Photocapacitance Investigation of Stoichiometry-dependent Deep Levels in InP

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Abstract. The photocapacitance measurements under constant capacitance condition is applied to *n*- and *p*-type InP crystals prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure. Samples used are InP bulk crystals grown by the conventional LEC method. Vapor pressure controlled-zone melting grown InP and LPE-grown InP are also investigated. The phosphorus vapor pressure dependence of the deep level density is shown. And the excitation photocapacitance method is also applied to show the precise optical transition mechanism of these deep levels. From these results, the defect formation mechanism is discussed in view of the deviation from the stoichiometric composition of InP.

1. Introduction

The most important factor to be controlled in compounds is the deviation from the stoichiometric composition[1]. Whereas InP is one of the most promising semiconductor material for the application of ultra-fast electronic devices, opto-electronic devices and so on, the deviation from the stoichiometric composition is more serious compared with Ga-As based compounds. Many reports on the deep levels have been published[2]. However, the results are far from crucial conclusion of the effects of stoichiometry on the defects in InP.
In this paper, the photocapacitance (PHCAP) measurements under constant capacitance condition is applied to various *n*- [3]and *p* -InP[4] crystals prepared by 4h-annealing at 700°C under controlled phosphorus vapor pressure followed by rapid cooling. Vapor pressure controlled-zone melting grown InP and LPE-grown InP are also investigated by PHCAP. The phosphorus vapor pressure dependence of the deep level density is shown. And the excitation photocapacitance method is also applied to show the precise optical transition of these deep levels.

2. Experiments

2.1 Sample preparation

The starting crystals used for annealing were LEC grown *n*-and *p*-InP. Carrier concentration of undoped crystal is 1.2-1.5x10^{16}cm^{-3} and that of Sn doped InP is 2.2x10^{16} cm^{-3}. Carrier concentration of *p*-InP doped with Zn is 3x10^{17} cm^{-3}. InP is placed in one end of a dumbbell-type quartz ampoule and 6N-red phosphorus in the other end. After sealing in vacuum, heat treatment was carried out at 700°C for 4h under controlled phosphorus vapor pressure. Phosphorus vapor pressure at the phosphorus zone, P_p, is determined from the temperature of red phosphorus [5]. The phosphorus vapor pressure at the crystal zone, P, was determined from the following equation.

$$P=P_p(T/T_p)^{1/2} \qquad (1)$$

where T and T_p are the temperature of InP crystals and red phosphor , respectively. After annealing, the ampoule was rapidly cooled by dipping into the water at nominal room temperature.

2.2 Photocapacitance measurements

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PHCAP measurement by constant capacitance method is applied at 77K to determine the level densities and their energy levels. Metal-semiconductor contact diodes were made by Au-evaporation as a barrier metal. Monochromatic light was fed into the depletion layer of the sample diodes. Deep levels was made to be neutral before each light irradiation. For this purpose, forward bias injection was carried out in the dark before each light irradiation. After light irradiation, bias voltage (ΔV_{ph}) changes to keep the junction capacitance constant according to the ionization of the levels. However, the depletion layer thickness is kept constant regardless of the change of ion density. The change of ion density, ΔNt, is given by the following equation.

$$\Delta V_{ph}=(\varepsilon/2C^2)\Delta Nt \qquad (2)$$

where C is the constant capacitance of the sample diode, ε is the dielectric constant and ΔV_{ph} is the change of bias voltage. Precise description of the PHCAP will be referred elsewhere[6].

3. Results and Discussion

3.1 n-type LEC InP crystal

Figure 1 shows the ion density PHCAP spectrum of undoped *n*-InP crystal before annealing. V_{dark} is attributed to the thermally ionized level density in the dark. Net ion density induced by the light irradiation is obtained by $\Delta V_{ph}=V_{ph}-V_{dark}$, where V_{ph} is the bias voltage after light irradiation. In Fig.1, it is shown that the ion density shows gradual increase at ~0.4eV and then increase at 0.63eV. The decrease of ion density at 0.74eV is induced by the neutralization of ionized deep level. In the wavelength region of 0.9-1.1eV, another ionization is observed at 1.1eV. In case of undoped *n*-InP, almost the same deep levels are observed even after 4h-annealing at 700°C.

Figure 2 shows the change of deep level density as a function of the phosphorus vapor pressure. It is shown that the Ec-0.63, 1.1eV and 0.74eV+Ev level density decreases with increasing vapor pressure in the range below 100 Torr. Then, the level densities increase when the vapor pressure exceeds 1000 Torr.

