Doping efficiency of Sb in ZnSe grown by MOVPE

Toshiyuki Ido [1)] , Hideo Goto [1)]

1) Deparatment of Electrical Engineering, Chubu University, 1200 Matsumoto−cho Kasugai, Aichi, 487−8501, Japan

1. Introduction

Zinc selenide has been investigated for a candidate to a blue light emitting diode and a blue laser for a long time. There are two problems for a practical use which are to obtain a low resistive p−type ZnSe and to get a good ohmic contact to p−type ZnSe by a simple method. In metalorganic vapor phase epitaxy (MOVPE) a nitrogen doping for an acceptor impurity was done by using NH_3. However, a nitrogen atom is partially inactive by a hydrogen termination and it is difficult to get a high acceptor concentration. On the other hand a Sb atom does not seem to be terminated by a hydrogen atom. Recently the Sb−doping in ZnSe was attempted to get low resistive p−type ZnSe by several groups.[1−3)] Until now the acceptor concentration in Sb−doping is also not enough high. In this study the Sb−doping efficiency in ZnSe grown by MOVPE was investigated and the mechanism of the low doping efficiency is shown.

2. Experimenal procedure

Sb−doped ZnSe epitaxial layers were grown by MOVPE in an atmospheric pressure. Substrates are (100) GaAs single crystals with the acceptor concentration of $10^{19}cm^{-3}$. Dimethyl Se(DMSe) and dimethyl Zn (DMZn) were used as the source materials, triethyl Sb (TESb) was used as the Sb source, and hydrogen was used as the carrier gas. The flow rates of DMSe, DMZn, and TESb were 15−30, 15, and 0−1.0 µmol/min., respectively. The growth temprature was 550ºC and the growth time is 2.5h. Photoluminescence (PL) measurement was done at the temperature range between 6 and 300K using a He−Cd laser. Four−crystals X−ray rocking curves were obtained by X−ray diffractometer. The concentration of Sb was measured by secondary ion mass spectrometry (SIMS). Net acceptor concentration was obtained from capacitance−voltage characteristicsat room temperature.

3. Results and discussion

ZnSe layers were epitaxially grown on GaAs substrates and the thickness of ZnSe layers was 4−6µm. Fig.1 shows the dependence of full width at half maximum (FWHM) of X−ray rocking curves reflected from (400) face on the flow rate ratio of DMSe and DMZn (VI/II) at TESb=0.01µmol/min. This shows that the crystalline quality of the epitaxial layer is the best at VI/II=2.45 and that its value of FWHM is 280 arc sec. This is constant up to TESb=0.1µmol/min. However, the peak of ZnSe (400) reflection becomes broader with increasing TESb as shown in Fig.2. Besides the additional diffraction peaks appear as shown in Fig.3. The additional peaks were identified as Sb_2Se_3, SbZn, and (SbZn)6H and the peaks become larger with the increase of TESb. By the observation of scanning electron microscopy the morphology of as−grown surface is smooth up to TESb=0.40 µmol/min. Above TESb=0.60 µ¼mol/min. there appear precipitates on the surface of ZnSe layer and at TESb=1.00 µmol/min. and the diameter of the precipitate becomes 20−30µm. Fig.4 gives the dependence of Sb concentration in ZnSe epitaxial layer on the flow rate ratio of VI/II at TESb=0.01µmol/min. obtained from the SIMS analysis. When VI/II increased from 2 to 3.3 at TESb =0.01 µmol/min., the Sb concentration decreases from $4x10^{19}/cm^3$ to $3x10^{18}/cm^3$. On the other hand, it is shown in Fig.5 that the Sb concentration becomes higher with increasing TESb at a constant VI/II. However, the net acceptor concentration is less than $10^{17}/cm^3$ as shown in Fig.6 obtaind from the capacitance−voltage characteristic. Fig.7 shows the dependence of PL spectrum at 30K on the flow rate of TESb at VI/II=2.88. Fig.8 shows the dependence of PL emission intensity on the flow rate ratio of VI/II at TESb=0.01µmol/min. The notations of I1, DEEP1, and DEEP2 are the emission from the exiton bound to the neutral acceptor peaked at 444.3nm, the broad emission peaked at 550nm, and the broad emission at 620nm, respectively. As shown in Fig.7 the PL spectrum of the sample grown at 0.01 µmol/min. shows I1 emission, donor−acceptor pair emission, and very weak broad emission peaked at 550nm, implying that the grown layer is a good crystalline quality. When TESb=0.016 µmol/min., the broad emission at 550nm becomes dominant. From

