MOVPE growth and DLTS study of Mn–doped ZnSe

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1. Introduction

The Mn atom has the magnetic spin whose compounds have a possibility of new functional devices such as the magnetic resistance and the magneto–optical effect. The dilute magnetic effect was intensively investigated in III–V and II–VI semiconductors by many researchers.[1–3)] The type and the concentration of the carrier can be controlled by doping an impurity independent of the amount of Mn–doping in the case of II–VI semiconductors because the Mn atom becomes +2 ion and substitutionally occupies the divalent cation site. This paper mentions the metalorganic vapor phase epitaxial (MOVPE) growth of Mn-doped ZnSe on GaAs substrates and the photoluminescence (PL) and the deep–level transient spectroscopy (DLTS) measurements on the epitaxial layers.

2. Experimental procedure

The epitaxial growth was done by MOVPE for 2 h using H_2 as a carrier gas under atmospheric pressure. Source materials were dimethyl Zn, dimethyl Se, triethyl Sb, and methylcyclopentadienyl tricarbonyl–Mn and their flow rates were 15–30, 15, 0.01 and 0.1–0.9 µmol/min, respectively. The substrate was (100) GaAs single crystal. The growth temperature was varied between 480 and 550ºC. Four–crystals X–ray rocking curves and secondary ion mass spectrometry (SIMS)studies were done. PL spectra were measured under the excitation of He–Cd laser at the temperature range between 6 and 300K. Double Schottky structure was formed on ZnSe surface by an evaporation of Au. A diameter of a small electrode is 0.5mmØ. DLTS spectra and capacitance–voltage characteristics were measured at 1MHz from 100 to 400K. On DLTS measurement a steady 5V reverse bias was used and the hight of the pulse bias, which filled with holes, is 5V.

3. Results and discussion

ZnSe was epitaxially grown on GaAs (100) substrate and the film thickness was between 1 and 4 µm. The film thickness was dependent not only with the growth temperature but also with the flow rate of Mn. The surface morphology changed with the flow rate ratio of DMSe and DMZn(VI/II) and was smooth for the films grown at VI/II=1. However the surface morphology became fairly rough for the films grown at VI/II=2. In Fig.1 the depth profiles of Zn, Se, As, and Mn by SIMS show that each concentration of Zn, Se, and Mn is nearly constant in ZnSe epitaxial layer, indicating that Mn is uniformly doped in ZnSe layer. The amount of Mn in ZnSe at Mn flow rate of 0.9µmol/min. is by three orders larger than that at 0.1µmol/min., which is enable to control the doping level of Mn. X–ray rocking curves show that the maximum amount of Mn is 12% by using the Vegard's law. As shown in Fig.2 PL spectrum at room temperature of samples grown at a Mn flow rate between 0.1 and 0.9µmol/min. shows the broad emission peaked at 580nm, which is due to the well–known Mn 3d transition from $^4T_1$ to $^6A_1$.[4)] Fig.3 shows PL spectra of the samples grown at various Mn flow rates and the undoped sample grorwn at the same growth condition. PL spectrum at 14K of the sample grown at Mn=0.1µmol/min. shows a broad emission peaked at 550nm and that at Mn=0.5µmol/min. shows a broad emission peaked at 630nm with a shoulder peaked at 550nm. The origins of PL at 550nm and 630nm seem to be due to the Mn 3d core transition and Mn–Mn cluster interaction, respectively.[6)] Fig.4 shows DLTS spectra of two samples A and B. The sample A is prepared at Mn =0.1µmol/min. and Sb=0.01µmol/min. The sample B is at Mn=0.5µmol/min. and without Sb flow. DLTS spectrum shows only one peak for the sample A and shows three peaks for the sample B. Both samples show p–type and the traps are the hole one. Arrenius plots for the traps obtained in Fig.4. The filled circule and open one correspond to (a) and (b) in Fig.4, repectively. The trap depth, the concentration, and the capture cross section are listed in Table 1. According to the trap depth all traps are different from PL emission centers shown in Fig.3. Trap parameters of both samples are different each other and the trap for the sample A does not seem to be the same trap as those for the sample B. We reported deep levels in ZnSe doped with $3.1\text{x}10^{15}$Sb cm^{-3} prepared by MOVPE in the previous paper.[7)] The activation energies are 0.54, 0.34, and 0.35eV. The capture cross sections are $2.6\text{x}10^{-15}$, $2.1\text{x}10^{-19}$,

and $5.3x10^{-17}cm^2$ for 0.54, 0.34, and 0.35eV, respectively. The concentration is in the order of $10^{13}cm^{-3}$ for three traps. Comparing with trap parmeters trap T4 is likely for 0.35eV trap in Sb−doped sample and seems to be related to Sb−doping. All traps in the sample B are different with those in Sb−doped ZnSe. Mn in the sample B is heavily doped and PL spectrum shows Mn−Mn cluster interaction. All traps in the sample B seems to be related to defects originated from Mn−doping.

4. Summary

Mn-doped ZnSe epitaxial layers on GaAs substrates were grown by MOVPE. They were examined by the photoluminescence and the deep−level transient spectroscopy measurements. The sample grown at Mn =0.1μmol/min. and Sb=0.01μmol/min. has one trap, which seems to be relalted to Sb−doping. On the other hand the sample grown at Mn=0.5μmol/min. and without Sb flow has three traps, which seem to be related to defects originated from Mn−doping.

