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Low Temperature Disordering Process of ZnSe/ZnS Superlattices Using Ion Implantation

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Disordering of ZnSe/ZnS superlattices was confirmed for the first time. Si,P,Zn ions were implanted ($1x10^{15}$ - $1x10^{16}$ ions/cm^2, 100 keV) into superlattices (140 A ZnSe - 140 A ZnS). Selective disordering of superlattices was confirmed by SEM observaton using an ion implantation mask. The inter-diffusion of S and Se was observed by SIMS analyses. By photoluminescence measurements, the emission of ZnS_xSe_{1-x} alloyed crystal was observed after thermal annealing. The disordering is mainly induced by the diffusion of defects generated by the ion implantation in the early stage of low temperature thermal annealing.

1. Introduction

Recently, much attention has been paid to the fabrication of superlattices, because of their novel properties using quantum size effects. ZnSe/ZnS superlattices, which has a direct and large bandgap, is a promising technology for use in blue light emitting devices. However, the process technology for II-VI compound semiconductors has yet to be established.

Selective disordering of superlattices is an attractive process technique for obtaining refractive index and bandgap distributions in the plane of the superlattice layer. Since the disordered region has a larger bandgap and a smaller refractive index compared with superlattice region, carriers and photons can be efficiently confined in the superlattice region. In fact, high quality GaAs/AlGaAs multi-quantum well lasers have been fabricated by using this technique[1]. In several papers, it has been reported that the disordering is induced by impurity diffusions on various superlattices, such as GaAs/AlAs[2], InGaAs/InP[3], and InGaAs/InAlAs[4].

In this paper, we report the first confirmation of disordering of ZnSe/ZnS superlattices by ion implantation and subsequent thermal annealing.

2. Experimental procedures

ZnSe/ZnS superlattices were grown on GaAs(100) substrates by low pressure metalorganic vapor phase epitaxy at 550 C at 75 Torr. Dimethylzinc, dimethlselenide and H_2S were used as source gases. The superlattices are composed of 10 periods of ZnSe(140 A) and ZnS(140 A).

Si, P, and Zn ions were implanted into ZnSe/ZnS superlattices at a dose of $1x10^{15}$ -$1x10^{16}$ ions/cm^2 with an ion energy of 100 keV. After the ion implantation, samples were annealed at 350 - 450 C for 3 - 24 hours. Annealing was carried out under selenium atmosphere in closed quartz ampoules.

3. Results and Discussion

3-1 Confirmation of Disordering

Disordering of ZnSe/ZnS superlattices was directly investigated by scanning electron microscopy (SEM). Si ions were selectively implanted (100 keV, $1x10^{16}$ ions/cm^2) into superlattices. The subsequent annealing was carried out at 350 C for 8 hours. Samples were tilted to 0.5 degrees by lapping. After lapping, ZnSe layers were selectively etched by H_2O_2. Figure 1 shows the shallow-angle cross section of ZnSe/ZnS superlattice after thermal annealing. Si ions were implanted only in the region shown on the left half of the photograph. At the non-implanted region (the right half of the photograph), the periodic superlattice structure is clearly seen. Without ion implantation, the superlattice structure is maintained even after thermal annealing. In the Si implanted region (the left half of the photograph), however, the interfaces of each layers are obscured. This shows that ZnSe/ZnS superlattice has been disordered by the ion implantation and the subsequent thermal annealing. We confirmed that ZnSe/ZnS superlattices can be selectively disordered by selective ion implantation. This technique will be very useful in fabricating optical waveguides or other devices.

