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Zn-induced impurity levels in layer semiconductor InSe

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The impurity levels in Zn-doped InSe have been investigated by photoluminescence (PL), Hall effect (HE), and deep-level transient spectroscopy (DLTS). Previous analysis by PL spectra shows that the radiative transition is dominated by donor-Zn acceptor pairs. In the present work, a search was made for the deep acceptor level using the combined data from HE and DLTS measurements. We find that the deep acceptor level, which is associated with defects or defect complexes formed by Zn atoms in the interlayer, is located about 0.6 eV above the valence band.

I. INTRODUCTION

Solar cells fabricated with *p*-InSe have been studied extensively in recent years.^{1,2} The elements of Zn or Cd have been used as dopants for *p*-InSe.³ It is necessary to know accurately detailed information on the impurity levels to discuss the applicability of InSe to highly efficient solar cells.

We have already reported the impurity levels in Zn-doped InSe.^{4,5} The emission band due to the Zn acceptor-donor pair recombination is observed by photoluminescence (PL) measurements and is well interpreted by self-activated luminescence in terms of a configurational coordinate model.⁴ The results of the thermal quenching of the PL intensity indicate that the Zn acceptor level is located at 0.16 eV above the valence band.

In electrical measurements, the activation energy of 0.31 eV associated with the Zn acceptor level is obtained from the slope of the Hall coefficient versus inverse temperature.⁵ The energy of 0.28 eV for the same level through Hall-effect (HE) measurements has also been reported by other workers.⁶ It is known that the presence of Zn atoms in InSe is essential for the appearance of these impurity levels. But there are serious discrepancies among the activation energies of the dominant acceptor levels reported in the PL and HE measurements. It is necessary to obtain the experimental results by other techniques to discuss the impurity levels in Zn-doped InSe.

In this paper, we report detailed results of PL, HE, and deep-level transient spectroscopy (DLTS) measurements. The activation energy of the deep acceptor level is determined from the combined data of DLTS and HE as a function of the concentration of Zn dopant.

II. EXPERIMENT

The *p*-InSe single crystals used in this study were grown by a conventional Bridgman technique. Zn of 99.999% purity was added at levels from 0.05 to 0.5 at. % to the stoichio-

metric melt of InSe. The samples were prepared by cleaving an ingot parallel to the crystallographic *c* plane.

PL measurements were carried out at 77 K by using a 514.5-nm Ar⁺ laser. A PbS photoresistor was used as a detector, and the PL spectra from the *c* plane were obtained by means of a lock-in amplifier technique.

The Hall coefficients were measured by a conventional dc method and by using a high-impedance electrometer in the temperature range from 210 to 430 K. The current flowed parallel to the *c* plane, and a magnetic field of 0.5 T was applied perpendicular to the *c* plane. Ohmic electrodes were made by In evaporation.

The DLTS measurements were performed on Schottky barriers formed by evaporating Al on the *c* plane. The ohmic contact on the other side was formed by In evaporation. The Schottky diode on the *p*-InSe showed forward condition when a negative voltage was applied to the Al contact. DLTS measurements were made with a circuit operating at 2 MHz and generally similar to the boxcar integrator circuit developed by Lang.⁷ The thermocouple was attached to the sample holder. The error in temperature measurements was estimated to be less than 1 K when the temperature was varied at a rate of 2 K/min.

III. RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of undoped and Zn-doped InSe. The initial Zn concentrations [Zn] in the growth solutions are also given in the figure. For the undoped samples, one emission band was observed at 1.33 eV. This band is attributed to the transition due to the annihilation of free excitons.^{8,9}

In addition to the 1.33-eV emission band, a new emission band of impurity center appeared at 1.17 eV in all Zn-doped samples. The temperature dependencies of peak shift and half-width of the 1.17-eV emission band are explained by a configurational coordinate model.⁴ This band was identified as emission due to a donor-Zn acceptor pair which is