Fig.8 this emission intensity becomes stronger with increasing VI/II, indicating that this emission seems to be related to zinc vacancy. There are several papers about the origin of deep levels. A.R. Reinberg et al.[4] reported that P and As give deep acceptor levels. K.W. Kwak et al.[5] reported that interstital atoms make the deep levels. D.J. Chadi[6] showed the possibility that the lattice relaxation leads to the formation of so−called DX centers for deep levels. We repoted that Sb is a shallow acceptor with the activation energy of 70meV.[1] Although we cannot define the origin of the deep level at present, the high doping of Sb in ZnSe seems to make a deep acceptor as well as a shallow one. It is concluded that the net acceptor concentration at the high doping of Sb is limited by the generation of the deep acceptor and the appearance of compounds such as Sb_2Se_3.

4. Summary

Sb−doped ZnSe epitaxial layers were grown on (100) GaAs substrates by MOVPE in an atmospheric pressure. In order to investigate the behaviour of Sb, photoluminescence measurement, four−crystals X−ray diffractometer, and secondary ion mass spectrometry were used. It is elucidated that a Sb atom does not only occupy the substitutional site but also makes compounds such as Sb_2Se_3 and/or the deep acceptor when the Sb−doing becomes high. It seems to be the reason why the effective acceptor concentration remains less than $10^{17}/cm^3$.

Acknowledgements

The authors are grateful to Dr. Sobue of Denso Co., Ltd. for SIMS analyses. This research was supported in part by a grant from the High−Tech Research Center Establishment Project of Ministry of Education, Culture, Sports, Science and Technology.

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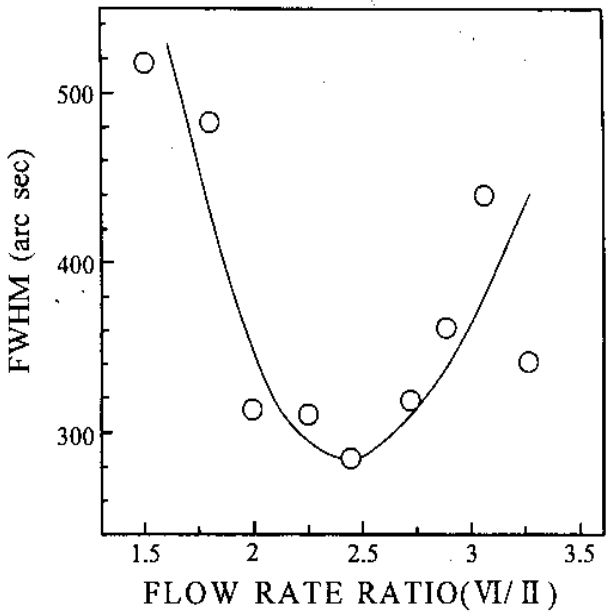

Fig.1 The dependence of FWHM of X-ray rocking curves reflected from (400) face on the flow rate ratio of VI/II at TESb=0.01 μmol/min.