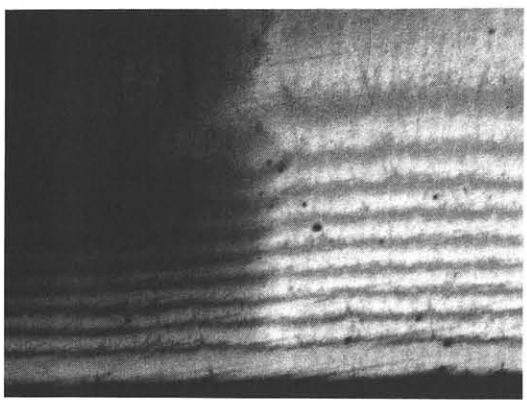

Fig.1 Shallow-angle cross section of ZnSe/ZnS superlattice after thermal annealing. Disordering is occured only in the Si implanted region (the left half of the photograph).

The inter-diffusion of S and Se is measured by secondary ion mass spectrometry (SIMS) using 3 keV - O_2^+ primary ion beam. Figure 2 shows the depth profiles of Se after crystal growth (a), after Si ion implantation (100 keV, $1x10^{16}$ ions/cm^2) alone (b), after thermal annealing (450 C, 3 hours) alone (c), and after ion implantation and subsequent thermal annealing (d). In Fig.2(a), (b) and (c), periodic depth profiles of Se are clearly seen. In Fig.2(d), however, the periodic profile is greatly damped. These results show that Se and S have inter-diffused by ion implantation and subsequent thermal annealing.

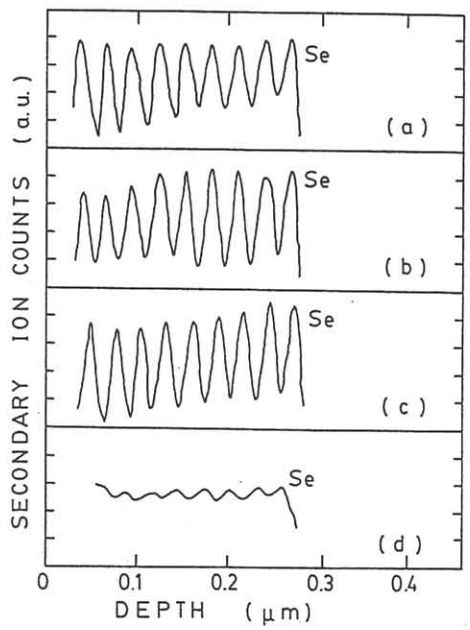

Fig.2 SIMS profiles of Se just after crystal growth(a), after ion implantation alone(b), after thermal annealing alone(c), and after ion implantation and subsequent thermal annealing(d).

Photoluminescence (PL) spectra were measured at 77 K using He-Cd laser (3250 A) as an excitation source. Before ion implantation, the emission line was observed at 2.81 eV. This emission is due to the transition between the quantum levels in ZnSe wells. Just after the ion implantation, no emission line was observed. This indicates that the crystalline quality was degraded by ion implantation damages. After annealing at 350 C for 5 hours, PL emission line was observed again, which shows the recovery of the crystalline quality. Figure 3 shows the PL spectrum after 5 hours annealing. The emission line is observed at 3.11 eV, which is about 300 meV higher than that of the as-grown sample. This result shows that the effective bangap has widened as a result of the disordering of superlattices.

We have confirmed, for the first time, the disordering of superlattices by SEM, SIMS, and photoluminescence. The disordering occurs at a much lower temperature than in the case of III-V compound semiconductors. This low temperature process will be useful in realizing high performance optical and electrical devices using II-VI compound semiconductors.

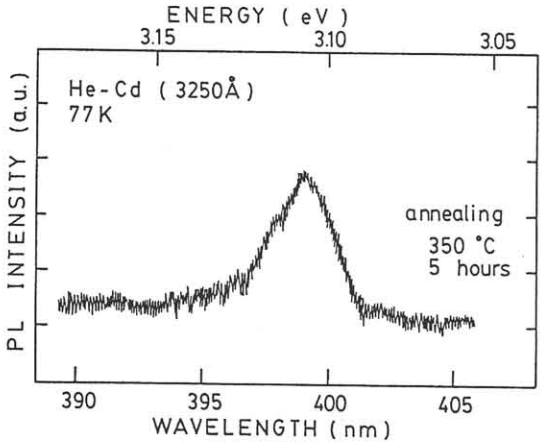

Fig.3 PL spectrum in the disorded layer. Annealing was carried out at 350 C for 5 hours.