Ion density PHCAP spectrum of S-doped InP crystal with the carrier concentration of $5x10^{17}cm^{-3}$ does not show the ionization at 0.63eV nor the neutralization at 0.74eV. Group VI impurity S will occupy the P-sublattices. Therefore, the doped impurity S will also reduce the V_P concentration. It is considered that these deep levels are stoichiometry-dependent and are related most possibly with at least the V_P. It is also considered that the annealing under extremely high vapor pressure induces non-equilibrium 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. In such highly degraded lattices, it is considered that both the excess phosphorus composition-related defect and the vacancy-related defects are generated. Excitation PHCAP method is applied to determine the precise energy level position at 40K. After 1.40eV

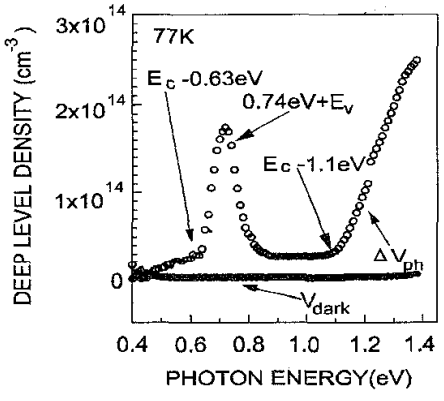

Fig.1 Ion density PHCAP spectrum of intentionally-undoped n-InP crystal before annealing

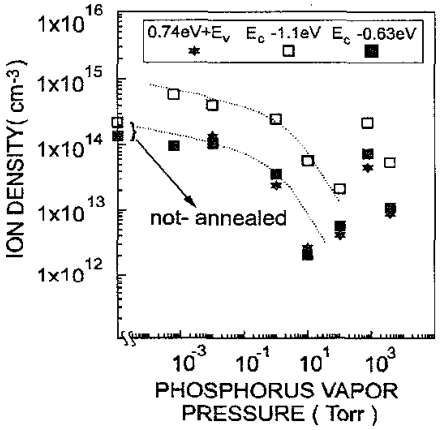

Fig.2 Phosphorus vapor pressure dependence of the deep level density in intentionally-undoped n-InP prepared by 4h-annealing at 700°C

light irradiation, the ion density PHCAP spectrum was measured from long wavelengths. It is shown that the decrease of ion density is induced at 0.43 and 0.45eV. This decrease of ion density is caused by the neutralization of ionized deep levels. The precise optical transition of deep levels in *n*-InP will be shown later with those in *p*-InP. In case of Sn-doped *n*-InP, the ion density PHCAP spectrum shows almost no ionized levels at around 0.63eV. However, after 4h-annealing at 700°C, Ec-0.63eV and 0.74eV+Ev levels are induced. The vapor pressure dependence of these deep levels shows gradual decrease in the range of $6x10^{-6} \sim 1x10^{-1}$ Torr. Above $1x10^{-1}$ Torr, the ion densities shows slight increase with increasing vapor pressure. Under the application of high vapor pressure, Sn-doped *n*-InP crystal is seriously degraded after annealing by the crystallographic inspection.

3.2 p-type InP LEC crystal doped with Zn

Figure 3 shows the ion density PHCAP spectrum of *p*-InP crystals prepared by 4 h-annealing at 700°C. It is shown that 1.05 eV+Ev level is detected before and after annealing. In addition, the deep level is detected at 0.74 eV above the valence band when *p*-InP crystals are annealed under lower vapor pressure of 1-100 Torr. It is already shown that PHCAP results revealed the electron capture at 0.74eV above the valence band even in undoped *n*-InP crystals. It is also shown that the 0.74eV+Ev level density in *n*-InP decreases with increase of vapor pressure in the 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*-InP. Therefore, it is concluded that the phosphorus vapor pressure dependence of the 0.74eV+Ev level density shows good correspondence between *n*- and *p*-InP crystals respectively. It is considered that 0.74eV+Ev level is at least related to V_P. 1.05 eV+ Ev level density increases monotonically with increase of vapor pressure. In view of vapor pressure dependence and the effect of impurity doping, 1.05 eV level may be due to defect- impurity complex with close relation to either In vacancy or P interstitial.

The excitation PHCAP was also carried out to 1.05eV+Ev level. After the primary light irradiation, ion density PHCAP spectrum was measured repeatedly from the long wavelength by changing the primary excitation light wavelength. After 1.08 eV light irradiation, neutralization is induced at 0.51 eV below the conduction band. From these results, schematic drawing of the optical transition

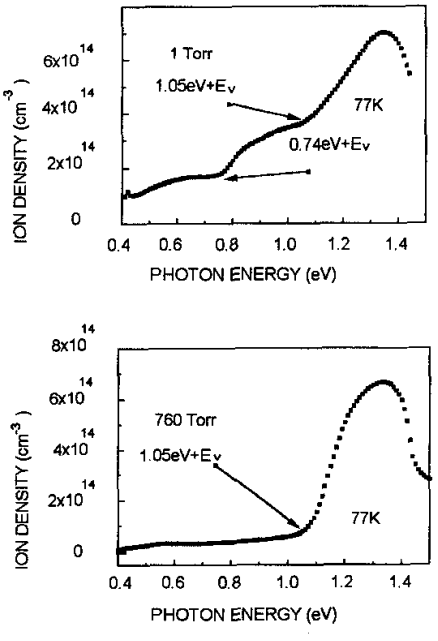

Fig.3 Ion density PHCAP spectra of intentionally Zn doped p-InP prepared by 4h-annealing at 700°C