Acknowledgements

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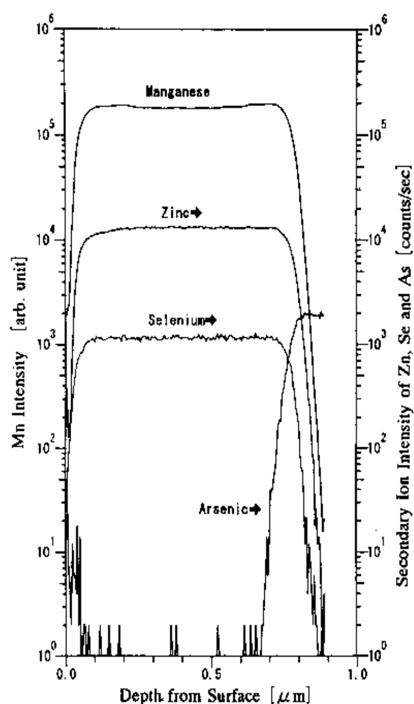

Fig.1 The depth profiles of Zn, Se, As, and Mn from the surface of ZnSe epitaxial layer by SIMS.

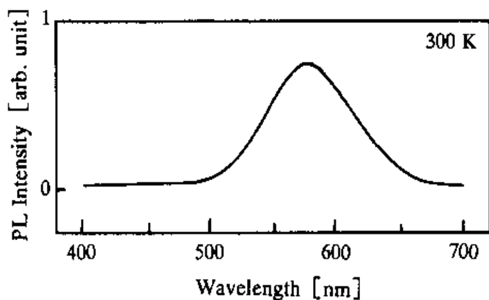

Fig.2 PL spectrum exited by He-Cd laser at room temperture for the sample grown at 550 ℃ and the Mn flow rate of 0.3 μmol/min.

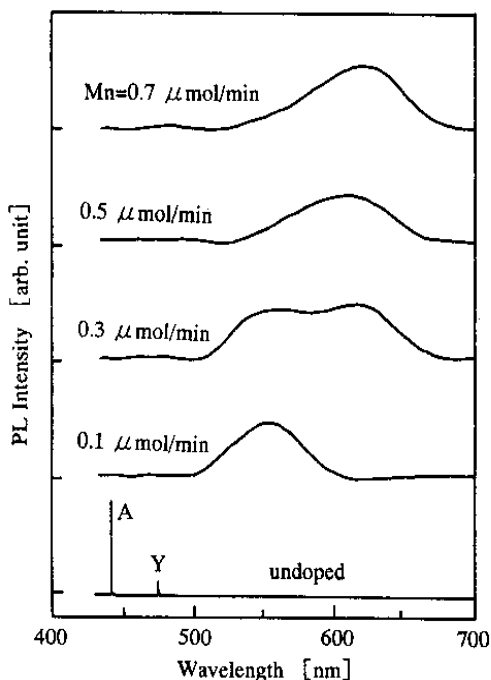

Fig.3 PL spectra exited by He-Cd laser at 30K for the sample doped with various Mn contents grown at 550 ℃ and PL spectrum at 14K for the undoped ZnSe epitaxial layer grown at 550 ℃. Notations of A and Y mean edge emission and Y emission[5], respectively.

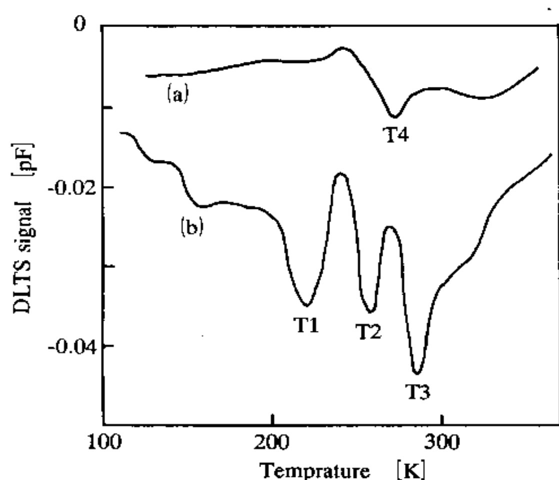

Fig.4 DLTS spectra for samples prepared at different Mn flow rates: (a) 0.1 μmol/min. and (b) 0.5 μmol/min.

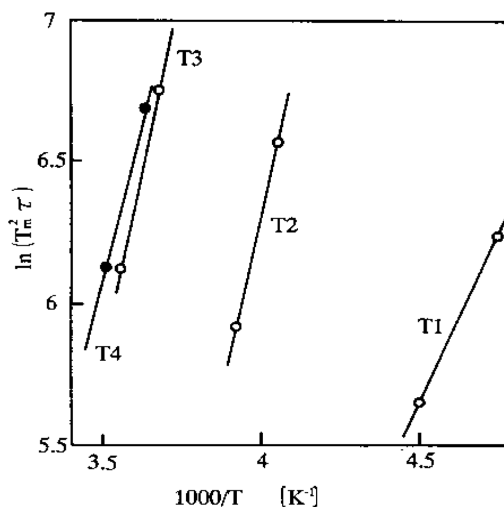

Fig.5 Arrehnius plots for the traps obtained in Fig.4. The filled circle and open one correspond to (a) and (b) in Fig.4, respectively.

Table 1 Trap parameters (depth, concentration, capture cross section) and net acceptor concentration for the Mn flow rate of 0.1 and 0.5 μ mol/min.

Mn flow rate μ mol/min.	net acceptor concentration(cm^{-3})	trap name	trap depth (eV)	trap concentration(cm^{-3})	capture cross section(cm^{2})
0.5	2.3×10^{14}	T1	0.22	5.9×10^{12}	1.0×10^{-16}
		T2	0.49	5.1×10^{12}	6.5×10^{-17}
		T3	0.46	7.1×10^{12}	7.8×10^{-16}
0.1	1.2×10^{16}	T4	0.38	1.1×10^{13}	1.0×10^{-17}