

## On p-Type Doping Limits in ZnMgSSe Quaternary Semiconductors

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p-Type doping limits in ZnMgSSe was calculated based on an amphoteric native defect model. The fitting to measurements considering the growth temperature showed that the band offset in ZnSe/ZnMgSSe will be localized to the valence band, i.e.,  $\Delta E_v = 0.95\Delta E_g$  or  $0.7\Delta E_g$  that is close to Shahzad's report ( $\Delta E_v \cong 0.9\Delta E_g$ ). It was found that the decrease of doping efficiency for the larger energy gap in ZnMgSSe is also similar in ZnSSe, but it can be improved by using ZnCdMgSe or ZnMgSe compound semiconductors.

### 1. Introduction

II-VI compound semiconductors such as ZnSe have wide band gap and are expected to play a major role for fabricating blue and shorter wavelength laser diodes, and active researches have been carried out. Basic II-VI heterostructures for this purpose will be based on ZnSe/ZnMgSSe systems lattice matched to GaAs. For example, if the active layer is ZnSe ( $E_g \cong 2.7\text{eV}$ ), the energy gap of ZnMgSSe cladding layer should be more than 3.1eV to prevent leakage currents<sup>1</sup>. However, there remains a problem on p-doping. The net acceptor concentration  $N_A - N_D$  is decreased for the larger energy gap in ZnMgSSe<sup>2</sup>. If this problem is intrinsic, the p-doping in ZnMgSSe cladding layers will be difficult. This phenomenon was explained by Kondo et al. with an amphoteric native defect (AND) model using the valence band offset of 33~45% ( $\Delta E_v = 0.33 \sim 0.45\Delta E_g$ ) for ZnSe/ZnMgSSe interfaces<sup>3</sup>. While Miyajima et al. reported that the band offset in ZnSe/ZnMgSSe is  $\Delta E_v \cong 0.60\Delta E_g$  with theoretical fitting to PL peak positions<sup>4</sup>, Shahzad et al. recently reported that the band offset is localized to valence band, i.e.,  $\Delta E_v \cong 0.90\Delta E_g$ <sup>5</sup>.

This paper re-examines the AND model on available doping experiments on ZnMgSSe, ZnSSe and ZnMgSe. The fitting to p-type doping in ZnMgSSe considering the growth temperature showed that the band offset in ZnSe/ZnMgSSe will be localized to the valence band from the viewpoint of the AND model. Although the decrease of p-type doping efficiency for the larger energy gap in ZnSSe is similar to ZnMgSSe, the AND model predicts that the p-type doping efficiency is much improved in ZnMgSe and ZnCdMgSe compound semiconductors. Although lattice matching is difficult for ZnMgSe ternary alloys, ZnCdMgSe can be lattice matched to InP substrates.

### 2. Amphoteric native defect model

Fundamental concept of the AND model is following<sup>6,7</sup>: The Fermi level stabilization energy ( $E_{FS}$ ) works as an energy reference among similar semiconductors. When a Fermi level is shifted from  $E_{FS}$ , creation of native defects limits the Fermi level separation from  $E_{FS}$ . On p-type doping,  $E_F$  shifts toward the lower energy below  $E_{FS}$  ( $E_F < E_{FS}$ ). This creates donor like defects, and this compensation mechanism prevents the Fermi level from separating from  $E_{FS}$ . This is expressed by the Fermi-level dependent formation energy of donor defects, and the formation energy is reduced for the larger separation of the Fermi level from  $E_{FS}$ . The maximum Fermi level separation from  $E_{FS}$  is known to be common among III-V semiconductors and the corresponding Fermi level position was assigned as  $E_{SI}$ <sup>6</sup>.  $E_{SI}$  was also shown to be common among II-VI semiconductors if the compensation mechanism is the same<sup>3,7</sup>.