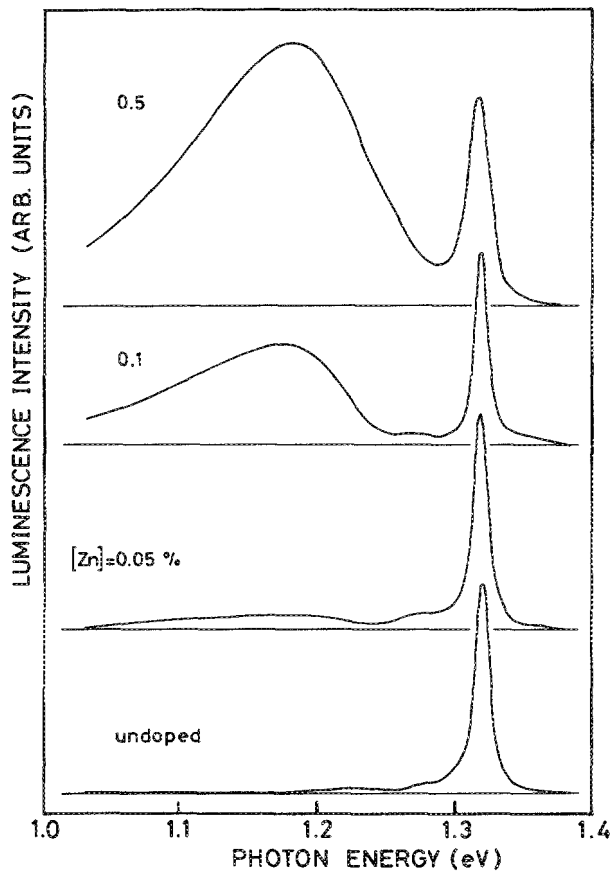


FIG. 1. PL spectra of undoped and Zn-doped InSe at 77 K. The initial Zn concentrations of [Zn] in the growth solutions are as indicated in the figure.

the localized electronic transition from the excited state of a vacancy to the ground state of a Zn acceptor level. From the experimental data of the thermal quenching of the PL intensity, the position of the Zn acceptor level was also estimated to be 0.16 eV above the valence band.

The feature presented in Fig. 1 indicates that the PL intensity of the 1.17-eV emission band increases with increasing [Zn]. The result suggests that the formation of a donor-Zn acceptor pair is greatly enhanced by the increase of [Zn].

Figure 2 shows the behavior of the carrier concentration as a function of the reciprocal temperature in undoped and Zn-doped InSe. The carrier concentrations of holes p and electrons n were calculated from the Hall coefficient by assuming a Hall factor of unity. The undoped sample showed

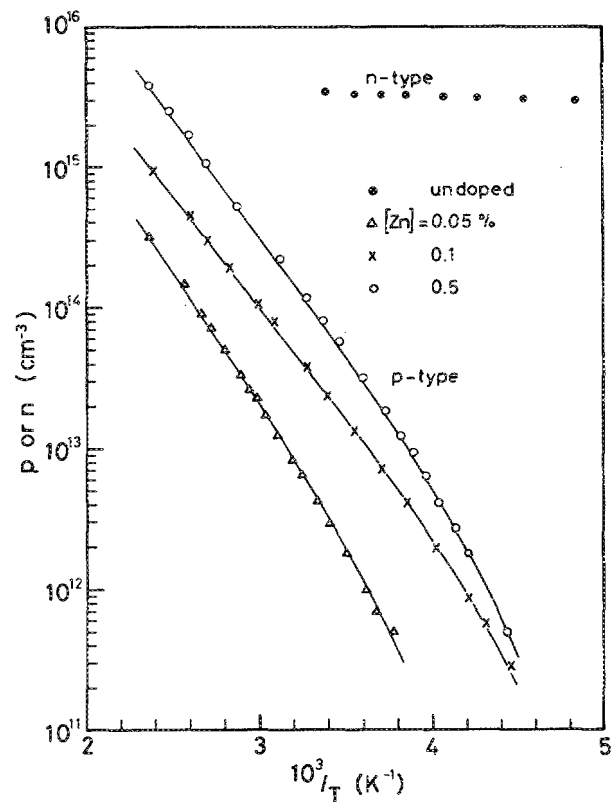


FIG. 2. Carrier concentration as a function of reciprocal temperature for undoped and Zn-doped InSe. The solid lines indicate the calculated hole concentrations from Eq. (1).

an n -type conduction, and n decreased slightly with decreasing temperature. The electrical conduction is dominated by the shallow donor level with an activation energy of 0.023 eV.¹⁰

