Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 360-362

Plasma-Assisted Epitaxial Growth of p-Type ZnSe in Nitrogen-Based Plasma

T. HAMADA, T. HARIU and S. ONO*

Department of Electronic Engineering,
*Research Institute of Electrical Communication,
Tohoku University, Sendai 980

P-type ZnSe have been successfully grown by plasma-assisted epitaxy in nitrogen-based plasma and the resistivity was reduced down to the order of 10Ωcm at room temperature. With relatively small N_2 flow rate around 0.073sccm, low-temperature photoluminescence intensities of donor-acceptor pair emission and acceptor-bound exciton emission from nitrogen-doped ZnSe were maximum with negligible deep level emission at partial pressure ratio $P_{N2}/(P_{N2}+P_{H2})$ around 80%. It has been found that, while hydrogen improves electronic property of ZnSe layers, excessive hydrogen can deteriorate the doping efficiency of shallow-acceptor nitrogen.

1. INTRODUCTION

ZnSe, a II-VI compound semiconductor with its direct bandgap around 2.67eV at room temperature, is a promising material for the fabrication of blue light emitting diodes (LED) and laser diodes (LD). However, the difficulty in making low resistivity p-type ZnSe with good electronic property has been widely recognized.

Both group Ia (Li, Na) and group Vb (N, P, As) elements have been attempted for p-type dopants in ZnSe, but stable and reproducible p-type ZnSe has only been demonstrated using Li and N. In the case of Li doping, the maximum value of N_A-N_D has been limited approximately to $1x10^{17}cm^{-3}$, probably due to compensation by donor-like interstitial Li and the problem of easy diffusion of Li has also been claimed. The effective incorporation of N as an acceptor into ZnSe films was prevented by low sticking coefficient of N. The plasma-excited nitrogen has been found to be useful for introducing shallow acceptors but the ZnSe layers grown in hydrogen-based plasma mixed partially with nitrogen still remained highly resistive.[1] Recently, some groups reported low resistivity p-type ZnSe:N by the same doping method employing a nitrogen plasma source for N doping during MBE growth of ZnSe.[2,3]

The plasma-assisted epitaxial growth (PAE), in which enhanced chemical reactivity and surface migration of atoms supplied through discharging plasma are employed, has been developed for reducing the temperature of epitaxial growth. The purpose of this paper is to describe the dependence of optical and electrical property of PAE-ZnSe on $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio in its plasma-assisted epitaxial growth in nitrogen-based plasma and then successful reduction of p-type resistivity down to the order of 10Ωcm at room temperature. It will be also indicated that the excessive hydrogen can deteriorate the doping efficiency of shallow acceptor nitrogen.

2. EXPERIMENTAL

An experimental PAE apparatus is shown in Figure 1. The details of growth procedure have been described elsewhere.[4]

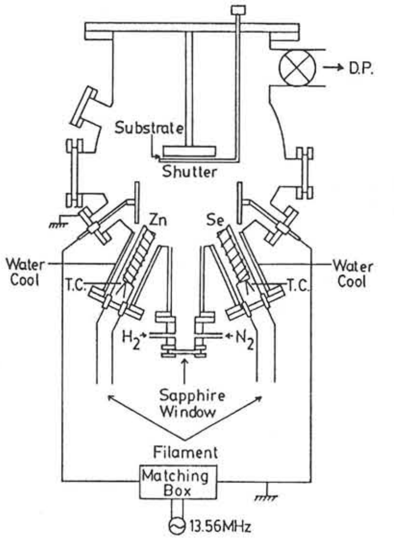

Fig.1 An experimental PAE apparatus for ZnSe.

