

STOICHIOMETRY CONTROL OF COMPOUND SEMICONDUCTOR CRYSTALS

PART TWO

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Effects of stoichiometry on various feature of III-V compounds are investigated. The application of the optimum vapor pressure of group V elements is shown to minimize the deviation from the stoichiometric composition. Temperature dependence of the optimum vapor pressure is also obtained from both the annealing and the liquid phase epitaxial (LPE) growth experiments. Vapor pressure technology is successfully applied to the bulk crystal growth. In view of the defect formation mechanism, role of the stable interstitial As atoms (I_{As}) in GaAs is emphasized. From the recent phot capacitance results, it is also shown that the excess group V atoms is also important for the formation of stoichiometry-dependent deep levels in InP and AlGaAs crystals. Even in the research field of surface science, it is shown that the precise control of stoichiometric composition should be required. Mechanism of the stoichiometry control is discussed on the basis of the equality of chemical potentials and the change of saturating solubility in the liquidus phase as a function of the vapor pressure. Stoichiometry-control should be also important in the field of the superconducting ceramics.

STOICHIOMETRY-DEPENDENT DEEP LEVELS IN *n*- AND *p*-TYPE InP CRYSTALS PREPARED BY ANNEALING UNDER CONTROLLED PHOSPHORUS VAPOR PRESSURE

The starting crystals used were liquid encapsulated Czochralski (LEC) grown *n*- and *p*- type InP with the {100}-oriented crystal surface. Carrier concentration of intentionally-undoped *n*-InP is $1.2\text{-}1.5 \times 10^{16} \text{cm}^{-3}$ and that of Zn-doped *p*-InP crystal is $3 \times 10^{17} \text{cm}^{-3}$ respectively. After cleaning and etching by a $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solution, a sample crystal is placed in one end of a dumbbell-type quartz ampoule and 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

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hours in the present experiments. Phosphorus vapor pressure at the phosphorus zone, P_0 , is determined from the temperature of red phosphorus referring to Honig [1]. The phosphorus vapor pressure at the crystal zone, P , was determined from the following equation:

$$P = P_0 (T / T_0)^{1/2}, \quad [4]$$

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 the water at nominal room temperature.

DEEP LEVELS IN N-TYPE InP [2]

Figure 1 shows the ion density PHCAP spectrum of intentionally-undoped n -type LEC InP crystal before annealing. The PHCAP measurements were carried out as follows. A sample diode was cooled and forward bias injection was applied in the dark in order to neutralize every deep level before light irradiation. Then, saturating bias voltage V_{dark} was obtained in the dark. V_{dark} is attributed to the thermally ionized level density in the dark. When monochromatic light was irradiated 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 $\Delta V_{\text{ph}} = V_{\text{ph}} - V_{\text{dark}}$. Under the constant capacitance condition, the depletion layer thickness is kept constant regardless of the change of the ion density. It is shown that almost constant V_{dark} at each wavelength confirms the neutralization of every deep level before each photo-excitation.

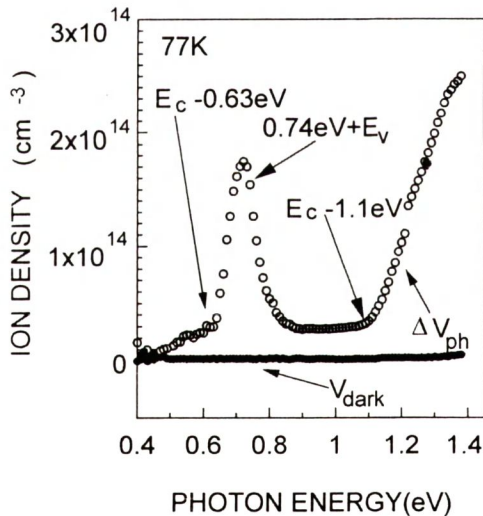


Fig. 1. Ion density PHCAP spectrum of intentionally-undoped n -type LEC InP crystal before annealing.

It is shown that almost constant V_{dark} at each wavelength confirms the neutralization of every deep level before each photo-excitation.

In Fig. 1, it is shown that the ion density shows gradual increase at ~ 0.4 eV and then rapid increase at 0.63 eV. The decrease of ion density at 0.74 eV is induced by the photo-neutralization of ionized deep level. In the wavelength region of 0.9-1.1 eV, another photo-ionization is observed at 1.1 eV.

