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# Stoichiometry-dependent deep levels in *p*-type InP

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Photocapacitance measurement is applied to investigate the stoichiometry-dependent deep levels in *p*-type InP crystals doped with Zn prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. Photocapacitance results reveal three dominant deep levels. A dominant deep level at 1.05 eV above the valence band is detected commonly before and after annealing, and the change of level densities is shown as a function of the phosphorus vapor pressure. Another two deep levels are also detected after annealing at 0.74 eV above the valence band and at 0.51 eV below the conduction band. In view of the deviation from the stoichiometric composition of InP, possible origins of these levels and their optical transition mechanism are discussed. © *1997 American Institute of Physics.* [S0021-8979(97)00107-2]

## I. INTRODUCTION

InP crystal is one of the most important semiconductor materials for the application of ultra-fast electronic devices, opto-electronic devices and so on. However, deviations from the stoichiometric composition can be significant compared to Ga–As based compounds. Therefore, the most important factor to be controlled in InP is the deviation from the stoichiometric composition.

Nishizawa[1–3] has previously pointed out the importance of stoichiometry control of compounds and the systematic research on the stoichiometry-dependent defects of III-V and II-VI compounds has been carried out.

Up until now, many reports on the deep levels have been published by means of deep level transient spectroscopy (DLTS),[4] photoluminescence (PL),[5] photo-induced transient spectroscopy (PITS) method.[6] In the case of InP crystal, understanding of the stoichiometry-dependent deep levels has been lacking compared with those of GaAs or GaP crystals. Recently, the authors[7] applied the photocapacitance (PHCAP) method to investigate the stoichiometry-dependent deep levels in intentionally-undoped *n*-type InP crystal prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. Photocapacitance (PHCAP)[8] measurement by constant capacitance method is a very useful method to determine the precise level densities and their energy levels. From the photocapacitance results on *n*-InP, it is shown that three dominant deep levels were detected at 0.63 and 1.1 eV below the conduction band and 0.74 eV above the valence band, respectively. The phosphorus vapor pressure dependence of these level densities has also been reported.

In this article, the 77 K-PHCAP method under constant capacitance conditions is applied to the intentionally Zn-doped *p*-type InP prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure followed by rapid cooling. The phosphorus vapor pressure dependence of the deep level density is shown, and excitation photocapacitance results show the precise optical transition mechanism of these deep levels.

## II. EXPERIMENT

The starting crystals used were liquid-encapsulated-Czochralski (LEC) grown *p*-type InP doped with Zn with the {100}-oriented crystal surface. Carrier concentration is $3\times10^{17}$ cm$^{-3}$. After cleaning and etching by a $H_2SO_4$–$H_2O_2$ solution, a sample crystal is placed in one end of a dumbbell-type quartz ampoule with 6N red phosphorus in the other end. After sealing in vacuum, the ampoule was put into a two-temperature zoned electric furnace. Heat treatment was carried out at 700 °C under controlled phosphorus vapor pressure. Heat treatment time was kept to be 4 h in the present experiments. Phosphorus vapor pressure at the phosphorus zone, $P_0$, is determined from the temperature of red phosphorus referring to Honig.[9] The phosphorus vapor pressure at the crystal zone, $P$, was obtained from the following equation:[10]

$$P=P_0(T/T_0)^{1/2}, \qquad (1)$$



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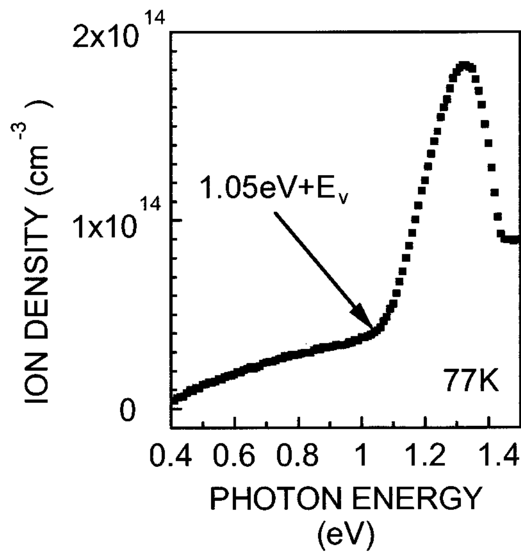