In case of thermal equilibrium, the ratio of N acceptor to defect concentration is given by<sup>3,6,7</sup>,

$$\frac{[N_{Se}]}{[D]} = \exp\left[\frac{E_{df}}{kT}\right] = \exp\left[\frac{2(E_F - E_{SI})}{kT}\right], \quad (1)$$

where  $[N_{Se}]$  is the N acceptor concentration,  $[D]$  is the donor defect concentration related to N,  $E_{df}$  is the formation energy of donor defects,  $k$  is the Boltzmann constant,  $T$  is the absolute growth temperature where the donor defects are created and  $E_F$  is the Fermi level. In Eq (1) the defect formation energy  $E_{df}$  is expressed to be dependent on the Fermi level as discussed above. If the defect formation energy is independent of the Fermi level position, the defect concentrations naturally increase for the higher growth temperature. But since the Fermi level is temperature dependent, the defect formation energy will be also temperature dependent through the Fermi level. Therefore the temperature dependence of the self-compensation by the created native defects may not be simple.

The donor defects are deeply related to nitrogen atoms, for example, interstitial nitrogen<sup>3</sup>, double-broken bonds related to substitutional N<sup>8</sup>, complex formation with Se vacancy<sup>9, 10, 11</sup>, or complex formation with Zn<sup>11</sup>. Then total nitrogen concentration  $[N]$  is expressed by,

$$[N] = [N_{Se}] + [D]. \quad (2)$$

The hole concentration  $p$  is assumed to be given by,

$$p = [N_{Se}] - [D] = N_v \mathcal{F}\left(\frac{-E_F}{kT}\right), \quad (3)$$

where  $\mathcal{F}$  is the Fermi-Dirac integral and  $N_v$  is the valence band effective density of states.

The energy position of  $E_{Si}$  is estimated from the saturation values of the net acceptor concentration or hole concentrations measured at room temperature by C-V and Hall measurements, respectively. Saturation of hole concentrations at around  $1.5 \times 10^{18} \text{cm}^{-3}$  is measured in ZnSe and this leads to  $E_{Si}$  value of 51.7 meV above  $E_v$  of ZnSe. In the following section, the doping properties will be calculated using this  $E_{Si}$  value common among II-VI semiconductors. The position of  $E_{Si}$  relative to the valence band top in other II-VI semiconductors is calculated with the respective band offsets to ZnSe.

### 3. Results and discussions

Figures 1 and 2 show the fitting of the AND model to the measured  $N_A - N_D$  values in ZnMgSSe. We assume an effective hole mass of  $m_v = 0.6m_0$  in ZnMgSSe similar to in ZnSe. The open circles show experimental data from refs. [2] and [12] in Figs. 1 and 2, where the growth temperature is 320°C and 280°C, respectively. Nitrogen concentrations and the valence band offsets were left as fitting parameters and the reasonable fits shown in Figs. 1 and 2 were obtained with  $[N] = 6.0 \times 10^{17} \text{cm}^{-3}$  and  $\Delta E_v = 0.95 \Delta E_g$ , and  $[N] = 1.5 \times 10^{17} \text{cm}^{-3}$  and  $\Delta E_v = 0.7 \Delta E_g$ , respectively. Although the nitrogen concentration used in Fig. 1 for the fitting is lower than the measured value with SIMS, the value of the nitrogen concentration does not influence the slopes of the lines for the higher energy gap. It only changes the saturation level of the net acceptor concentration at lower energy gap. In both cases, nice fitting was possible with the valence band offset closer to the report of ref. [5],  $\Delta E_v \approx 0.90 \Delta E_g$ . The difference of the valence band offsets used for the fitting of the measurements on ZnMgSSe shows the limited accuracy of the present AND model. Both results show that the decrease of maximum doping concentration for the larger energy gap is serious in ZnMgSSe.