Figure 2 shows the ion density PHCAP spectrum of intentionally-undoped n -type InP prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure. Deep levels are observed nearly at the same pho-

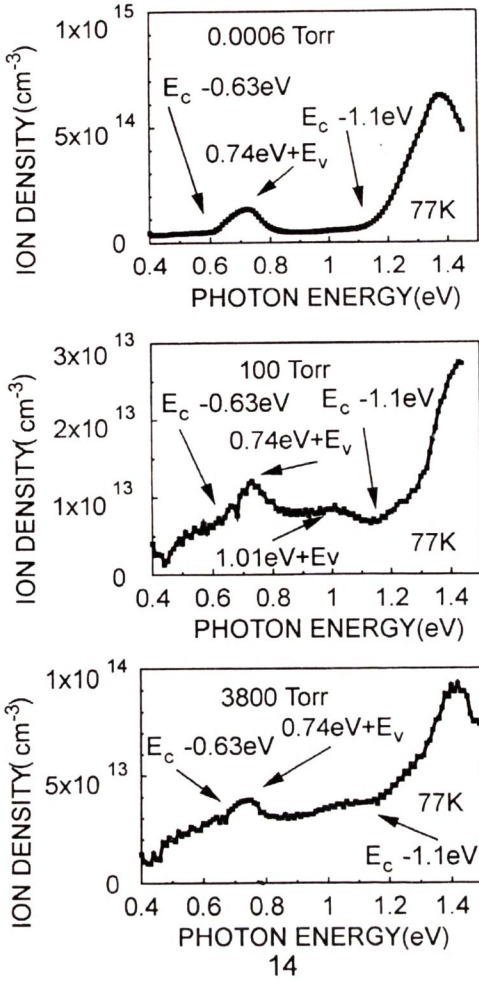


Fig. 2. Ion density PHCAP spectrum of intentionally-undoped *n*-type InP prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure.

phosphorus vapor pressure exceeds 1000 Torr. These levels are commonly detected in intentionally-undoped *n*-type LEC InP crystals before and after annealing. Even in *p*-type InP crystals doped with Zn ($p=3 \times 10^{17} \text{cm}^{-3}$), the ion density PHCAP measurements reveal the photoionization at 0.74 eV and 1.1 eV respectively as shown in Fig. 4. The photo-ionization at 0.74 eV in *p*-type InP corresponds to the electron capture at 0.74 eV in *n*-type crystal. Therefore, it is considered that these deep levels are not induced by the unexpected impurity contamination during annealing; but most probably by the intrinsic defects.

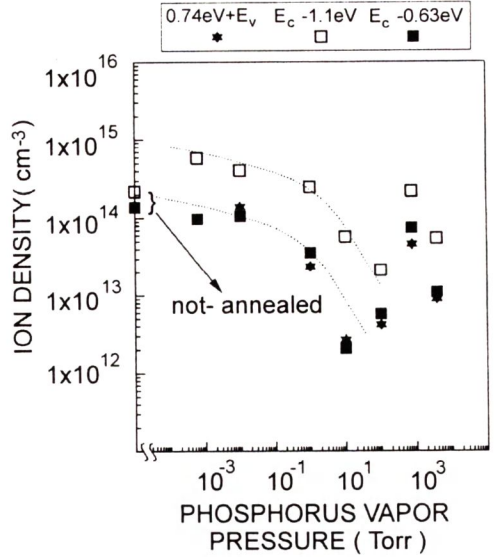


Fig. 3. Change of deep level density in *n*-InP as a function of the applied phosphorus vapor pressure.

ton energies as those for the samples before annealing. However, it is noticed that InP crystal annealed under the phosphorus vapor pressure of 100 Torr shows another photoionization at $E_v + 1.01 \text{ eV}$.