After adding Zn to the stoichiometric melt of InSe, the type of conduction changed to p type. The hole concentration increased with increasing [Zn] and drastically decreased with decreasing temperature. Since the donor exists certainly in Zn-doped InSe by the results of PL measurements, we assumed that the Zn-doped samples behave as partially compensated p -type semiconductors. Despite the strong structure anisotropy of layer InSe, the anisotropy of the hole effective mass is not large.¹¹ We used a usual three-dimensional expression for the density of states of the valence band N_v . The temperature dependence of p is given by¹²

$$p = 2(N_a - N_d) / \left[1 + \frac{\beta N_d}{N_v} \exp\left(-\frac{E_a}{kT}\right) \right] + \left\{ \left[1 + \frac{\beta N_d}{N_v} \exp\left(-\frac{E_a}{kT}\right) \right]^2 + \frac{4\beta(N_a - N_d)}{N_v} \exp\left(-\frac{E_a}{kT}\right) \right\}^{1/2} \quad (1)$$

with

$$N_v = 4.82 \times 10^{15} T^{3/2} (m_h/m_0)^{3/2} \quad (\text{cm}^{-3}),$$

where E_a is the acceptor activation energy, k is Boltzmann's

constant, and N_a and N_d are the concentrations of the acceptor and the donor, respectively. The hole effective mass ratio of $m_h/m_0 = 1.3$ and the degeneracy factor for the acceptor level of $\beta = 2$ were used in these calculations.¹³ The solid

TABLE I. Electrical properties of Zn-doped InSe. The values of N_a , N_d , and E_a were obtained from HE, and the value of E_t was estimated from DLTS.

| Initial Zn concentration (%) | N_a ($\times 10^{17} \text{ cm}^{-3}$) | N_d ($\times 10^{12} \text{ cm}^{-3}$) | E_a (eV) | E_t (eV) |
|------------------------------|--------------------------------------------|--------------------------------------------|------------|------------|
| 0.05 | 0.89 | 4.2 | 0.63 | 0.64 |
| 0.1 | 2.6 | 0.82 | 0.58 | 0.59 |
| 0.5 | 9.8 | 6.4 | 0.62 | 0.62 |

lines are the hole concentrations calculated from Eq. (1). The values of N_a , N_d , and E_a for these fits are shown in Table I. The activation energy of about 0.6 eV was obtained from all samples and the values of N_a increased with increasing [Zn]. The initial Zn concentrations in the growth solutions with [Zn] = 0.05%–0.5% are the region of orders of 7×10^{18} – $7 \times 10^{19} \text{ cm}^{-3}$. The atomic absorption spectroscopy analysis performed by Chevy showed that the segregation coefficient of Zn in middle region of an ingot was on the order of 0.1–0.3.³ Therefore, the Zn concentrations in the final crystals with [Zn] = 0.05%–0.5% are estimated at the range of 1×10^{18} – $1 \times 10^{19} \text{ cm}^{-3}$. The obtained values of N_a in Table I are about one order of magnitude lower than those determined from the segregation coefficient. One possibility of its origin is considered that the Zn atoms in InSe are associated with the formation of the donor-Zn acceptor pairs, defects, or defect complexes, as will be described later. A certain Zn concentration in the final crystal is not clear at present. However, the values of N_a are significantly influenced by adding an amount of Zn. We conclude that the deep acceptor level arises from the doping process of Zn atoms.

Figure 3 shows the DLTS spectra of Zn-doped InSe for various [Zn]. The diodes were reverse biased at 1.0 V with a trap filling pulse of 1.0 V for 0.1 ms. One broad peak was observed at near 310 K. The DLTS signal intensity was greatly enhanced with increasing [Zn]. Since the pulse bias did not exceed the dc bias throughout the experiments, only majority-carrier (hole) traps were investigated. When the holes are emitted to the maximum of the valence band, the emission rate e_p is given by¹⁴

$$e_p = (\sigma_p v_p N_v / g) \exp(-E_t / kT_m), \quad (2)$$

where σ_p is the hole-capture cross section, v_p is the hole average thermal velocity, g is the degeneracy of the trap level, T_m is the peak temperature of the DLTS signal, and E_t is the activation energy of the trap level. If we assume that v_p varies as $T^{1/2}$ and N_v as $T^{3/2}$, the activation energy of the trap level can be obtained from the slope of an Arrhenius plot of e_p / T_m^2 vs $1/T_m$. Figure 4 shows the Arrhenius plots for the traps in each Zn-doped InSe sample. The solid, dotted, and dot-dashed lines are the least-squares fit lines, and the obtained values of E_t are also shown in Table I. The activation energy of traps evaluated by the fitting is about 0.6 eV and shows nearly the same value for each Zn-doped sample. The value of 0.6 eV agrees with the activation energy of the deep acceptor level obtained from HE measurements.