FIG. 1. Ion density PHCAP spectrum of intentionally Zn-doped $p$-type InP with the carrier concentration of $3\times10^{17}$ $cm^{-3}$ before annealing.

where $T$ and $T_0$ are the temperature of InP crystals and red phosphorus, respectively. After annealing, the ampoule was rapidly cooled by dipping into water. Metal–semiconductor contact diodes were made by Au evaporation as a barrier metal, and AuZn/Au was used for the ohmic contact on the back surface. Monochromatic light was fed into the depletion layer of the sample diodes. PHCAP measurement was carried out at 77 K.

To determine the level density and their energy levels, the charge state of the deep levels in the depletion layer was made to be neutral before each light irradiation at 77 K. For this purpose, forward bias injection was carried out in the dark before each light irradiation. After light irradiation, bias voltage, $\Delta V_{ph}$, changes to keep the junction capacitance constant according to the ionization of the deep levels. The change of the ion density, $\Delta Nt$, is given by the following equation:

$$\Delta V_{ph}=(\epsilon/2C^2)\Delta Nt, \tag{2}$$

where $C$ is the predetermined constant capacitance of the sample diode, $\epsilon$ is dielectric constant, and $\Delta V_{ph}$ is the change of bias voltage. Precise description of the PHCAP measurement and the equipment is reported elsewhere.[11]

The PHCAP measurements were carried out as follows. A sample diode was cooled and the forward bias injection was applied in the dark in order to neutralized deep levels before light irradiation. Then, a saturating bias voltage $V_{dark}$ was obtained in the dark. $V_{dark}$ is attributable for the thermally ionized level density in the dark. When monochromatic light was fed into the depletion region of the sample diode, bias voltage $V_{ph}$ changed according to the ionization of deep levels and the saturating bias voltage was obtained. Net ion density induced by the light irradiation is obtained by $\Delta V_{ph}=V_{ph}-V_{dark}$. Under constant capacitance conditions, the depletion layer thickness is kept constant regardless of the change in the ion density.

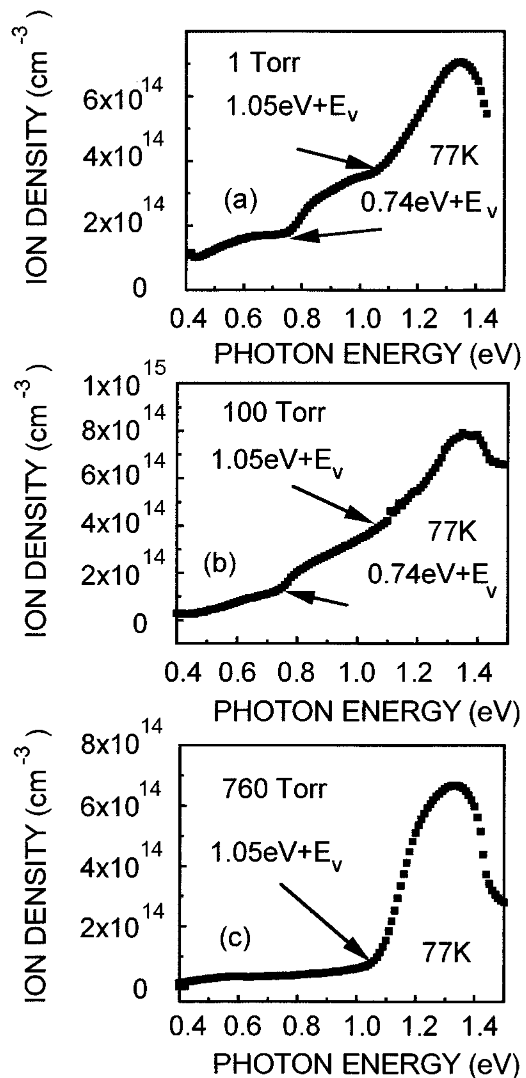


FIG. 2. Ion density PHCAP spectra of intentionally Zn-doped $p$-type InP prepared by 4 h annealing at 700 °C under phosphorous vapor pressure of (a) 1 Torr, (b) 100 Torr, and (c) 760 Torr, respectively.