Figure 3 shows the change of deep level density as a function of the applied phosphorus vapor pressure. It is shown that the $E_c - 0.63 \text{ eV}$, $E_c - 1.1 \text{ eV}$ and $E_v + 0.74 \text{ eV}$ level density decreases with increasing phosphorus vapor pressure in the range below 100 Torr. Then, the level densities increase when the applying phos-

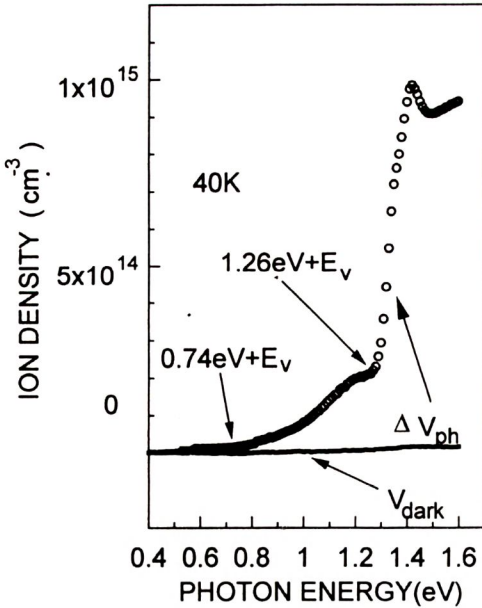


Fig. 4. Ion density PHCAP spectrum of *p*-type InP crystals doped with Zn ($p=3 \times 10^{17} \text{ cm}^{-3}$).

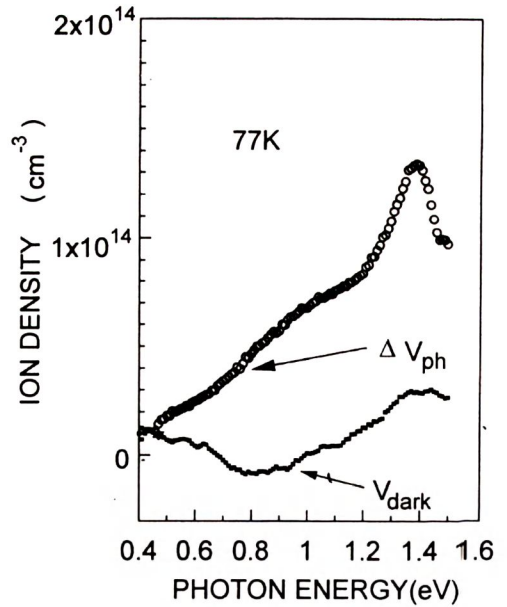


Fig. 5. Ion density PHCAP spectrum of Sn-doped LEC InP crystal with the carrier concentration of $2.2 \times 10^{16} \text{ cm}^{-3}$.

On the $E_c - 0.63 \text{ eV}$ and $E_v + 0.74 \text{ eV}$ level, it is shown that the amphoteric impurity doping annihilates the formation of these deep levels. Figure 5 shows the ion density PHCAP spectrum of Sn-doped LEC InP crystal with the carrier concentration of $2.2 \times 10^{16} \text{ cm}^{-3}$. The carrier concentration is almost the same as that of intentionally-undoped LEC InP ($n = 1.1 \times 10^{16} \text{ cm}^{-3}$).

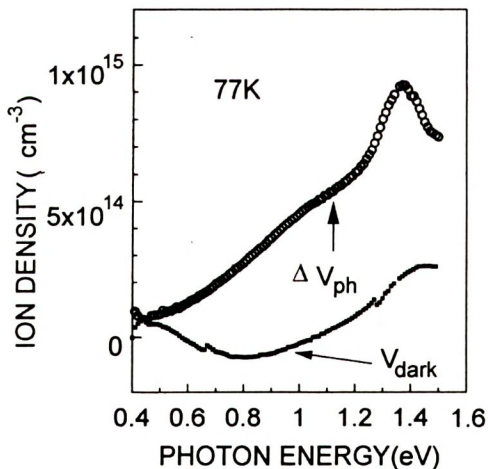


Fig. 6. Ion density PHCAP spectrum of S-doped InP crystal with the carrier concentration of $5 \times 10^{17} \text{ cm}^{-3}$.

As shown in Fig. 6, ionization and neutralization cannot be detected at around 0.63 eV and 0.74 eV respectively. It is considered that the doped impurity Sn will occupy both In and P sublattices. Therefore, In and/or P vacancies are thought to be annihilated by Sn doping. In addition, ion density PHCAP spectrum of S-doped InP crystal with the carrier concentration of $5 \times 10^{17} \text{ cm}^{-3}$ does not show the ionization at 0.63 eV nor the neutralization at 0.74 eV (Fig. 6). Group VI impurity S will occupy the P-sublattices. Therefore, it is considered that

the doped impurity S will also reduce the phosphorus vacancy concentration. In view of the phosphorus vapor pressure dependence of the level density, it is considered that these deep levels are stoichiometry-dependent and are related most possibly with at least the phosphorus vacancy. It is also considered that the annealing under extremely high vapor pressure induces nonequilibrium defects in the lattice. Indeed, in the case of GaAs, it is noticed that high-pressure annealing induces not only the interstitial arsenic atom-related point defects but structural defects like stacking faults and extended dislocations [3]: In such highly degraded lattices, it is considered that both the excess phosphorus composition-related defect and the vacancy-related defects are generated [4].