3-2 Disordering mechanism

Figure 4 shows the PL emission peak energy of disordered layers as a function of annealing time. The annealing temperature was 350 C. The S composition x in ZnS_xSe_{1-x} alloyed crystal is calculated from the PL emission peak energy. S composition x is also shown in Fig. 4. The emission peak energy is almost constant at about 3.1 eV (x=0.31) for more than 5 hours annealing. Since the thicknesses of the ZnSe and ZnS layers in the superlattice are 140 A each, the composition x of completely disordered layer is x=0.5. Therefore, the superlattice has not been disordered completely, which is in agreement with the results of SEM observation and SIMS analysis. Since the disordering does not proceed even after more than 5 hours of annealing in spite of incomplete disordering, the inter-diffusion of S and Se occurs only in the early stage of a few hours annealing. This tendency agrees well with the defect induced disordering mechanism reported by J.Cibert et al.[5].

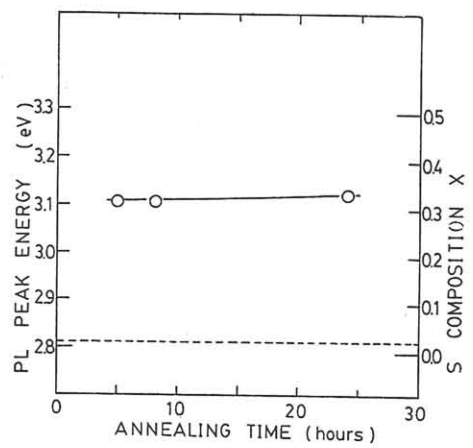

Fig.4 PL emission peak energy and S composition as a fuction of annealing time.

Just after the ion implantation, a great number of defects exist. At the early stage of annealing, an inter-diffusion of S and Se is strongly promoted by the diffusion of these defects. However, the number of defects rapidly decreases by annealing and no more disordering occures after the crystalline quality is recovered. We have concluded that the dominant disordering mechanism is the diffusion of defects. In this mechanism, thermal diffusion of impurities is unnecessary to disorder the superlattices, therefore, the disordering can be realized at such a low temperature of about 400 C.

Disordering of superlattices were examined at various ion implantation conditions by SEM observation. Annealing condition was fixed at 450 C for 3 hours. Table 1 shows ion implantation sources and total doses. Circles inducate disordering while the X indicates no disordering. At a total dose of $1x10^{16}$ ions/cm^2, superlattices are disordered independent of ion implantation sources. Superlattices are disordered by implantation of Zn, of which the superlattices are composed, as well as Si and P impurities. This result also suggests that the disordering is induced by the diffusion of defects in our experiments. At a dose of $1x10^{15}$ ions/cm^2, a clear superlattice structure was observed by SEM even after thermal annealing. Therefore, it is thought that the amount of defects generated at this implantation condition is insufficient to induce the inter-diffusion. We have found that a high dose of ion implantation, as much as $1x10^{16}$ ions/cm^2, is necessary to disorder at such a low temperature.

Table 1 Implantation elements and their dosage

element	dose(ions/cm^2)	disordering
Si	1×10^{16}	○
P	1×10^{16}	○
Zn	1×10^{16}	○
Si	1×10^{15}	×

4. Conclusion

We have confirmed the disordering of ZnSe/ZnS superlattices by ion implantation and subsequent thermal annealing by SEM, SIMS and photoluminescence. Superlattices can be disordered at about 400 C by a high dose of ion implantaion. We have found that the disordering is dominantly induced by the diffusion of defects generated by the ion implantation. This low temperature process will be useful to fabricate novel optical and electrical devices using II-VI compound semiconductors.

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