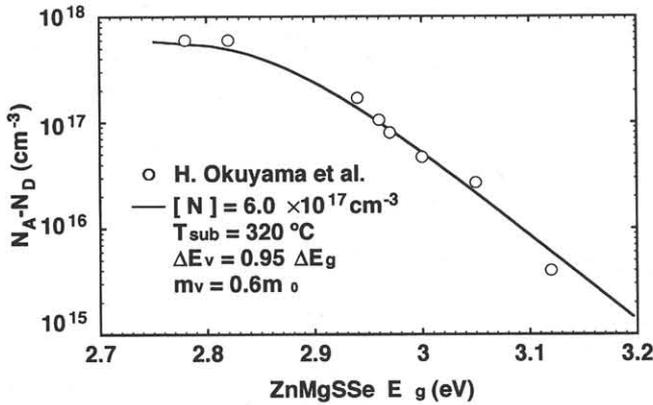


Fig. 1. The dependence of  $N_A - N_D$  on the energy gap of ZnMgSSe. The solid line shows calculated result. The open circles show experimental data from ref. [2].

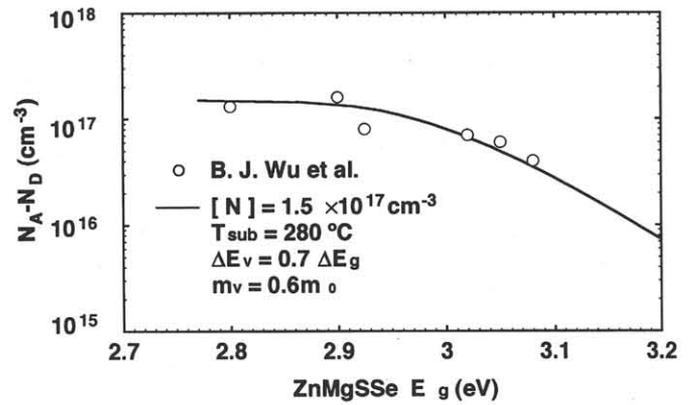


Fig. 2. The dependence of  $N_A - N_D$  on the energy gap of ZnMgSSe. The solid line shows calculated result. The open circles show experimental data from ref. [12].

The net acceptor concentrations measured in ZnSSe were also studied with the AND model. The MBE growth at 300°C reported by Teraguchi et al. [13] was well fitted with the AND model using the reported valence band offsets  $\Delta E_v = 0.927 \Delta E_g$  for ZnSe/ZnSSe system and assuming  $[N] = 1 \times 10^{18} \text{cm}^{-3}$  and  $m_v = 0.49m_0$  and the results are shown in Fig. 3. The decrease of the maximum net acceptor concentration for the larger energy gap is also clear in ZnSSe due to the compensation predicted by the AND model.

Figure 4 (a) is the results of n-type doping in ZnMgSe. The net donor concentration measured on ZnMgSe doped with  $\text{ZnCl}_2$  at the growth temperature of 330°C is shown with the open circles<sup>14)</sup>. The n-type doping limit of ZnSe was assumed to be  $2 \times 10^{19} \text{cm}^{-3}$  and then the upper limit of ZnSe Fermi level,  $E_{Si}$ , is estimated to be 165 meV above the conduction band. This  $E_{Si}$  level is also common among II-VI semiconductors in the AND model. Using the electron effective mass of  $0.16m_0$  and assuming the total Cl concentration of  $2 \times 10^{19} \text{cm}^{-3}$ , the measurements are well fitted by the band offset of  $\Delta E_c = 0.8 \Delta E_g$ .

The p-type doping property of ZnMgSe was calculated with the resultant valence band offset of  $\Delta E_v = 0.2 \Delta E_g$ . The nitrogen concentration of  $1.5 \times 10^{18} \text{cm}^{-3}$  and the growth temperature of 300°C were assumed. The decrease of the p-type doping efficiency in ZnMgSe for the larger energy gap is not so significant as those in ZnMgSSe and ZnSSe. But