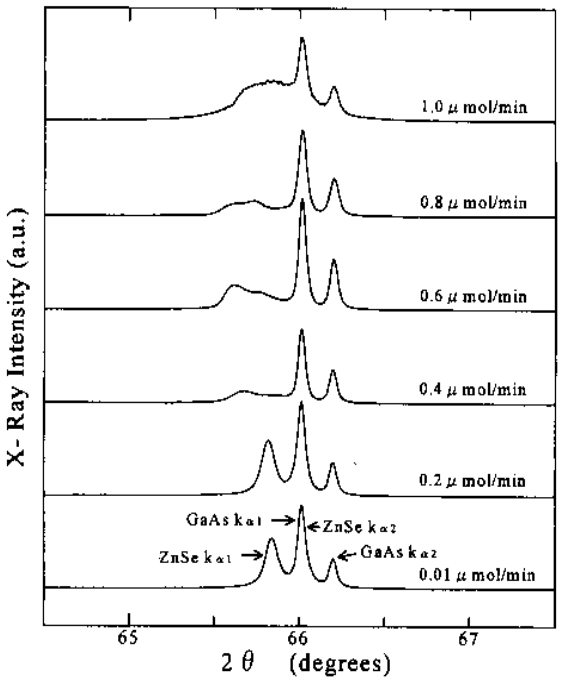

Fig.2 The dependence of X-ray rocking curves reflected from (400) face on the flow rate of TESb at VI/II=1.5.

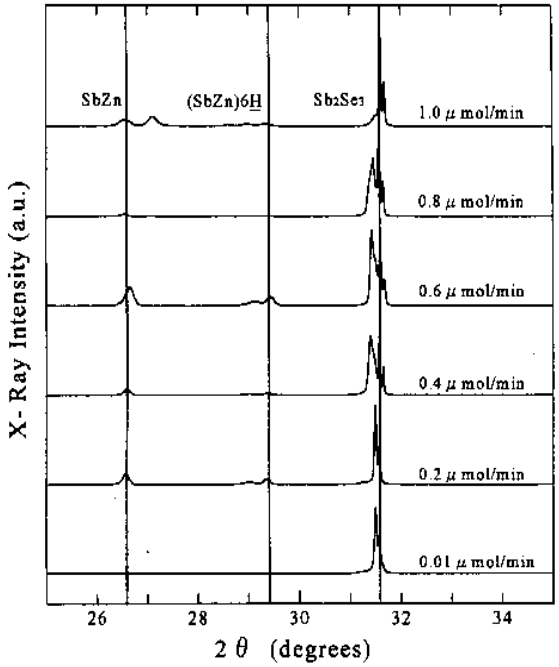

Fig.3 The change of X-ray diffraction intensity of Sb compounds by the flow rate of TESb at VI/II=1.5.

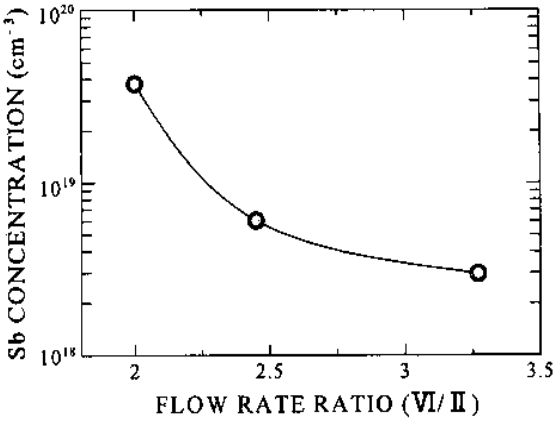

Fig.4 The dependence of Sb concentration in ZnSe epitaxial layer on the flow rate ratio of VI/II at TESb=0.01 μmol/min. from the SIMS analysis.

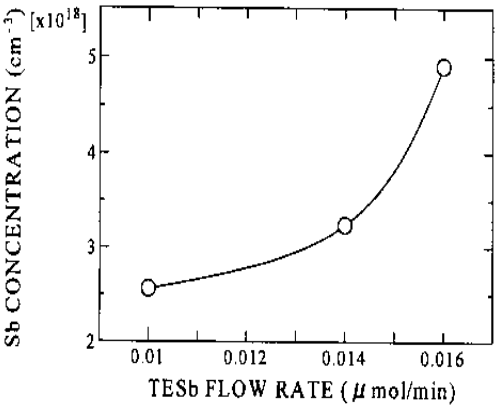

Fig.5 The dependence of Sb concentration in ZnSe epitaxial layer on the flow rate of TESb at VI/II=2.88 from the SIMS analysis.