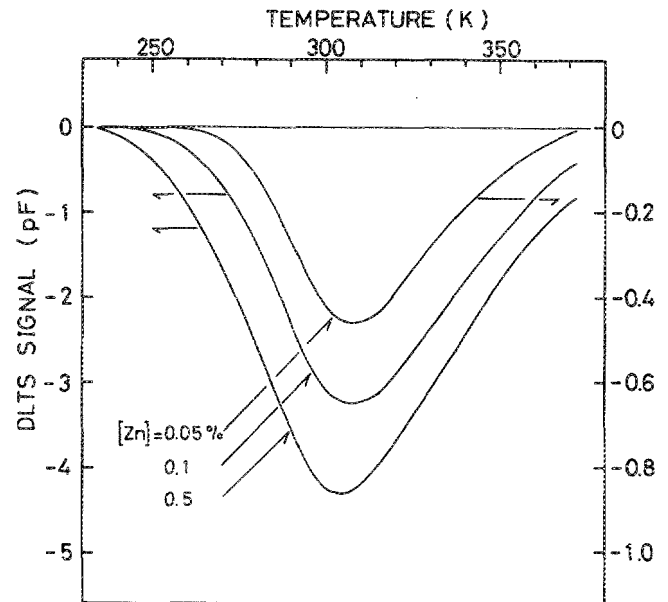


FIG. 3. DLTS spectra of Zn-doped InSe. The samples were reverse biased at 1.0 V with a trap filling pulse of 1.0 V for 0.1 ms. The rate window was 511 s^{-1} ($t_1 / t_2 = 0.5/5 \text{ ms}$).

From the results of PL measurements, the acceptor level attributed to the substitutional Zn is introduced at 0.16 eV above the valence band. The acceptor level obtained by HE and DLTS measurements is deeper than the level of the substitutional Zn. However, the deep acceptor level is certainly caused by the doping of Zn atoms in the crystal growth.

InSe crystal consists of a pile of packets in which atoms are bound by covalent and ionic-covalent bonds, whereas between the packets there are only weak van der Waals

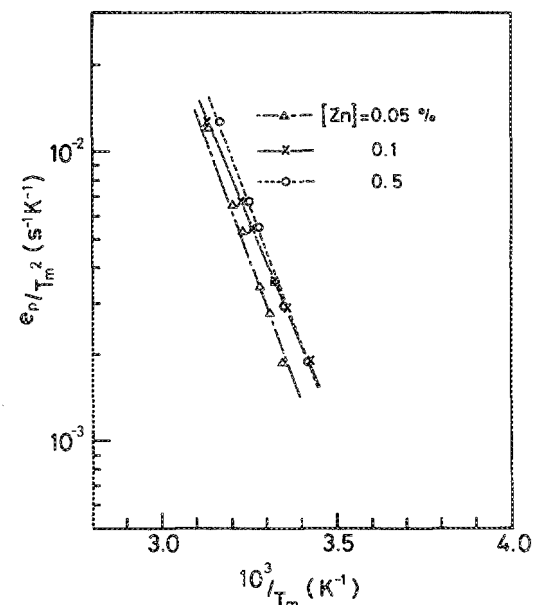


FIG. 4. Arrhenius plots of e_p / T_m^2 for the reciprocal of peak temperature shown in Fig. 3.

forces.¹⁵ By the characteristic of layer structure, the dopant atoms tend to precipitate in the interlayer region⁶ and form defects or defect complexes. Since the concentration of the deep acceptor level increases with increasing [Zn], as seen in the HE measurements, it may be reasonable to speculate that the defects or defect complexes are associated with Zn atoms precipitated in the interlayer.

IV. CONCLUSIONS

Measurements of PL, HE, and DLTS were carried out for Zn-doped InSe as a function of [Zn]. It was revealed from PL that the formation of a donor-Zn acceptor pair is greatly enhanced by the increase of [Zn]. The activation energy of the deep acceptor, which was associated with the defects or defect complexes formed by Zn atoms in the interlayers, was determined to be about 0.6 eV above the valence band using both HE and DLTS measurements. It is concluded that the optical transition is dominated by the donor-Zn acceptor pair, whereas the electrical transition is governed by the defects or defect complexes.

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