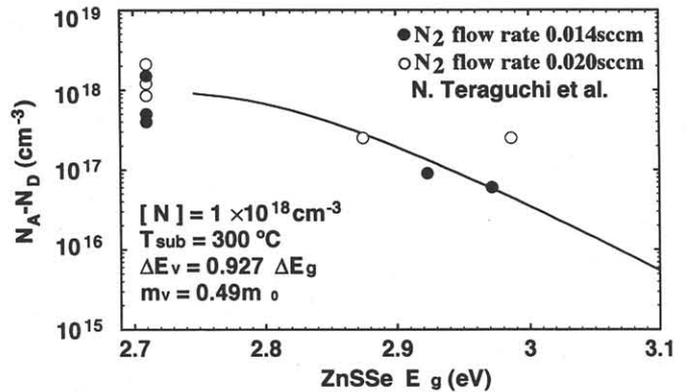
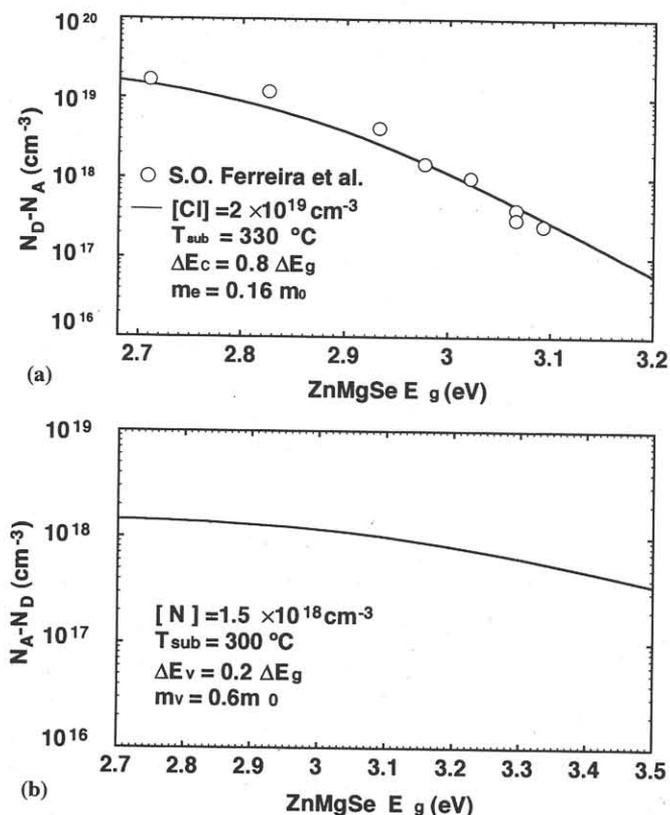
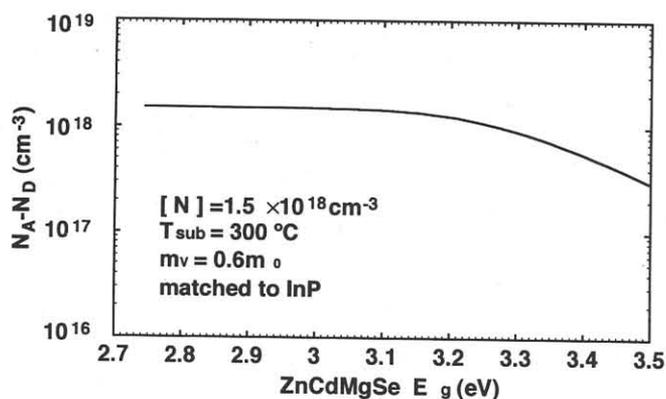


Fig. 3. The dependence of  $N_A - N_D$  on the energy gap of ZnSSe. The solid line shows the calculated results. The closed and open circles show experimental data at 300 °C from ref. [13].



**Fig. 4.** (a) Dependence of  $N_A - N_D$  on the energy gap for n-type ZnMgSe. The solid line shows the calculated result. The open circles show experimental data from ref. [14]. (b) The p-type doping limits of ZnMgSe calculated with AND model.



**Fig. 5.** The p-type doping limits of ZnCdMgSe calculated with AND model.

since the lattice constant of MgSe is larger than that of GaAs by 4.2%, the problems of the dislocation formation due to lattice mismatch to GaAs substrates will be serious.

