Extended Abstracts of the 22nd (1990 International) Conference on Solid State Devices and Materials, Sendai, 1990, pp. 469-472

Layer Disordering of ZnSe/ZnS Strained Layer Superlattices by N^+ or Li^+ Ion-Implantation and Low Temperature Annealing

Toshiya Yokogawa, Tohru Saitoh, Edmund L. Wolak and Tadashi Narusawa
Opto-Electronics Research Laboratory, Semiconductor Research Center,
Matsushita Electric Ind. Co., Ltd.
3-15 Yagumo-Nakamachi, Moriguchi, Osaka 570, Japan

We demonstrate layer-disordering of ZnSe/ZnS strained layer superlattices (SLSs) induced by low-damage N^+ or Li^+ ion-implantation and low temperature annealing. The interdiffusion of Se and S atoms was observed by secondary-ion mass spectrometry analyses. By spectrophotometer measurements, a significant decrease in the refractive index, which is useful for waveguiding application, was confirmed in the disordered SLS. In photoluminescence (PL), a slight red shift of the PL peak was observed in the early stage of annealing. This shift is related to the relaxation of misfit strain by the interdiffusion. For longer annealing times, the PL peak for implanted SLS shifted towards the higher energy side, which clearly indicates disordering of the SLS.

1. INTRODUCTION

Impurity-induced disordering of semiconductor superlattice (SL) is a useful technique for patterning the refractive index and bandgap distribution in the plane of the SL layer[1)-3)]. This capability provides the foundation for new types of semiconductor devices as well as optoelectronic integrated circuits. Much attention has been paid to ZnSe/ZnS strained layer superlattice (SLS) having a direct and large bandgap because of the application for blue light emitting devices[4)]. Recently, we demonstrated, for the first time, the possibility to modify the structure of the ZnSe/ZnS SLS using the Si ion-implantation at a dose of 1×10^{16} ions/cm^2 [5)]. However, such a high dose implantation of Si has the disadvantage of creating defects which are not eliminated easily by subsequent thermal annealing. The N^+ and Li^+ are, in contrast, preferred as ion species because the radiation damage can be removed easily, the diffusion constants are high, and these impurities do not generate deep levels such as self-activated centers.

In this paper we report, for the first time, on layer disordering of ZnSe/ZnS SLSs by N^+ or Li^+ ion-implantation and low temperature annealing, and demonstrate a large refractive index change induced by interdiffusion in SLSs.

2. EXPERIMENTAL PROCEDURE

ZnSe/ZnS SLSs were grown by low pressure MOVPE using dimethylzinc (DMZ), dimethylselenium (DMSe) and H_2S. Substrates were Cr-doped (100) GaAs. The growth temperature and pressure were 550 C and 75 Torr, respectively. Typical flow rates of DMZ, DMSe and H_2S were 0.4, 1.6 and 3 sccm, respectively. One structure used for the implantation experiments consisted of a 40 period superlattice with alternating layers of 30 A ZnSe and 70 A ZnS. Ion-implantations were performed at room temperature with an energy of 100 keV at an angle of 7 degrees. Samples were implanted using either a 5×10^{14} ions/cm^2 dose of N^+ or a 1×10^{15} ions/cm^2 dose of Li^+. The cal-

culated projected range Rp of N and Li are 0.18 and 0.35 um, respectively, by the Lindhard-Scharff-Schiott (LSS) theory. Post-annealing was carried out in a Se and S ambient at 400 C. The Se and S depth profiles were measured by secondary ion-mass spectrometry (SIMS), using a Cs^+ primary ion beam at 1.5 keV. Photoluminescence (PL) measurements were carried out using a 3250 A He-Cd laser (10 mW) for an excitation.

3. RESULTS AND DISCUSSION

ZnSe/ZnS interdiffusion was investigated using SIMS. Figure 1 shows the S depth profiles for the SLS after the growth (a), and after N^+-implantation and subsequent anneal at 400 C for 3 h (b). In Fig.1 (a), the superlattice structure was clearly observed, but in Fig.1 (b), the periodic profile disappeared. These results indicate that the superlattice structure was disordered by the thermal anneal after the implantation.

