Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 399-402

Oxygen-Doped ZnSe Grown by Molecular Beam Epitaxy

K. Akimoto, T. Miyajima, and Y. Mori

Sony Corporation Research Center, 174 Fujitsuka, Hodogaya, Yokohama 240, Japan

Photoluminescence spectra of oxygen-doped ZnSe grown by molecular beam epitaxy was studied. The oxygen-related peaks were observed at 4437 and 4550 A with phonon replicas, and they are thought to be due to oxygen-bound exciton and donor to oxygen-acceptor emission, respectively. Oxygen, an isoelectronic impurity in ZnSe, acts as shallow acceptor with acceptor level of 83 meV. A model for oxygen acting as an acceptor is proposed.

1. INTRODUCTION

Oxygen substituted for selenium in ZnSe is an isoelectronic impurity. It is well known that isoelectronic substitutions in semiconductors have a profound effect on the optical properties caused by the exciton bound at the impurities. Examples recognized so far are N or Bi substituting for P in $Gap^{(1,2)}$ or $GaAsP^{(3)}$ and O substituting for Te in ZnTe.⁽⁴⁾ These systems are classified as isoelectronic acceptor or isoelectronic donor depending on whether the impurity attracts electrons or holes, respectively. Oxygen as an electronegative impurity in ZnSe is an isoelectronic acceptor, and has interesting optical properties.

In this paper, the optical properties of oxygen-doped ZnSe are discussed in reference to photoluminescence spectra (PL).

2. EXPERIMENTAL

ZnSe films were grown in a Riber MBE

2300 system. The substrates were semi-insulating (100)-oriented GaAs which, prior to being loaded into the system, were chemically etched in a 2% KOH: H_2O_2 (20:1) solution for 5 min. The source materials used were metallic Zn and Se, both of six-nine purity. ZnO with five-nine purity was used as the source of the oxygen dopant.

The beam-pressure ratio of Zn to Se was maintained at about unity, and the growth temperature was kept at 240 C. The growth rate was about 0.8 μ m/h and the film thickness was about 2 μ m.

PL measurements were made at 4K using 10 mW of unfocussed 325 nm radiation from a He-Cd laser with a beam diameter of about 2 mm.

3. RESULTS AND DISCUSSION

A typical PL spectrum at 4K from an unintentionally doped ZnSe film is shown in Fig.1. The spectrum is dominated by I_2 line at 4431 A caused by the recombination

of excitons bound to neutral shallow Another peak at 4424 A is donors. attributed to the radiative recombination of free excitons (E_y) . A small peak at 4453 A denoted as I_1^{xd} is believed to be associated with an exciton bound to a intensity of native The defect. deep-level emission at about 6000 A (not shown in the Figure) is three orders of magnitude smaller than that of the I peak, suggesting high quality ZnSe.

Figure 2 shows the photoluminescence spectra of oxygen-doped ZnSe. The oxygen concentration of this sample measured by secondary ion mass spectroscopy was 2.2x10¹⁷cm⁻³. Two peaks denoted as I, and D-A followed by phonon replicas were spectrum of observed but not in the unintentionally doped ZnSe.





Fig. 1 PL spectrum of unintentionally doped ZnSe at 4K.



The spectrum of oxygen-doped ZnSe is very similar to that of nitrogen-doped ZnSe⁽⁵⁾.

The PL spectrum of an oxygen ion implanted ZnSe is shown in Fig. 3. The oxygen ions were implanted into unintentionally doped ZnSe at a dose of $3.4 \times 10^{12} \text{ cm}^{-2}$ with an acceleration energy of 240 KeV, then the implanted sample was annealed at 470 C for 5 min. in N_2 I2, I1, I1 and D-A peaks with ambient. phonon replicas were observed. The position of the I, and D-A peaks are the same as those observed in the oxygen-doped ZnSe sample shown in Fig. 2, so the I, and D-A peaks can be concluded as the oxygen-related luminescence.

The PL spectra ranging from 4500 to 4650 A of oxygen doped ZnSe measured under different excitation density are shown in

Fig. 4. The position of the D-A peak is shifted toward shorter wavelength about 3 meV, and the full width at half maximum of the peak was changed from 18.2 meV to 14.6 meV by an excitation density varied from 16 mW/cm^2 to 320 mW/cm^2 . Since this change is generally observed for donor to acceptor emission, it is reasonable to assign the D-A peak as donor to oxygen-acceptor emission.

Observation of the donor to acceptor emission including an isoelectronic impurity is the first time. Judging from the PL spectra, the oxygen acts as an acceptor having almost the same optical property as an impurity of group I or V elements.

The mechanism of oxygen acting as an acceptor in ZnSe may be as follows: the





Fig. 4 Variation of PL spectra for D-A peak with excitation density.

electrons of the host lattice near the oxygen atom are attracted to the oxygen by its large electronegative character, i.e., charge transfer occurs and charged oxygen is Then the positive charge left in formed. the host lattice is bound to the charged oxygen by a long-range Coulomb potential in an acceptor-like wave function. This state may be very similar to that of the acceptor generally used, such as N or Li.

The acceptor level and the effective charge of oxygen in ZnSe were estimated using the position of the D-A peak and the effective mass approximation.

The transition energy of donor to acceptor is given by

$$h \gamma = E_{g} - (E_{A} + E_{D}) + (Ze^{2}/\epsilon r),$$
 (1)

where E_g is the bandgap energy, E_A and E_D are the acceptor and donor binding 3 energies, is the low frequency dielectric constant, e is the electronic charge. r is the donor-acceptor separation, and Z is the effective charge of the central atom.

The binding energy of the hydrogen-like atom that has an effective charge Z is given by

$$E_{A} = \frac{z^{2} e^{4} m^{*}}{2 \pi^{2} n^{2} \epsilon^{2}} = z^{2} E_{A0}, \qquad (2)$$

where m is the effective mass and E_{AO} is the binding energy for Z=-1. Using Eq.(1) and (2) and values for E_g , E_D , $e^2/\epsilon r$ and E_{AO} of 2.819 eV, 28 meV, 18 meV, and 110 meV, the acceptor level and the effective charge of oxygen in ZnSe can be estimated as 83 meV and -0.87, respectively.

The acceptor level is the shallowest thus far reported. It can be considered that the oxygen is a promising impurity for growing p-type ZnSe.

References

- (1) D. G. Thomas, M. Gershenzon, and J. J. Hopfield, Phys. Rev. 131 2397 (1963).
- J. D. Cuthbert and D. G. Thomas, (2)
- (3) D. R. Scifres, N. Holonyak, Jr., C.
 B. Duke, G. G. Keiman, A. B. Kunz, M.
 G. Craford, W. O. Gruves, and A. H. Herzog, Phys. Rev. Lett. <u>27</u> 191 (1971).
 (4) J. L. Merz, Phys. Rev. <u>176</u> 961 (1968).
 (5) W. Stutius, Appl. Phys. Lett. <u>40</u> 246
- (1982).