Next, in order to clarify the optical transition mechanism of $E_c-0.63$ eV level, ion density PHCAP spectrum was measured from long wavelength and short wavelength respectively.

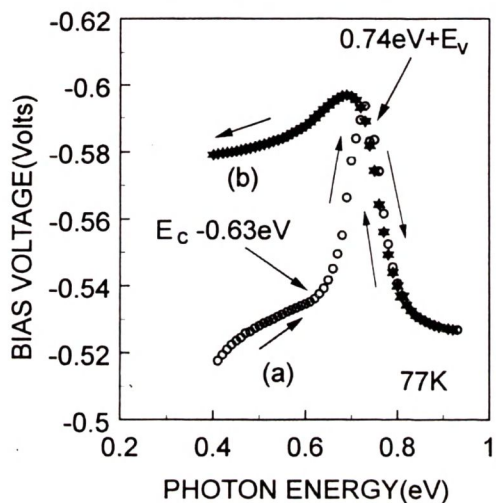


Fig. 7. Ion density PHCAP spectrum obtained from (a) long wavelength and from (b) short wavelength light irradiation. Sample used was intentionally-undoped *n*-type InP without any heat-treatment.

Therefore, from these results, it is considered that the $E_c-0.63$ eV level is photo-ionized by the 0.63 eV-monochromatic light irradiation and can be neutralized by the 0.74 eV monochromatic light irradiation via electron transition from the valence band to the ionized $E_c-0.63$ eV level. And the neutral $E_c-0.63$ eV level is ionized in the wavelength region of 0.63-0.79 eV.

Figure 8 shows the excitation PHCAP spectrum of an intentionally-undoped InP crystal before annealing. After 1.40 eV light irradiation, the ion density PHCAP spectrum was measured from long wavelengths at 40K. In Fig.8, it is shown that the decrease of ion density is induced at 0.43 and 0.45 eV after 1.40 eV light irradiation. This decrease of ion density is caused by the neutralization of deep levels ionized by the 1.40 eV light irradiation. By changing the primal excitation wavelength, it is

Figure 7 shows the ion density PHCAP spectrum obtained from: (a) long wavelength and from (b) short wavelength light irradiation. Sample used was intentionally-undoped *n*-type InP without any heat-treatment. When the monochromatic light is irradiated from the long wavelength, the ionization is induced at 0.63 eV and the neutralization occurred at 0.74 eV respectively. However, when the light is irradiated from the short wavelength, the ionization is induced at 0.79 eV and then the ion density decreases a little. This decrease of ion density is considered to be due to thermal neutralization.

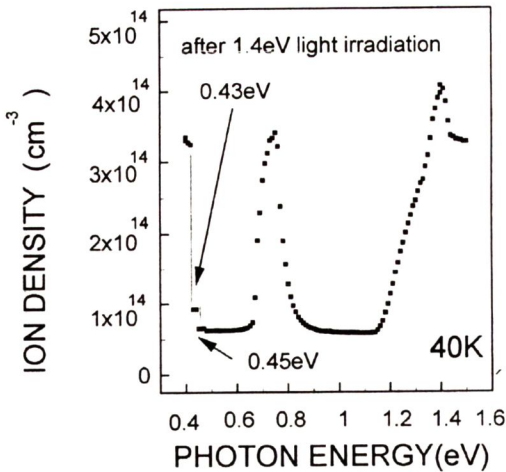


Fig. 8. Excitation PHCAP spectrum of an intentionally-undoped n -InP crystal before annealing.

shown that the neutralization at 0.43 and 0.45 eV is attributable for the ionized level of $E_c - 1.1$ eV via electron transition from the valence band. In addition, it is noticed that the ionization at 1.1 eV is not caused by the interband transition from $E_c - 0.63$ eV to the X valley, because ion density PHCAP spectrum of our LPE InP crystal shows photo-ionization at 1.1 eV but the $E_c - 0.63$ eV level cannot be detected in LPE sample (not shown here.).

