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Nitrogen-Doped ZnSe Grown on Vicinal (100)-Oriented and (211)-Oriented GaAs Substrates by Molecular Beam Epitaxy

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This letter presents the growth and characterization of N-doped ZnSe grown on vicinal (100) and (211)GaAs. The effects of the surface step and the step density on the formation of deep donors are investigated by comparison of the PL property and net-acceptor concentration of N-doped ZnSe epilayers grown on the vicinal surfaces with those on the exact (100) surface. It is shown that the use of the vicinal substrate suppresses the generation of deep donor. The effects of bonding natures at Zn sites on the N-incorporation process are studied through the comparison of the net-acceptor concentration of N-doped ZnSe epilayers grown on the (211)A-surfaces with those on the (211)B-surface. It is found that the N incorporation is limited by single-dangling bond at the Zn sites.

1. INTRODUCTION

The low resistive p-type ZnSe material has been achieved using a plasma source for nitrogen (N) doping during molecular beam epitaxy (MBE).[1,2] This progress in p-type doping of ZnSe has led to the demonstration of a blue-green diode laser in ZnSe-based heterostructures.[3,4] The net acceptor concentration (N_A-N_D) in p-type ZnSe increases monotonically with increasing the concentration of incorporated nitrogen up to ~10^{18}cm^{-3},[5,6] while it decreases when the N concentration exceeds ~5×10^{18}cm^{-3}. Under optimal conditions, net acceptor concentration up to 1×10^{18}cm^{-3} in p-type ZnSe epilayer with N concentration of 5.2×10^{18}cm^{-3} was obtained.[5] One of the main causes of the upper limit on the attainable net acceptor concentration is compensation related to the formation of N-associated donors.[7,8] The formations of defects in ZnSe during growth depend on the surface structure, bond configuration, type of surface steps, and their density. The purpose of this study is to examine the effects of these parameters on the quality of ZnSe and the nitrogen-doping behavior. We have performed three types of experiments: comparison of growth on exact (100)-oriented GaAs with that on (100) misoriented 2° and 4° off toward (110); comparison of growth on exact (100) with that on (100) misoriented 4° off toward (110) and (010); comparison of N-doping of ZnSe on (211)A-oriented GaAs with that on (211)B. The use of vicinal (100) allows us to study the effect of the surface steps and the step density, and the use of both the (211)A and (211)B orientations to determine the effect of change in the single and double bonding natures of Zn and Se sites. This letter presents the growth and characterization of N-doped ZnSe grown on vicinal (100) and (211)GaAs. We show that the use of the vicinal substrate improves the crystal quality of N-doped ZnSe and suppresses the compensation by the deep donor, and that the N-incorporation process depends strongly on the surface bonding nature.

2. EXPERIMENTAL

The N-doped ZnSe films were grown on (100)- and (211)-oriented GaAs substrates by MBE. The active nitrogen flux produced by a microwave plasma source was injected into the MBE chamber through a quartz glass pipe. The N concentration incorporated in ZnSe films was controlled by changing microwave power in a range of 50-200W or the flow rate of N_2. For each growth, the samples to be compared were grown simultaneously on substrates mounted side by side. The samples grown were characterized by photoluminescence (PL) and capacitance-voltage (C-V) measurements. The PL measurement was performed with a He-Cd laser excitation of 10mW at 14K. N_A-N_D value was determined by C-V profiling using Au as a Schottky barrier metal.

3. RESULTS AND DISCUSSION

The growth conditions for the samples grown on exact and vicinal (100)GaAs were as follows: the beam pressure ratio of Zn to Se was fixed at unity and the substrate temperature was at 230°C, which yielded the Zn-rich condition; the growth rate was 0.7μm/h and the thicknesses of the films were about 2.8μm; the microwave power was kept at 120W and the flow rate of N_2 was at constant at which the background pressure during the growth was 2×10^{-6} torr. Figure 1 shows PL spectra from N-doped ZnSe epilayers grown simultaneously on the exact (110)GaAs, (100)GaAs misoriented 4° off toward (110) and (010) at substrate temperature of 230°C. The N_A-N_D values are measured to be 5×10^{16}cm^{-3} for the samples grown on (100),

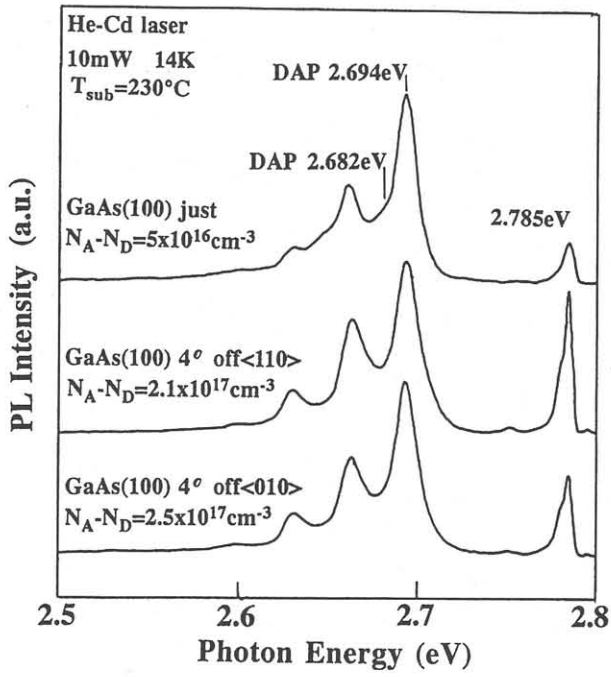

Fig.1 PL spectra from the N-doped ZnSe epilayers grown on the exact (110), (100)GaAs misoriented 4° off toward (110) and (010). The deep DAP emission at 2.682eV is not observed from the samples grown on vicinal surfaces.