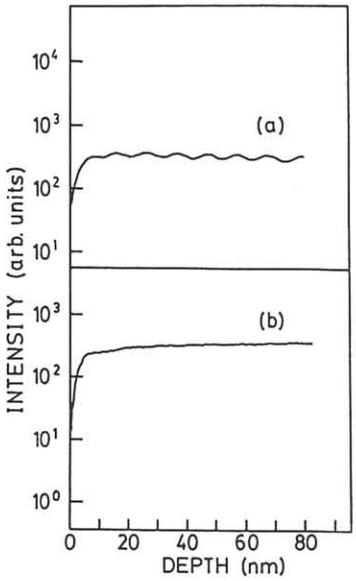

FIG.1 Depth profiles of S by SIMS analyses just after growth (a) and N^+-ion implantation and subsequent thermal annealing at 450 C for 3 h (b). The superlattice was composed of 40 periods of 30 A-ZnSe and 70 A-ZnS.

The refractive indices of the SLSs were estimated by spectrophotometer measurements and computor simulation. These indices were calculated by using the reflectance measured from superlattice layer surface at normal incidence. Since the superlattice layer is a Fabry-Perot etalon sandwiched by air and the GaAs substrate, an interference ripple was observed in the spectrum of reflectance. In order to estimate the refractive indices, we simulated the reflectance spectrum of the air/II-VI/GaAs system, assuming that the single-effective-oscillator approximation is valid for the II-VI material at the energies sufficiently below the direct band edge[6]. The values for the complex refractive index of GaAs were taken from reference 7. We used two energies E_d and E_0 (of Eq.(10) in Ref.6) as fitting parameters. In the best fit of single-effective-oscillator fomula, the results of the simulation are in extremely good agreement with the measured reflection spectra, as shown in Fig. 2. Figure 3 and 4 show the dispersions of the refractive index in N^+ and Li^+ implanted SLSs, respectively. A significant decrease in the refractive in-

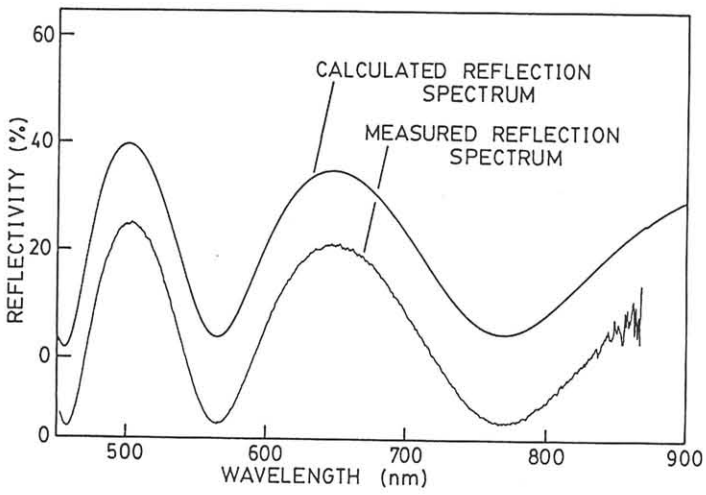

FIG.2 Comparison of calculated and measured reflection spectra in the superlattice on the GaAs substrate.

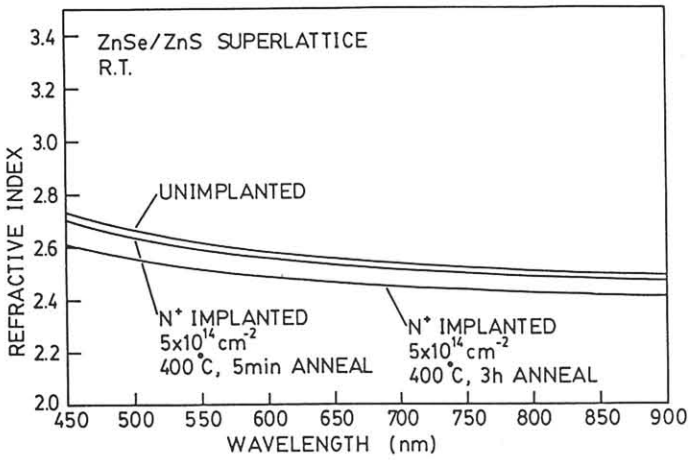

FIG.3 Refractive indices for the as-grown superlattice and the superlattices annealed after N^+-implantation as a function of the wavelength.