In view of optical transition mechanism of major deep levels, it is concluded that the ionized $E_c - 0.63$ eV level locates at 0.74 eV above the valence band at 77K and that the neutral state of $E_v + 0.43$ and $E_v + 0.45$ eV (at 40K) level locates at 1.1 eV below the conduction band.

In summary, the photocapacitance method was applied in the constant capacitance condition to investigate the stoichiometry-dependent deep levels in intentionally-undoped n -type InP crystals. Samples were prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure. The present photocapacitance measurements revealed three dominant deep levels at 0.63 and 1.1 eV below the conduction band and 0.74 eV above the valence band respectively. These level densities decreased by increasing phosphorus vapor pressure in the range below 100 Torr. When the phosphorus vapor pressure exceeded 1000 Torr, the deep level densities increased. The excitation photocapacitance results have revealed the electron capture at 0.43 and 0.45 eV corresponding to the ionized state of $E_c - 1.1$ eV level. In view of the phosphorus vapor pressure dependence of the level density and the effects of impurity doping on the annihilation of deep levels, it was suggested that $E_c - 0.63$ eV and $E_v + 0.74$ eV levels would relate most probably with the phosphorus vacancy.

DEEP LEVELS IN P-TYPE InP [5]

Figure 9 shows the ion density PHCAP spectrum of intentionally Zn-doped p -type LEC InP crystal before annealing. It is shown that the ion density increases 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 electron from the valence band to the neutral deep acceptor levels.

Figure 10 shows the ion density PHCAP spectrum of intentionally Zn-doped InP

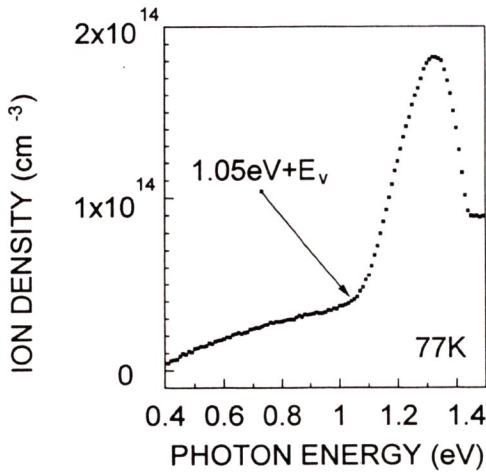


Fig. 9. Ion density PHCAP spectrum of intentionally Zn-doped *p*-type LEC InP crystal before annealing.

crystals prepared by 4 h-annealing at 700°C under various phosphorus vapor pressure. In Fig. 11, it is shown that $E_v + 1.05$ eV level can be detected commonly before and after annealing. In addition, the photo ionization 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, $E_v + 0.74$ eV level cannot be detected, when phosphorus vapor pressure applied was above ~760 Torr. In view of the $E_v + 0.74$ eV deep level, we have already reported in previous section on *n*-type InP 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 $E_v + 0.74$ eV level density in *n*-type InP decreases with the increase of applying phosphorus vapor pressure in the vapor pressure range below <100 Torr. It means that the photoresponse at $E_v + 0.74$ 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 $E_v + 0.74$ eV level density shows good correspondence between *n*- and *p*-type InP crystals respectively.

