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Photoluminescence Spectra of Silver-Doped ZnSe Grown by MBE

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Photoluminescence spectra of silver-doped ZnSe grown by molecular beam epitaxy was studied. The silver-related peaks were observed at 2.726 eV with phonon replicas, and are thought to be due to the radiative recombination of donor to silver-acceptor (D-A) emission. The acceptor level of silver in ZnSe is estimated to be about 85 meV from the peak energy of donor-acceptor emission, which would be consistent with the activation energy of thermal quenching of the D-A emission.

1. INTRODUCTION

The transition metal Ag forms acceptors in II-VI compound semiconductors when introduced substitutionally on the cation site. Silver in ZnTe and CdTe acts as a normal acceptor in a d^{10} configuration, while the ZnS host makes Ag_{Zn} open shell d^9-type acceptor(1). Since the d^9-type acceptors have a hole in the d-state, the acceptor level is deep. Dean et al. concluded that silver in ZnSe grown by LPE acts as a conventional d^{10} acceptor. However, optical measurements have established that silver in ZnSe acts as a deep acceptor with an activation energy ranging from 240 to 435 meV (1)-(3). In this paper, the optical properties of silver doped ZnSe grown by MBE are discussed in reference to photoluminescence (PL) spectra .

2. EXPERIMENTAL

ZnSe films were grown by molecular beam epitaxy. The substrates were semi-insulating (100)-oriented GaAs, which prior to being loaded into the chamber were chemically etched in a 2% KOH : H_2O_2 (20 : 1) solution for 5 minutes. Metallic Zn and Se of six-nine purity were used as source materials. The dopant material was metallic silver of seven-nine purity. 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 μm/hour and the film thickness was about 2 μm.

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

3. RESULTS AND DISCUSSION

A typical PL spectra at 4°K from an intentionally doped ZnSe film is shown in Fig.1. The spectra is dominated by a I_2 line at 2.798 eV (4431 Å) caused by the recombination of excitons bound to neutral shallow donors. Another peak at 2.802 eV (4421 Å) is attributed to the radiative recombination of free excitons (Ex). The intensity of deep level emission at about 2.1 eV (about 6000 Å), not shown in the figure, is three orders of magnitude smaller than that of the I_2 peak, suggesting high quality ZnSe.

Figure 2 (a) and (b) shows the photoluminescence spectra of silver doped ZnSe.

During the crystal growth, the temperature of the silver cell was kept at 600°C. Two peaks denoted as I_2 and D-A emission followed by phonon replicas were observed. The D-A emission was not observed in the spectrum of unintentionally doped ZnSe. Another peak at 2.25 eV (green emission) could be ascribed to native defects. ODMR (Optically Detected Magnetic Resonance) results have established that the green emission is due to the acceptor like center, whose most likely structure is $(Ag_{Zn}\text{-}Se\text{-}Ag_i)^0$ (4).

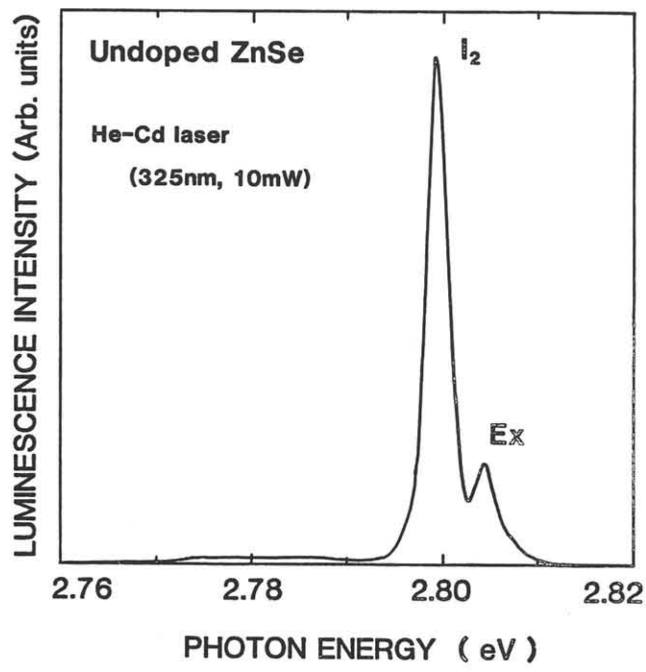

Fig.1 Photoluminescence spectrum of undoped ZnSe at 4 K.