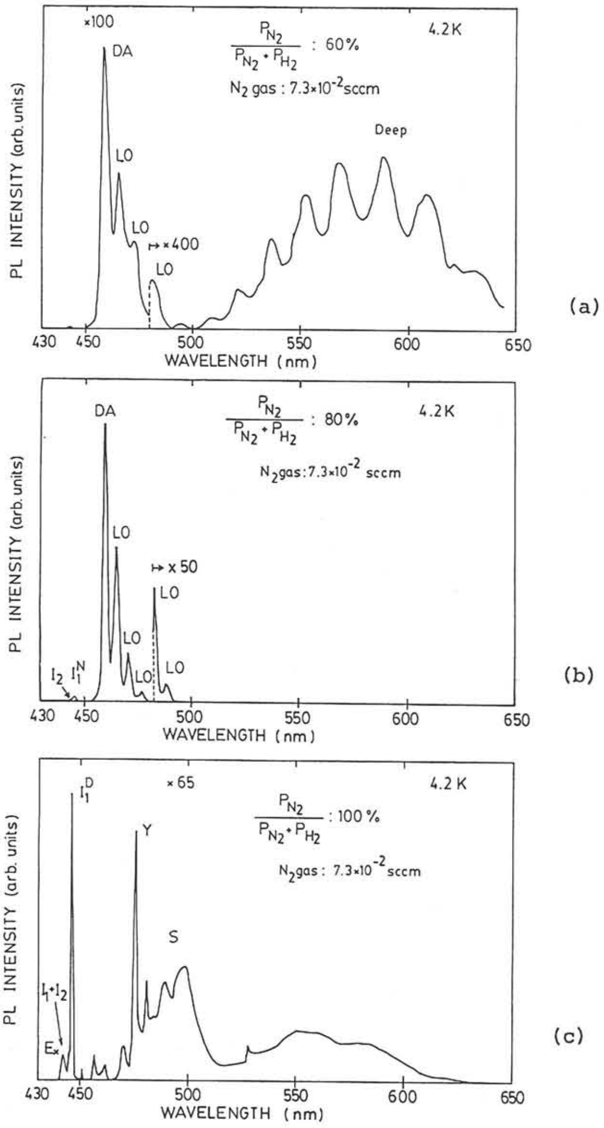

Fig.2 PL spectra of N-doped ZnSe layers grown on (100) GaAs at N_2 gas flow rate of 0.073sccm with different $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratios (a)60, (b)80 and (c)100%.

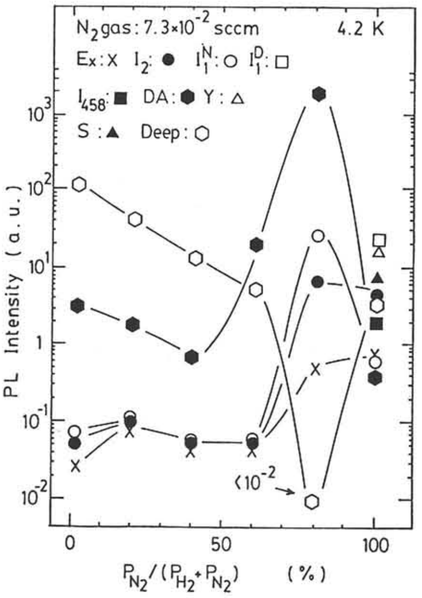

Fig.3 The dependence of PL intensities of various emission peaks on $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio. (N_2 gas flow rate of 0.073sccm)

Elemental metallic Zn and Se shots (99.9999% pure) were evaporated by resistive heating and supplied toward the growing surface after excitation and partial ionization in (H_2+N_2) mixed or N_2 plasma. Hydrogen gas (99.99999% pure was further purified by a palladium diffuser), mixed with N_2 gas (99.9995% pure) for doping was introduced into the chamber and excited through capacitive coupling by rf power at 13.56MHz.

The ZnSe films were grown on semi-insulating (100) GaAs substrates at substrate temperature of 320°C with typically 10W rf power applied to excite the plasma. The total pressure at growth was 0.004Torr. The N_2 gas flow rate was varied between 0.073 ~ 1.4sccm, while the Zn and Se crucible temperatures were fixed at 350 and 185°C, respectively. The growth rate of ZnSe:N ranged from 0.6 ~ 0.8μm/h, and the thickness of films was between 1.2 and 1.6μm.

The low temperature photoluminescence (PL) spectra were measured at 4.2K with excitation by ultraviolet (UV) light of a 500W Hg(Xe) lamp through a filter UVD-36A for cutting off the light of wavelength longer than 400nm.

3. RESULTS AND DISCUSSION

The 4.2K PL spectra of N-doped ZnSe layers grown with N_2 gas flow rate fixed at 0.073sccm, are shown in Figure 2 for different $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratios 60, 80 and 100%. Figure 3 summarizes the dependence of PL intensities of various emission peaks on $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio. Although deep level emission is dominant in the low partial pressure ratio, the intensity of donor-acceptor (DA) pair emission as well as deep level emission decreases gradually with the increased partial pressure ratio, but further increase of partial pressure ratio leads to the increase of DA and I_1^N (acceptor-bound exciton peak) emissions. At partial pressure ratio around 80%, DA and I_1^N emissions show maximum with negligible deep level emission as shown in Figures 2 and 3. P-type conductivity of this layer was confirmed by Hall measurement using Au electrodes and the resistivity was the order of 10Ωcm. It has been indicated that excited hydrogen is useful to remove residual impurities in the growth ambient[5] and it is also speculated that a small quantity of hydrogen can possibly enhance nitrogen-