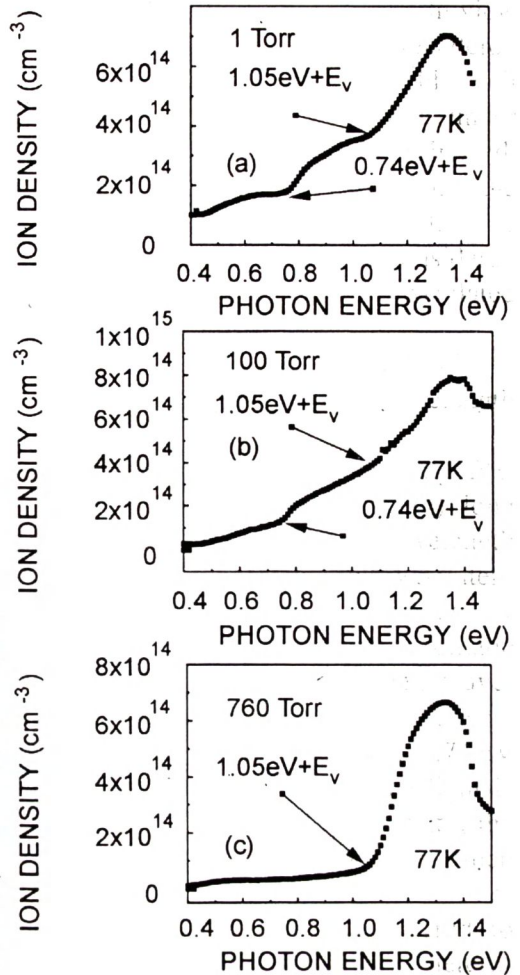


Fig. 10. Ion density PHCAP spectrum of intentionally Zn-doped InP crystals prepared by 4 h-annealing at 700°C under various phosphorus vapor pressure.

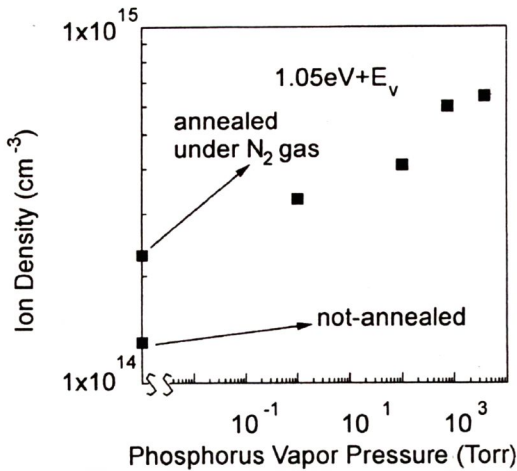


Fig. 11. Phosphorus vapor pressure dependence of the 1.05 eV deep level density in *p*-InP doped with Zn. It is shown that $E_v + 1.05$ eV level density increases with increasing phosphorus vapor pressure.

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

Figure 11 shows phosphorus vapor pressure dependence of the 1.05 eV deep level density. It is shown that $E_v + 1.05$ 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, origin of 1.05 eV may include defect-impurity complex with relation to either In vacancy or P interstitial, alternatively.

We perform the excitation PHCAP to investigate the optical transition mechanism of ~ 1.05 eV level above the valence band. Figure 12(a) shows the excitation PHCAP spectrum of an intentionally Zn-doped *p*-InP sample prepared by 4h-annealing at 700°C under phosphorus vapor pressure of 760 Torr. After the primary light irradiation at interval of 0.02 eV in the spectral range from 1.0 eV to 1.4 eV, ion density PHCAP spectrum was measured repeatedly from the long wavelength by changing

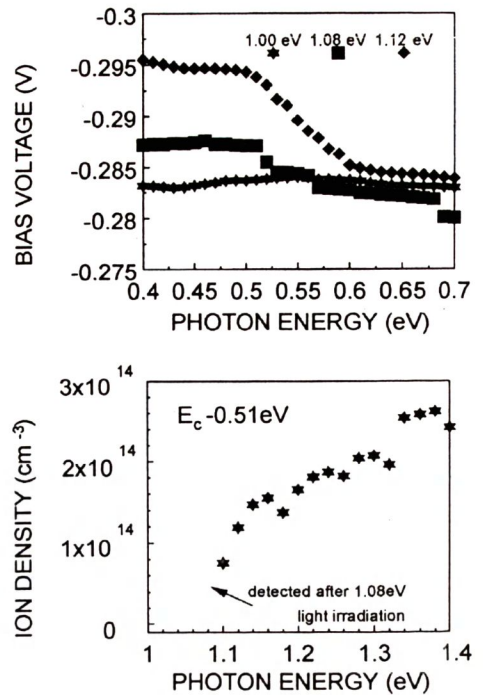


Fig. 12. (a) Excitation PHCAP spectrum of an intentionally Zn-doped *p*-InP sample prepared by 4h-annealing at 700°C under phosphorus vapor pressure of 760 Torr. (b) Change of ion density of $E_c - 0.51$ eV level in *p*-InP as a function of primary excitation light wavelength in the range of 1.08-1.4 eV.

the primary excitation light wavelength. As shown in Fig. 12(a), after 1.08 eV light irradiation, the neutralization is induced at 0.51 eV below the conduction band. Fig. 12(b) shows the change of ion density of $E_c-0.51$ eV level as a function of primary excitation light wavelength in the range of 1.08 -1.4 eV. Ion density of $E_c-0.51$ eV level looks to be saturated above ~ 1.20 eV light irradiation.