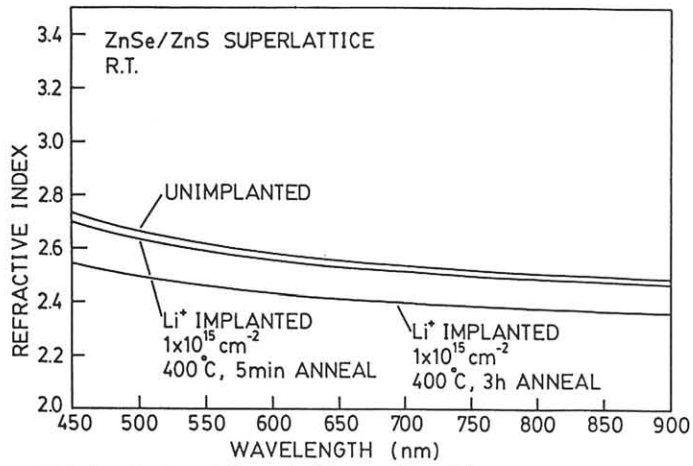

FIG.4 Refractive indices for the as-grown superlattice and the superlattices annealed after Li^+-implantation as a function of the wavelength.

dex was observed in both SLSs which are N^+ and Li^+ implanted and annealed at 400 C for 3 h. This behavior is very useful for the fabrication of the optical devices in ZnSe/ZnS SLSs.

PL measurements also show the layer-disordering of ZnSe/ZnS superlattices. Before the ion implantation, the excitonic emission line, which is related to the transition between quantum energy levels in ZnSe wells, was observed at 2.925 eV. Just after the ion implantation, no emission was observed because of crystalline damage due to the implantation. Emission was observed after ion-implantation and anealing, however, which indicates the recovery of crystalline quality. After annealing at 400 C, a strong excitonic emission around 400 nm was observed in implanted SLSs. Figure 5 shows the relationship between PL peak energy and annealing time in both N^+-implanted and Li^+-implanted superlattices. The post-annealing was done at 400 C for 1.5 hours and for 3 hours. A slight red shift of the PL peak was observed in the early stage of annealing. We calculated the difference of band gap energy between strained ZnSe well layer and bulk ZnSe by the deformation theory[8], assuming that the SLS is free-standing. The value of 59 meV was found, which agrees well with the red shift of the PL peak. Therefore, we confirmed that this shift is related to the relaxation of misfit strain by partial interdiffusion. For longer annealing times, the PL peak for the implanted SLS is shifted towards the higher energy side, which clearly indicates layer disordering of the SLS.

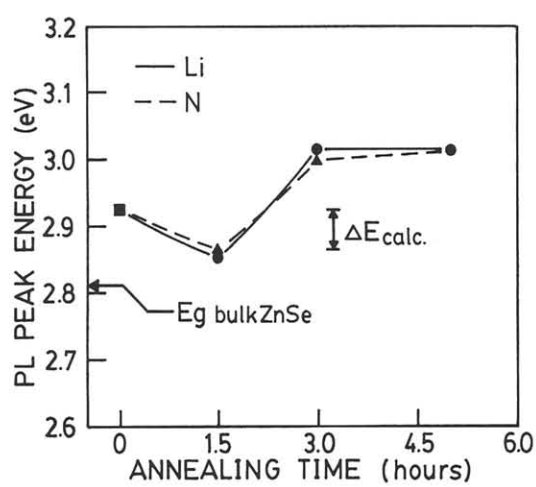

FIG.5 Photoluminescence peak energy vs annealing time for the superlattices which were N^+-implanted (dashed line) or Li^+-implanted (solid line).