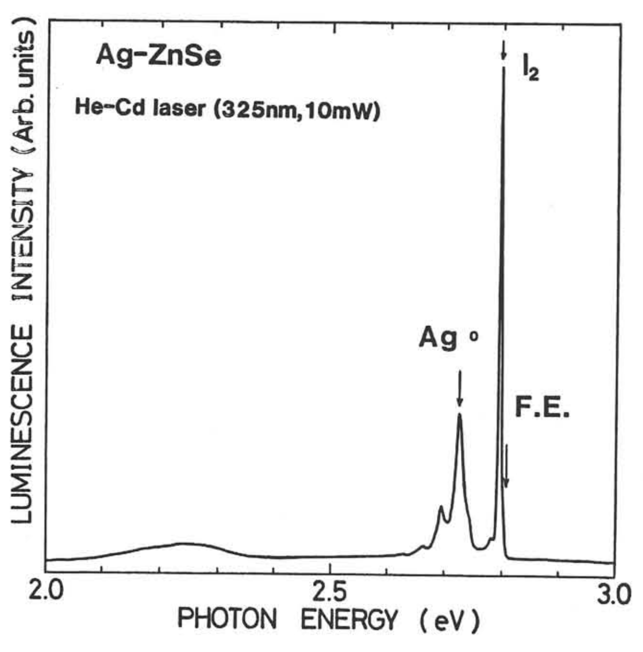

Fig.2 (a) Photoluminescence spectra of silver-doped ZnSe at 4 K. Spectral range is 2.0 to 3.0 eV.

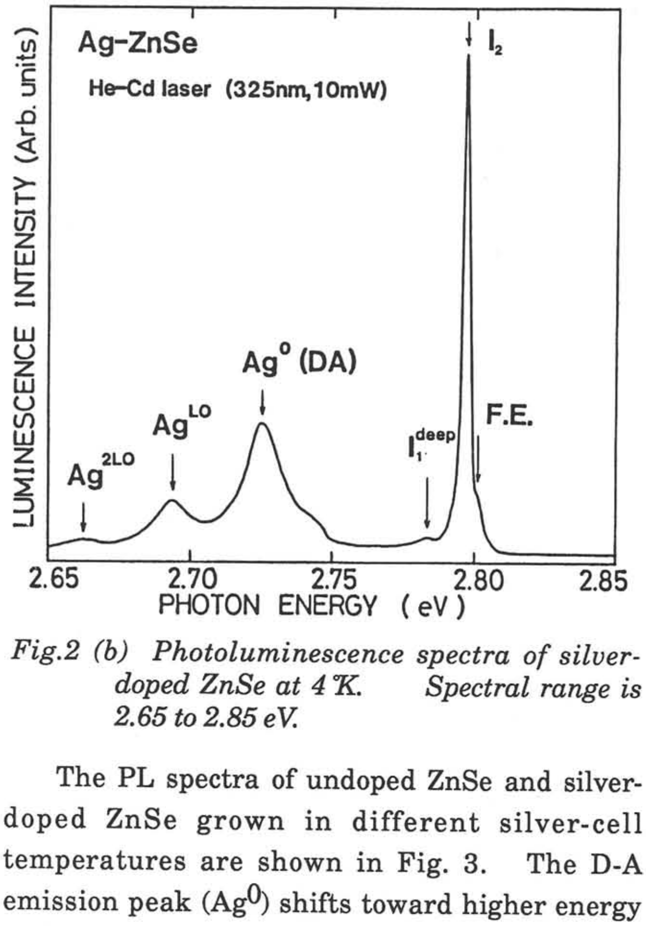

Fig.2 (b) Photoluminescence spectra of silver-doped ZnSe at 4 K. Spectral range is 2.65 to 2.85 eV.

The PL spectra of undoped ZnSe and silver-doped ZnSe grown in different silver-cell temperatures are shown in Fig. 3. The D-A emission peak (Ag^0) shifts toward higher energy with increasing silver-cell temperature. Figure 4 shows the PL spectra of silver-doped ZnSe measured under different excitation energies. The D-A emission peak (Ag^0) and the phonon replicas (Ag^{LO}, Ag^{2LO}) shift toward lower energy as the excitation energy is reduced from 10 mW to 0.5 mW. The position of the donor-bound exciton (I_2) peak does not change. Since these changes are generally observed in donor-to-acceptor emission, it is reasonable to assign the D-A peak (Ag^0) as donor to silver-acceptor emission.