$2.1x10^{17}cm^{-3}$ for the sample on (100) misoriented toward (110) and $2.5x10^{17}cm^{-3}$ for the sample on (100) misoriented toward (010). The N_A-N_D values of the epilayers grown on vicinal surfaces are 4-5 times larger than that grown on the (100). All the three samples show dominant shallow DAP emissions at 2.694eV. The deep DAP emission appears at 2.682eV in the spectrum from the sample grown on exact (100), while it is not observed from the samples grown on vicinal surfaces, indicating the reduction in the deep donors in N-doped ZnSe epilayers grown on vicinal surfaces. These facts indicate that the crystal quality of N-doped ZnSe is improved by using the vicinal surface, which results in suppression in the defect formation and increase in the N_A-N_D value. No significant difference between the samples grown on (100) misoriented toward (110) and (010) was found.

The N-incorporation process is dependent on the surface bonding nature. The polar (211) surface, on which there are two kinds of dangling bonds: single- and double-dangling bonds, provides a tool for studying incorporation process of impurities.[9,10] An ideally flat ZnSe(211) surface is shown in Fig.2. N-acceptor sites are the ones with a single back bond on the (211)A surface, whereas they are the ones with double back bond on the (211)B surface.

In this study, the (211)A- and (211)B-GaAs wafers was used as substrates for (211)-oriented ZnSe growth. Prior to ZnSe growth, the substrates, which had been etched in 5 H_2SO_4 : 1 H_2O_2 : 1 H_2O, were cleaned thermally at temperature of 580°C. The growth conditions for N-doped ZnSe epilayers grown on (211)A- and (211)B-GaAs were as follows: the beam pressure ratio of Zn to Se was fixed at 3 and the substrate temperature was at 250°C, which yielded the Zn-rich conditions; the growth rate was 0.7μm/h and the

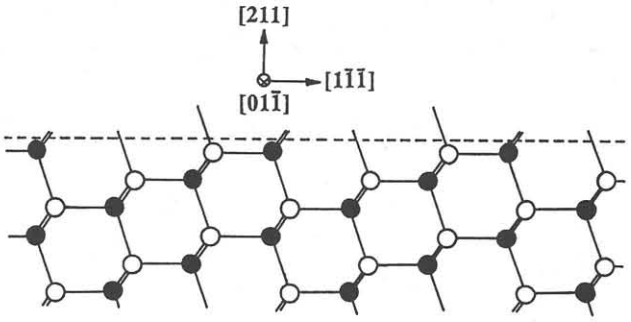

Fig.2 Crystallographic model of ideal ZnSe(211) surface. On the (211)A surface, the white circles represent Zn atoms, the black ones Se atoms, on the (211)B surface the arrangement is reversed.

thicknesses of the films were about 2.8μm; the microwave power was kept at 120W and the flow rate of N_2 was at constant at which the background pressure during the growth was $2x10^{-6}$ torr.

Figure 3 shows PL spectra from N-doped ZnSe epilayers grown simultaneously on (211)A- and (211)B-GaAs. The PL spectra from both the samples show dominant shallow donor-acceptor emission at 2.690eV and the emissions associated with deep acceptors (I_1^d) at 2.782eV. The N_A-N_D values are estimated as $8x10^{15}cm^{-3}$ for (211)A, which is 16 times larger than that for (211)B ($5x10^{14}cm^{-3}$) indicating that the the N incorporation is limited by the single-dangling bond at Zn sites. The two possible reasons for the N-incorporation rate into the (211)A surface much larger than into the (211)B surface are given in the following: (i) the density of N-acceptor (Se sublattice) sites on the (211)A surface is twice of that on the (211)B surface; (ii) N would form bonds to Zn atoms with the single-dangling bond on the (211)A easier than those with the double-dangling bonds on the (211)B, since the double-dangling bonds of Zn atoms would form dimers.

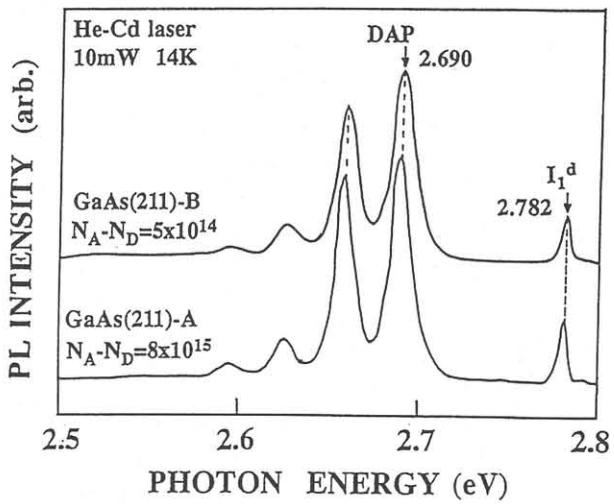

Fig.3 PL spectra from the N-doped ZnSe epilayers grown on (211)A- and (211)B-GaAs.

4. CONCLUSION

We have investigated the effects of the surface steps and the step density on the formation of deep donor through the comparison of the PL property and net-acceptor concentration of N-doped ZnSe epilayers grown on vicinal (100) surfaces with those on the exact (100) surface. It is shown that the use of the vicinal substrate improves the crystal quality of N-doped ZnSe and suppresses the generation of deep donor. The effects of bonding natures at Zn sites on the N-incorporation process are studied by comparison of the net-acceptor concentration of N-doped ZnSe epilayers grown on the (211)A-surfaces with those on the (211)B-surface. It is found that the N incorporation is limited by single-dangling bond at Zn sites.

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