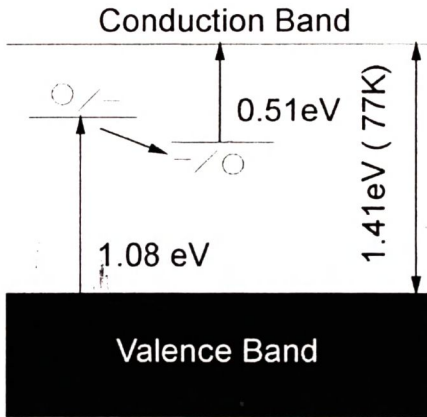


Fig. 13. Schematic drawing of the optical transition process of $E_v + 1.08$ eV in *p*-InP level by the simple flat band diagram.

levels at 0.74 eV and 1.05 eV above valence band. $E_v + 1.05$ 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-defects with relation to the impurity-intrinsic defect. $E_v + 0.74$ eV level is formed by the annealing under a low phosphorus vapor pressure. $E_v + 0.74$ eV level is probably contributed 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 $E_v + 1.08$ eV level locates at 0.51 eV below the conduction band.

InP BULK CRYSTAL GROWTH BY THE VAPOR PRESSURE CONTROLLED ZONE MELTING METHOD

Vapor pressure control technique has been also applied to the InP bulk crystal growth in combination with the zone melting method (VZM method). Figure 14 shows the phosphorous vapor pressure dependence of the carrier concentration and

Fig.13 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 level is induced by the electron transition at 0.51 eV below conduction band by Frank-Condon shift of about 0.09 eV. Therefore, in view of optical transition mechanism, it is concluded that the neutral $E_v + 1.08$ eV level corresponds to the ionized $E_c-0.51$ eV level.

In summary, the photocapacitance measurement is applied to investigate the stoichiometry-dependent deep levels in intentionally Zn-doped *p*-type InP crystals prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure.

The PHCAP spectrum revealed two deep levels at 0.74 eV and 1.05 eV above valence band. $E_v + 1.05$ 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-defects with relation to the impurity-intrinsic defect. $E_v + 0.74$ eV level is formed by the annealing under a low phosphorus vapor pressure. $E_v + 0.74$ eV level is probably contributed 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 $E_v + 1.08$ eV level locates at 0.51 eV below the conduction band.

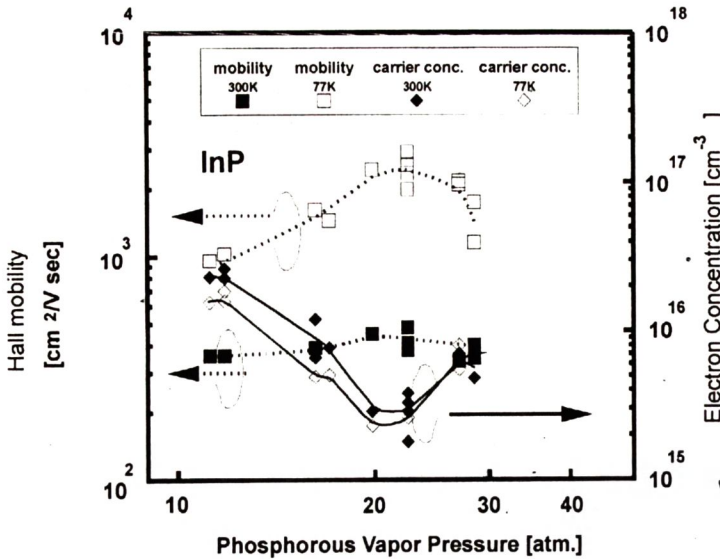


Fig. 14. Phosphorus vapor pressure dependence of the carrier concentration and the Hall mobility in vapor pressure controlled zone melting method (VPC-ZM) grown InP.