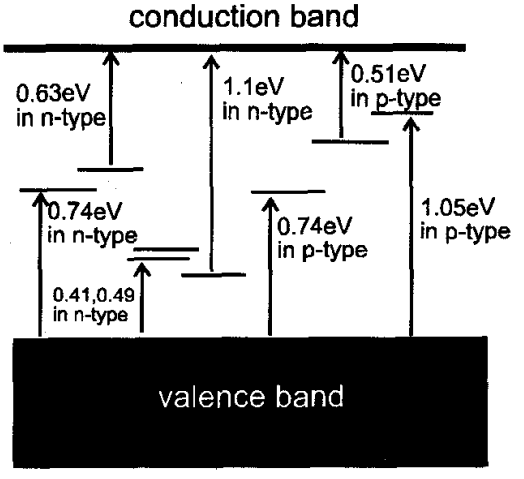

Fig.4 Schematic drawings of the optical transition process of stoichiometry-dependent deep levels in LEC-grown InP prepared by 4h-annealing at 700°C

process in InP is shown in Fig.4.

3.3 Vapor pressure controlled InP crystal growth

The vapor pressure control technology has been extensively applied to the liquid phase epitaxy (LPE) and bulk crystal growth of InP by the pressure controlled zone melting method. Contrary to the conventional method, LPE growth has been carried out by the temperature difference method under controlled vapor pressure (TDM-CVP)[7]. Figure 5 shows the ion density PHCAP spectrum of LPE-grown InP under controlled vapor pressure. As shown in Fig.5, almost no deep level is detected in the spectral range below 1.1eV. This indicates that the high quality LPE InP with stoichiometric composition can be grown by the pressure controlled LPE method.

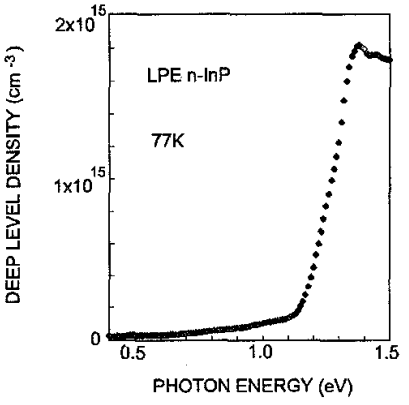

Fig.5 Ion density PHCAP spectrum of LPE-grown n-type InP epitaxial layer.

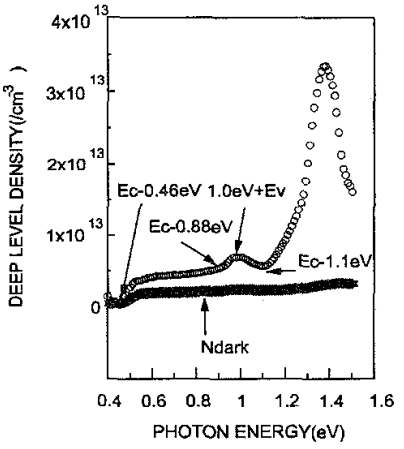

Fig.6 Ion density PHCAP spectrum of n-type InP bulk crystal grown by the vapor pressure controlled zone melting method.

Figure 6 shows the ion density PHCAP spectrum of InP bulk crystal by the pressure controlled zone melting method. From our previous results, it has been shown that the electron concentration shows its minimum and the Hall mobility shows its maximum under a specific phosphorus vapor pressure of ~22.7 atm[8]. As shown in Fig.6, the PHCAP method revealed deep donors at 0.46, 0.86 and 1.1eV below the conduction band and ~1.0eV above the valence band respectively. These deep levels are quite different from those observed in conventional LEC InP except Ec-1.1eV level. In addition, the level density is extremely low compared with the LEC InP. Therefore, vapor pressure control technology has a possibility to obtain high quality bulk crystals with stoichiometric composition.

4. Conclusion

PHCAP measurements revealed stoichiometry-dependent deep levels at Ec-0.63eV, 0.74eV+Ev, Ec-1.1eV in both intentionally-undoped and Sn doped *n*-type InP , and 0.74eV+Ev and 1.05eV+Ev levels have been revealed in Zn-doped *p*-type InP respectively. 0.74eV+Ev level was detected commonly in both *n*-and *p*-type InP when annealed under lower phosphorus vapor pressure. From the results, it is considered that Ec-0.63eV, 0.74eV+Ev and Ec-1.1eV levels relate at least with V_P. 1.05eV+Ev level in *p*-InP is considered to be related with excess phosphorus composition. Vapor pressure control has been extensively applied to the LPE and bulk crystal growth of InP. PHCAP results indicates that the high quality crystals with stoichiometric composition will be obtained by the vapor pressure control during crystal growth.

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