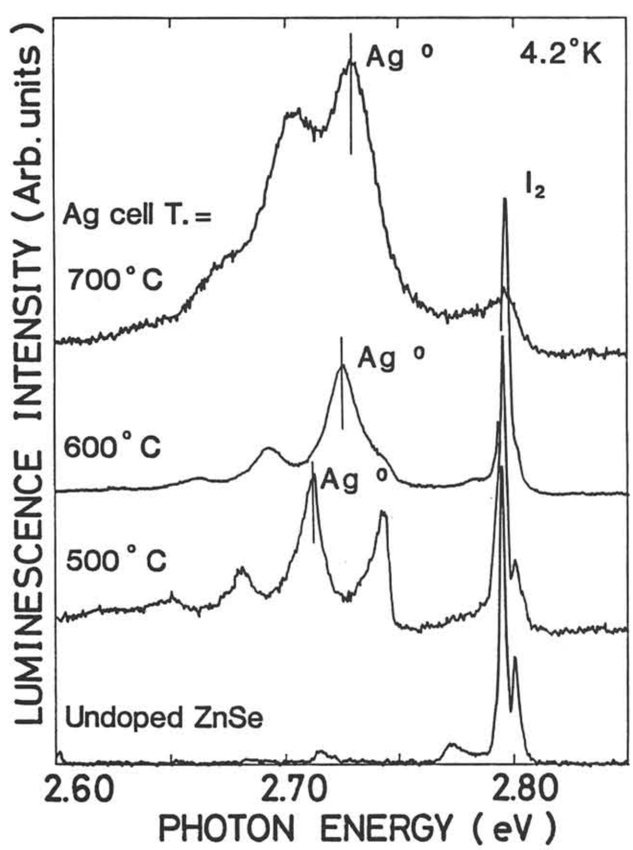

Fig.3 Variation of photoluminescence spectra of silver-doped ZnSe for D-A emission peaks with silver-cell temperature.

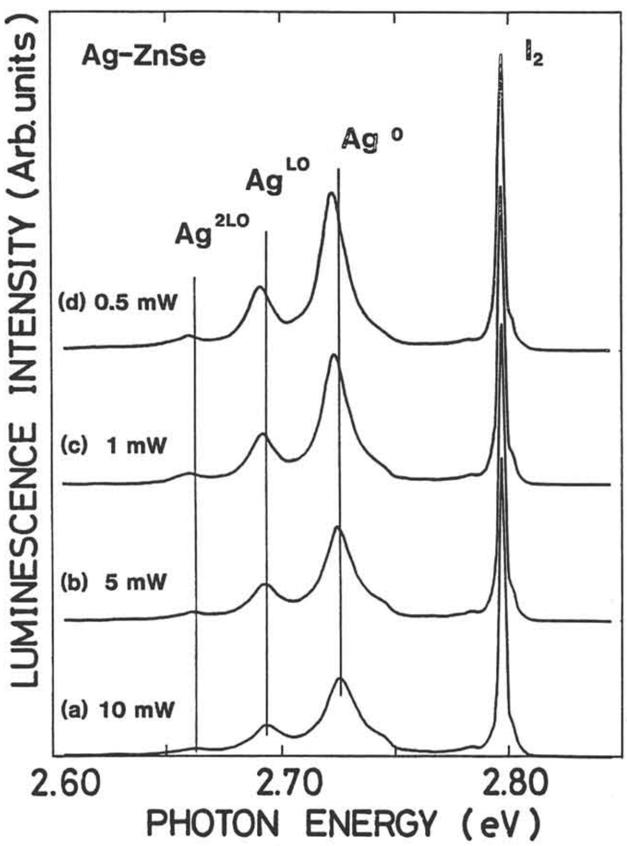

Fig.4 Variation of photoluminescence spectra of silver-doped ZnSe for D-A emission peaks with excitation energy

The acceptor level of silver in ZnSe was estimated using the position of the D-A emission peak (Ag^0). The emission energy $h\nu$ of the 'isolated' pair, donor to acceptor, is given by

$$h\nu = Eg - (Ea + Ed) + e^2 / (\varepsilon \cdot r). \qquad (1)$$

Here the last term (coulomb interaction) take into account the electrostatic interaction between the ionized donor and acceptor in the final state of the transition. Eg is the band-gap energy, Ea and Ed are the acceptor and donor binding energies, ε is the low-frequency dielectric constant, e is the electronic charge, and r is the distance between donor and acceptor. While the donor and acceptor, which both number 1×10^{19} cm^{-3}, distribute in ZnSe at random, the average distance R is calculated to be about 88 Å. The coulomb energy is estimated as

$$e^2 / (\varepsilon \cdot R) = 18 \text{ meV}. \qquad (2)$$

Using Eg=2.818 eV, Ed=26 meV, the peak energy of D-A emission (Ag^0) $h\nu$=2.726 eV, and Equation (1) and (2), the acceptor level of silver in ZnSe can be estimated as 85 meV.