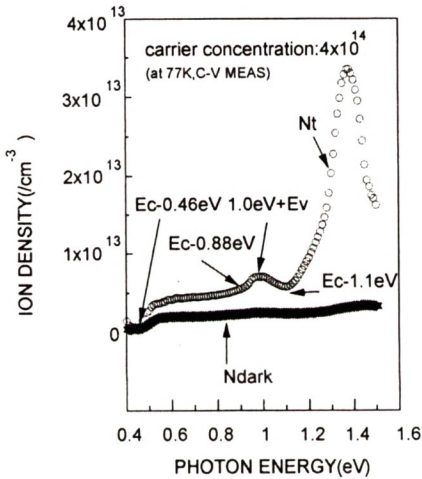


Fig. 15. Ion density photocapacitance spectrum of VZM-grown *n*-type InP bulk crystal with the residual carrier concentration of $5 \times 10^{14} \text{ cm}^{-3}$.

the Hall mobility. The carrier concentration and the Hall mobility at 77K shows minimum and maximum value under a specific phosphorous vapor pressure of about 22.5 atm. at the melting point. The present value of mobility is greater than that obtained from the conventional LEC method.

Figure 15 shows the ion density photocapacitance spectrum of VZM-grown *n*-type InP bulk crystal with the residual carrier concentration of $5 \times 10^{14} \text{ cm}^{-3}$. It is shown that the P-vacancy related deep level in *n*-InP at $E_c - 0.63 \text{ eV}$ and $E_v + 0.74 \text{ eV}$ cannot be revealed in this sample. These deep levels are commonly detected in intentionally-undoped LEC grown *n*-InP crystals. Further photocapacitance investigation is to be continued at present.

GaP PURE GREEN LED WITHOUT NITROGEN DOPING

Luminous efficiency of LED is strongly influenced by a small amount of defects. Therefore, the characteristics of LED is very sensitive to the crystal perfection.

It was shown that the TDM-CVP enables the LPE GaP almost free from disloca-

tion, and GaP pure green LED was fabricated by this method. At that time, it has been believed that the nitrogen should be doped to improve the luminous efficiency, because GaP has indirect transition. But the emission wavelength shifts to a longer one by N doping, and the color of GaP:N LED is close to yellow rather than green. The GaP LED grown by the TDM-CVP exhibits a pure green emission ($\lambda=550$ nm) with high luminous efficiency without N doping. Wavelength of this emission light

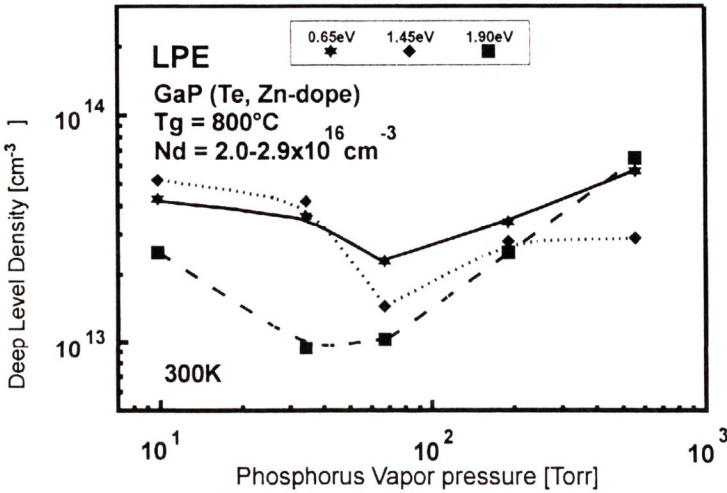


Fig. 16. Phosphorus vapor pressure dependence of deep level density in TDM-CVP grown LPE GaP measured by the conventional PHCAP method. Deep level density shows minimum under a specific optimum phosphorous vapor pressure.

corresponds to the direct energy gap of GaP crystal.

Figure 16 shows the phosphorus vapor pressure dependence of deep level density measured by the conventional PHCAP method. Deep level density shows minimum under the optimum phosphorus vapor pressure. These levels were shown to be stoichiometry-dependent and act as a nonradiative recombination center. It is shown that the TDM-CVP controls the introduction of these deep levels caused by the deviation from the stoichiometric composition.

EDITORIAL NOTE

The paper submitted by the authors was divided by the editor into three parts which are successively published. Part one, published “Materiały Elektroniczne” nr 4-1996 was dealing with deep levels related to GaAs stoichiometry. In part two, published in this issue, deep level defects induced by the phosphorus pressure changes during growth and annealing of InP and GaP are discussed. Part three, which will be presented in the next issue, is dedicated to stoichiometry related defects in AlGaAs.

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