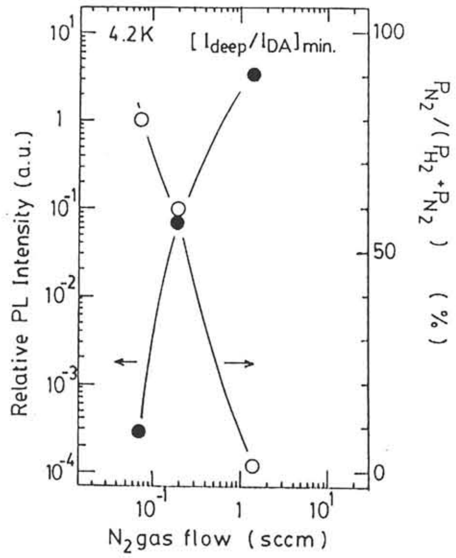

Fig.4 The minimum of I_{deep}/I_{DA} PL intensity ratio of ZnSe:N grown in (H_2+N_2) mixed plasma at a constant N_2 gas flow rate, and $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio at which this minimum is obtained.

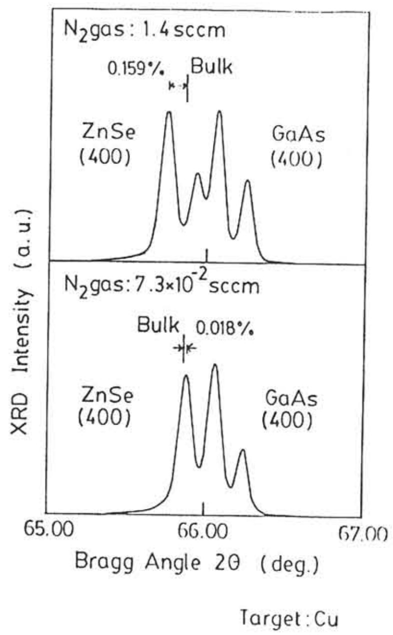

Fig.5 The (400) X-ray diffraction patterns of N-doped ZnSe layers with minimum I_{deep}/I_{DA} PL intensity ratio grown at N_2 gas flow rate of 0.073 and 1.4sccm.

acceptor doping by generating atomic nitrogen through Penning effect. However, it is here to be noted that excessive hydrogen should compensate nitrogen-acceptors by forming, for example, H-N bonding.

Figure 4 shows the minimum of I_{deep}/I_{DA} PL intensity ratio of ZnSe layers grown in (H_2+N_2) mixed plasma at a constant N_2 gas flow rate, and $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio at which this minimum is obtained. When the N_2 gas flow rate was increased, the minimum of I_{deep}/I_{DA} ratio was increased by many orders of magnitude and the optimum $P_{N2}/(P_{H2}+P_{N2})$ ratio was drastically decreased. The larger hydrogen partial pressure required at higher N_2 flow rate to reduce deep level PL emission seems to indicate that hydrogen can be useful to remove residual impurities in the growth ambient, as shown before[5], but the above result also suggests that some nitrogen species in the growth ambient can induce unknown deep complex defects.

Figure 5 shows the (400) X-ray diffraction (XRD) patterns for N-doped ZnSe with minimum I_{deep}/I_{DA} grown with N_2 gas flow rate of 0.073 and 1.4sccm. A ZnSe layer grown with large N_2 flow rate has larger lattice constant than bulk ZnSe, while that with smaller flow rate has smaller lattice constant than bulk ZnSe. This result also supports the incorporation of inert nitrogen such as interstitial N, N_2 molecule, SeN[5] etc. which can form complex defects suggested in the above.

4. CONCLUSIONS

P-type ZnSe:N layers with resistivity of the order of 10Ωcm, with strong shallow nitrogen-acceptor-related PL and with negligible deep level PL, was grown epitaxially on semi-insulating (100) GaAs by plasma-assisted epitaxy in nitrogen-based plasma. The N_2 flow rate and $P_{N2}/(P_{H2}+P_{N2})$ partial pressure ratio have profound effects on the electronic property of PAE-ZnSe:N. Further study on optimized growth conditions is required for further improvement.

REFERENCE

1) S. Yamauchi and T. Hariu, Appl. Sur. Sci. 33/34(1988) 862.
2) R.M. Park, M.B. Troffer, and C.M. Rouleau, J.M.DePuydt and M.A. Haase, Appl. Phys. Lett. 57(1990) 2127.
3) K. Ohkawa, T. Karasawa and T. Mitsuyu, J. Cryst. Growth 111 (1991) 797.
4) H. Sato, O. Osada, K. Matsushita, T. Hariu and Y. Shibata, Vacuum 36(1986) 133.
5) S. Yamauchi and T. Hariu, Mat. Res. Soc. Symp. Proc. Vol.161,(1990) 147.