## III. RESULT AND DISCUSSION

Figure 1 shows the ion density PHCAP spectrum of intentionally Zn-doped $p$-type liquid-encapsulated crystal (LEC) InP crystal before annealing. It is shown that the ion density increases sharply at 1.05 eV above the valence band. In the case of $p$-type semiconductors, the increase of ion density is induced by the optical transition of electrons from the valence band to the neutral deep acceptor levels.

Figure 2 shows the ion density PHCAP spectrum of intentionally Zn-doped InP crystals prepared by 4 h annealing at 700 °C under various phosphorus vapor pressure. In Fig. 2, it is shown that the 1.05 eV$+Ev$ level can be detected commonly before and after annealing. In addition, the photoionization of another deep level is detected at 0.74 eV above the valence band when $p$-InP crystals are annealed under lower phosphorus vapor pressure in the range of 1–100 Torr. However, 0.74 eV$+Ev$ level cannot be detected, when phosphorus vapor pressure applied was above ~760 Torr. In view of the 0.74 eV$+Ev$ deep level, we have already re-



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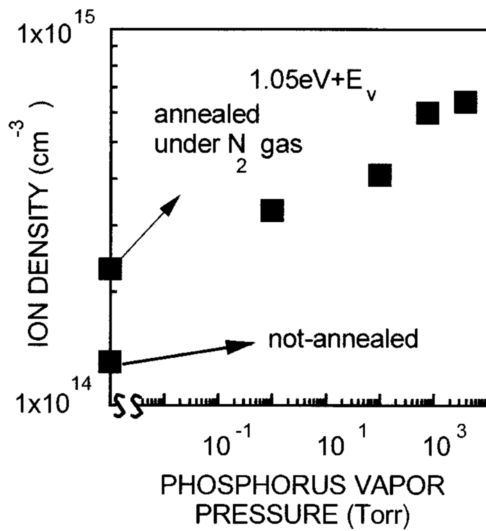


FIG. 3. Phosphorous vapor pressure dependence of deep level density of 1.05 eV in Zn-doped InP samples prepared by annealing at 700 °C under various phosphorous vapor pressure.

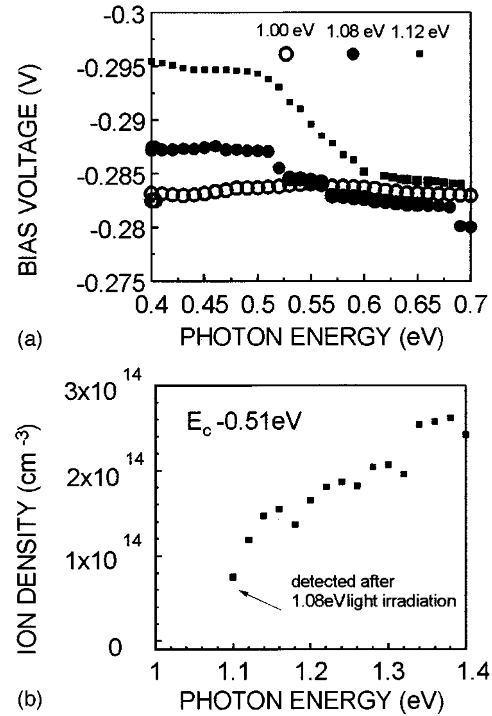


FIG. 4. (a) Ion density PHCAP spectra measured from long wavelength after the primary excitation light irradiation. (b) The change of ion density of $Ec-0.51$ eV level as a function of the primary excitation light wavelength. Sample used was intentionally Zn-doped $p$-type InP prepared by 4 h annealing at 700 °C under phosphorous vapor pressure of 760 Torr.

ported in our previous article on $n$-type InP[7] that photocapacitance results revealed the electron capture at 0.74 eV above the valence band even in intentionally undoped $n$-type InP sample before and after annealing under various phosphorus vapor pressure. It is also shown that the 0.74 eV$+Ev$ level density in $n$-type InP decreases with increasing phosphorus vapor pressure in the vapor pressure range below $<100$ Torr. It means that the photoresponse at 0.74 eV$+Ev$ in Zn-doped $p$-InP corresponds to the electron capture at 0.74 eV in $n$-type InP. Therefore, it is concluded that the phosphorus vapor pressure dependence of the 0.74 eV$+Ev$ level density shows good correspondence between $n$- and $p$-type InP crystals, respectively.