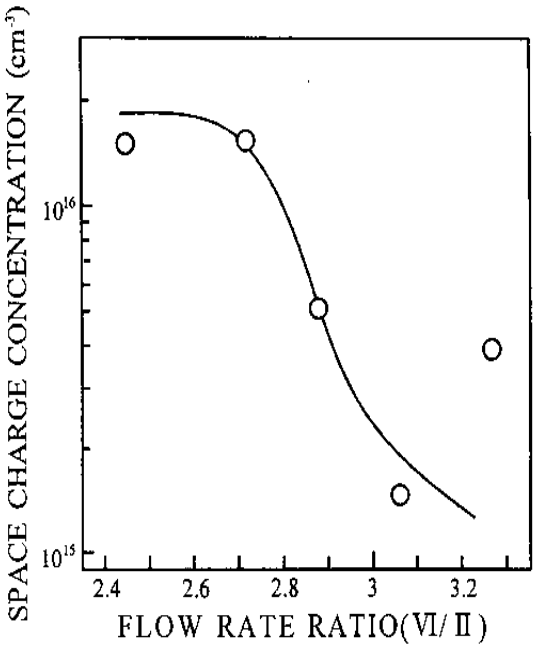

Fig.6 The dependence of space charge concentration in ZnSe epitaxial layer on the flow rate ratio of VI/II at TESb=0.01 μmol/min. from the capacitance-voltage measurement.

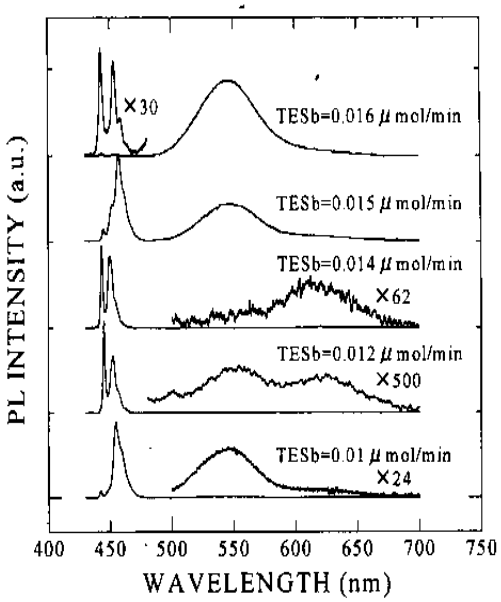

Fig.7 The dependence of PL spectrum at 30K on the flow rate of TESb at VI/II=2.88.

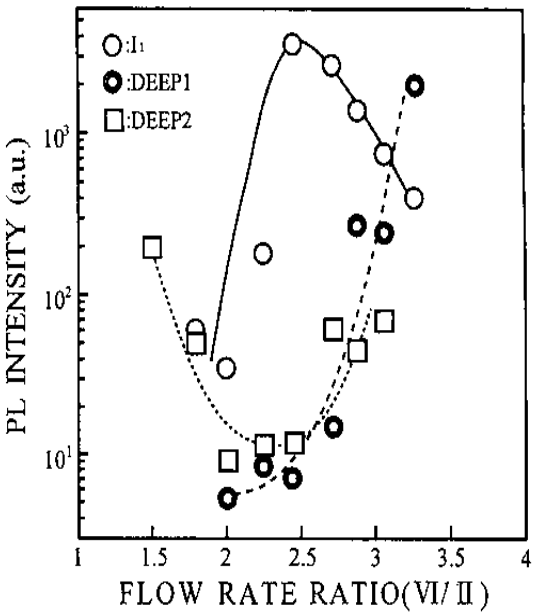

Fig.8 The dependence of PL emission intensity on the flow rate ratio of VI/II at TESb=0.01 μmol/min. I1, DEEP1, and DEEP2 are the emission from the exiton bound to the neutral acceptor peaked at 444.3nm, the broad emission peaked at 550nm, and the broad emission at 620nm, respectively.