Temperature dependences of PL show a reduction of quasi-two-dimensional exciton binding energy with disordering. Figure 6 shows the PL intensity as a function of reciprocal temperature. PL quenching properties, which are related to the dissociation of exciton and strong electron-phonon interaction[9], were observed in both samples. In as-grown ZnSe/ZnS SLSs, a strong excitonic emission and a large activation energy of quenching were obtained due to the large oscillator strength and large binding energy of quasi-two-dimensional excitons in a quantum well. However, the activation energy for disordered SLS was estimated to be 16 meV, much smaller than that for th as-grown SLS. These results indicate that the confinement of excitons in quantum well becomes weak by the interdiffusion in the heterointerface of SLS, which results in a reduction of the exciton binding energy. Consequently, the large change of oscillator strength as well as energy gap induces the large refractive index change.

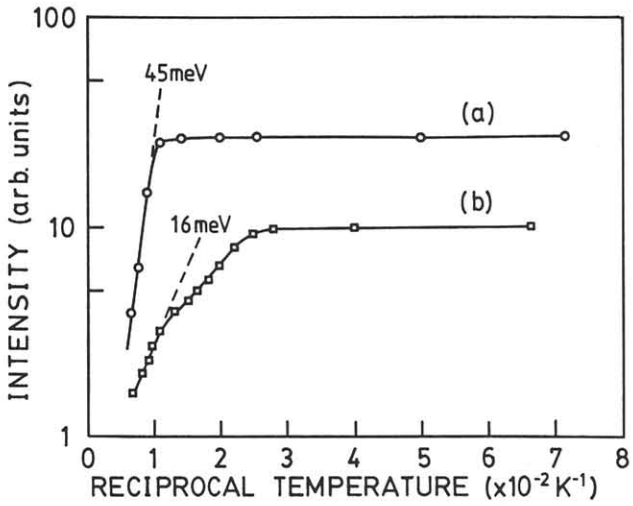

FIG.6 Photoluminescence intensity for the as-grown superlattice (a) and the disordered superlattice (b) as a function of the reciprocal measuring temperature.

4. CONCLUSION

We have confirmed interdiffusion in ZnSe/ZnS SLSs induced by low-damage N^+ or Li^+ ion-implantation and low temperature annealing, and demonstrated a large refractive index change. Secondary-ion mass spectrometry analyses show the periodic depth profiles of Se and S disappeared after ion-implantation and subsequent thermal annealing at 400 C. A significant decrease in the refractive index was observed in the disordered SLS. This low temperature planar process will be very useful for the fabrication of II-VI semiconductor opto-electronic devices.

ACKOWLEDGMENT

We are grateful to T. Onuma of Opto-Electronics Research Laboratory for continuous encouragement and discussion.

REFERENCES

1)W.D.Laidig, N.Holonyak,Jr. and M.D.Camras; Appl. Phys. Lett. 38(1981)776.

2)N.Holonyak,Jr., W.D.Laidig, M.D.Camras, J.J.Coleman and P.D.Dapkus; Appl. Phys. Lett. 39(1981)102.

3)E.Kapon, N.G.Stoffel, E.A.Dobisz and R.Bhat; Appl. Phys. Lett. 52(1988)351.

4)T.Yokogawa, M.Ogura and T.Kajiwara; Appl. Phys. Lett. 52(1988)120.

5)T.Saito, T.Yokogawa and T.Narusawa; Appl. Phys. Lett. 55(1989)735.

6)S.H.Wemple and M.Didomenico,Jr.;Phys. Rev. B3(1971)1338.

7)"Handbook of Optical Constant of Solids" edited by E.Palik, Academic Press, Orlando FL, 1985.

8)B.J.Skromme, M.C.Tamargo and J.L.de Miguel; Appl. Phys. Lett. 53(1988)2217.

9)T.Yokogawa, H.Sato and M.Ogura; J. Appl. Phys. 64(1988)5201.