.7768 eV) dominantly appeared in the PL spectrum of ZnSe/GaAs:vac epilayer. The I_2 is consistent with the donor and the I_1-like emission corresponds to the acceptor.

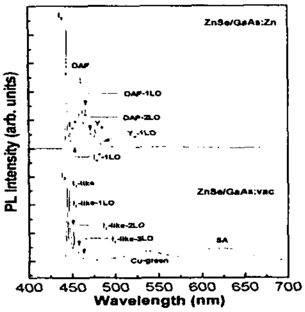

Fig. 5. Photoluminescence spectra at 10 K for the ZnSe/GaAs:vac and ZnSe/GaAs:Zn.

Also the peaks related to LO phonon replicas of the I_1-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_v^o 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 ℃ (ZnSe/GaAs:Zn epilayer).

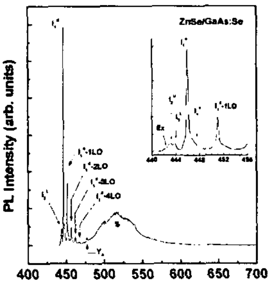

Fig. 6. Photoluminescence spectrum at 10 K for the ZnSe/GaAs:Se.

became the dominant peak after the Se-atmosphere treatment. This indicates that the origin of the I_1^d 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_{Se}. 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.

4. 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 ℃ and 670 ℃, respectively. FWHM from the x-ray rocking curves and thickness were obtained to be 195 arcsec and 1.8 m, 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 (D^o, 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 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_1^d, was also seen. However, the I_1^d 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_1^d is related to V_{Zn}. The acceptor-impurity binding energy of the I_1^d was estimated to be 268 meV. The I_1^d 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

[1] J. Nishizawa, R. Suzuki, and Y. Okuno, J. Appl. Phys. 59 (1986) 2256.