This estimation is consistent with the thermal activation energy of D-A emission shown in Fig. 5. Figure 5 shows the integral intensity versus the reciprocal temperature, and that there are two competing ionization mechanisms with different activation energies. The activation energies are ε_1=20.4 meV and ε_2=97.9 meV, which values are ascribed to the binding energy of donor and acceptor, respectively. The acceptor level of silver in ZnSe is less than 100 meV and is comparable to N (Ea=85 to 100meV) [(5),(6)], O (Ea=83 meV) [(7)], Li (Ea=114meV) [(8),(9)] in ZnSe.

The energy of silver-acceptor bound exciton (E_{bx}) is calculated to be E_{bx}=2.793 eV, using the energy level of silver-acceptor (Ea) and the relation E_{bx}/Ea=0.1 [(10)]. This slight peak can be observed as the shoulder of I_1 peak in Fig. 2. The green emission at 2.25 eV could be due to the recombination of donors with deep acceptors. The energy level of the deep acceptor can be

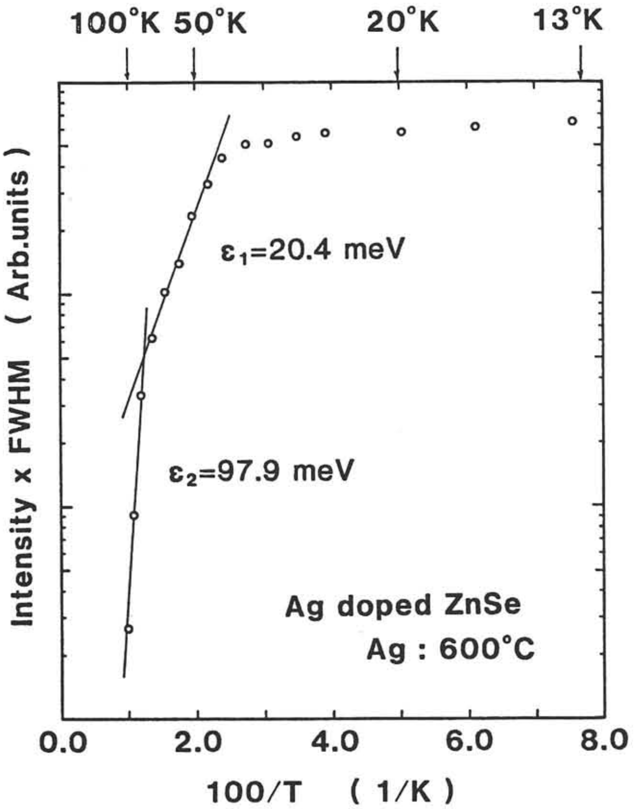

Fig.5 Variation of the integrated luminescence intensity of D-A emission (Ag^0) with sample temperature.

clculated to be 560 meV by equation (1). The energy of excitons bound to deep acceptors is estimated to be 2.745 eV. This emission peak can be observed in the photoluminescence spectra of Fig.3.

4. SUMMARY

Photoluminescence spectra of silver-doped ZnSe grown by MBE were measured. Silver-doped peaks appeared at about 2.726 eV. The origin of these peaks is thought to be due to the radiative recombination of donor to silver-acceptor. The acceptor level of the silver in ZnSe is estimated to be Ea=85 meV, as shallow as that of nitrogen, oxygen or lithium in ZnSe. The green emission at 2.25 eV is believed to be associated with defects.

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REFERENCES

(1) P. J. Dean, B. J. Fitzpatrick, and R. N. Bhargava, Phys. Rev. B26 2016 (1982)
(2) P. O. Holtz, B. Monemar, and H. J. Lozykowski, Phys. Rev. B32 986 (1985)
(3) V. Swaminathan and L. C. Greene, J. Luminescence 14 357 (1976)
(4) N. R. J. Poolton, J. J. Davies, J. E. Nicholls, and B. J. Fitzpatrick, J. Cryst. Growth 72 336 (1985)
(5) R. N. Bhagava, J. Cryst. Growth, 59 15 (1982)
(6) K.Kosai, B. J. Fitzpatrick, H. G. Grimmeiss, R. N. Bhargava, and G. F. Neumark, Appl. Phys. Lett. 35 194 (1979)
(7) K. Akimoto, T. Miyajima, and Y. Mori, Phys. Rev. B39 3138 (1989)
(8) J. L. Merz, K. Nassau, and J. W. Shiever, Phys. Rev. B8 1444 (1973)
(9) H. Tews, H. Venghaus, and P. J. Dean, Phys. Rev. B19 5178 (1979)
(10) R. E. Halsted and M.Aven, Phys. Rev. 14 64 (1965)