Therefore, it is considered that this level is not induced by the unexpected impurity contamination, but is probably related to phosphorus vacancies or a vacancy. Further, from the present PHCAP spectrum, we conclude that the 0.74 eV $+Ev$ level is related to the phosphorus vacancy due to the deviation from stoichiometry, because this deep level is formed by annealing under a lower phosphorus vapor pressure.

Figure 3 shows phosphorus vapor pressure dependence of the 1.05 eV deep level density. It is shown that 1.05 eV $+Ev$ level density increases with increasing phosphorus vapor pressure. Deep level at 1.05 eV was not detected in undoped InP but can be observed in Zn-doped $p$-InP. In view of phosphorus vapor pressure dependence of this deep level and the effect of impurity doping, the origin of 1.05 eV may include defect-impurity complex with relation to either In vacancies or P interstitials.

We performed excitation PHCAP to investigate the optical transition mechanism of the $\sim$1.05 eV level above the valence band. Figure 4(a) shows the excitation PHCAP spectrum of an intentionally Zn-doped $p$-InP sample prepared by 4 h annealing at 700°C under a phosphorus vapor pressure of 760 Torr. After the primary light irradiation at all interval of 0.02 eV in the spectral range from 1.0 to 1.4 eV, ion density PHCAP spectrum was measured repeatedly from the long wavelength by changing the primary excitation light wavelength. As shown in Fig. 4(a), after 1.08 eV light irradiation, it is shown that the neutralization is induced at 0.51 eV below the conduction band. Figure 4(b) shows the change of ion density of $Ec-0.51$ eV level as a function of primary excitation light wavelength in the range of 1.08–1.4 eV. The ion density of the $Ec-0.51$ eV level looks to be saturated above $\sim$1.20 eV light irradiation.

Figure 5 shows schematic drawing of the optical transition process of this level by the simple flat band diagram. This level at 1.08 eV above valence band is ionized after 1.08 eV light excitation light. Then, the neutralization of the

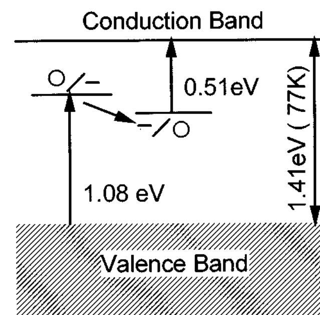


FIG. 5. Schematic drawing of the optical transition of $Ec-0.51$ eV and 1.05 eV$+Ev$ levels in $p$-type InP deduced from the present excitation PHCAP results.



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level is induced by the electron transition at 0.51 eV below conduction band by the Frank–Condon shift of about 0.09 eV. Therefore, in view of optical transition mechanism, it is concluded that the neutral 1.08 eV$+Ev$ level corresponds to the ionized $Ec-0.51$ eV level.

## VI. CONCLUSION

The photocapacitance measurement is applied to investigate the stoichiometry-dependent deep levels in intentionally Zn-doped $p$-type InP crystals prepared by 4 h annealing at 700 °C under controlled phosphorus vapor pressure. The PHCAP spectrum revealed two deep levels at 0.74 and 1.05 eV above valence band. The 1.05 eV$+Ev$ level has been detected in common before and after annealing and the ion density increased with increasing phosphorus vapor pressure. This level is considered to be a complex defect with relation to the impurity-intrinsic defect. The 0.74 eV$+Ev$ level is formed by annealing under a low phosphorus vapor pressure. 0.74 eV$+Ev$ level is attributed to phosphorus vacancy at least due to the deviation from stoichiometry. In view of the optical transition mechanism of these deep levels, the excitation PHCAP results revealed the neutralization at 0.51 eV just after 1.08 eV light irradiation. Therefore, it is concluded that the ionized level of the neutral 1.08 eV$+Ev$ level locates at 0.51 eV below the conduction band.


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