Figure 5 examines another possibility of p-type doping in ZnCdMgSe. This quaternary compound can be matched to InP substrates and the band gap can be controlled from 2.4eV to 3.5eV. The valence band offset was linearly interpolated using  $\Delta E_v = 0.19\text{eV}$  for ZnSe/MgSe discussed in Fig.4 and  $\Delta E_v = 0.56\text{eV}$  of MgSe/ $\text{Zn}_{0.46}\text{Cd}_{0.54}\text{Se}$ .<sup>15)</sup> The improvement of p-type doping efficiency for the larger energy gap will be possible in ZnCdMgSe.

#### 4. Conclusions

The experimental doping data of ZnMgSSe, ZnSSe, and ZnMgSe were examined with the AND model. The band offset in ZnSe/ZnMgSSe was suggested to be localized to the valence band,  $\Delta E_v = 0.7 \sim 0.95 \Delta E_g$ . It is closer to  $\Delta E_v = 0.90 \Delta E_g$  reported by Shahzad et al. The decrease of the doping efficiency in ZnMgSSe and ZnSSe for the larger energy gap was well reproduced with the AND model. Based on this model, this problem in ZnMgSSe and ZnSSe may be cleared in ZnMgSe or ZnCdMgSe. High-quality heterostructures will be possible with ZnCdMgSe by lattice matching to InP substrates<sup>16,17)</sup>.

#### 5. Acknowledgements

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#### References

- 1) I. Suemune: Jpn. J. Appl. Phys. **31** (1992) L95
- 2) H. Okuyama, Y. Kishita, T. Miyajima, A. Ishibahi, and K. Akimoto: Appl. Phys. Lett. **64** (1994) 904.
- 3) K. Kondo, H. Okumura, and A. Ihibahi: Appl. Phys. Lett. **64** (1994) 3434.
- 4) T. Miyajima, F. P. Logue, J. F. Donegan, J. Hegarty, H. Okuyama, A. Ishibahi, and Y. Mori: Appl. Phys. Lett. **66** (1995) 180.
- 5) K. Shahzad, J. Petruzzello, J. M. Gaines, and C. Ponzoni: Appl. Phys. Lett. **67** (1995) 695.
- 6) W. Walukiewicz: Materials Science Forum **143-147** (1994) 519.
- 7) W. Walukiewicz: private communication.
- 8) C. H. Park and D. J. Chadi: Phys. Rev. Lett. **75** (1995) 1134.
- 9) Y. Marfaing: J. Cryst. Growth **138** (1994) 305.
- 10) I. S. Hauksson, J. Simpson, S. Y. Wang, K. A. Prior, and B. C. Cavenett: Appl. Phys. Lett. **61** (1992) 2208.
- 11) A. García and J. E. Northrup: Phys. Rev. Lett. **74** (1995) 1131.
- 12) B. J. Wu, J. M. DePuydt, G. M. Haugen, G. E. Höfler, M. A. Haase, H. Cheng, S. Guha, J. Qiu, L. H. Kuo, and L. Salamanca-Riba: Appl. Phys. Lett. **66** (1995) 3462.
- 13) N. Teraguchi, S. Hirata, H. Mouri, Y. Tomomura, A. Suzuki, H. Takiguchi: J. Cryst. Growth **150** (1995) 803.
- 14) S. O. Ferreira, H. Sitter and W. Faschinger: Appl. Phys. Lett. **66** (1995) 1518.
- 15) M. W. Wang, J. F. Swenberg, M. C. Philips, E. T. Yu, J. O. McCaldin, R. W. Grant, and T. C. McGill: Appl. Phys. Lett. **64** (1994) 3455.
- 16) T. Morita, A. Kikuchi, I. Nomura, and K. Kishino: Proc. of IPPRM '95, p. 805.
- 17) N. Dai, A. Cavus, R. Dzakpasu, and M. C. Tamargo: Appl. Phys. Lett. **66** (1995) 2742.