

Deep levels in heavily Zn-doped InP layers implanted with Ti and Ti/P

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We have investigated deep level peaks observed in the photoluminescence spectrum of heavily Zn-doped InP layers grown by metalorganic chemical vapor deposition at energies centered at 0.89 and 0.94 eV. These peaks are enhanced when the samples are implanted with Ti. When P is co-implanted, however, the intensity of these peaks decrease, and at an increased dosage, the peaks disappear from the spectrum. The peaks are, therefore, dependent on the phosphorus vacancy produced by the excessive Zn doping or the implant damage. Hall measurement data show that the Ti/P-implanted p-type InP layer is converted to n type with its sheet resistance decreasing and the donor activation of Ti increasing for higher P co-implant dose. In addition, the photoluminescence intensity of the deep level peaks is highly correlated with the sheet resistance. © 1998 American Institute of Physics. [S0021-8979(98)00204-7]

Zn is a commonly used *p*-type dopant in InP based compounds grown by metalorganic chemical vapor deposition (MOCVD). Because of its characteristics such as electrical activity, controllable incorporation with no memory effect, and low residual toxicity,¹⁻³ Zn is often the preferred choice in InP over other *p*-type dopants such as Be, Cd, and Mg. High doping concentrations are desirable in many semiconductor devices for reduced parasitic resistances and RC constants. However, it is known that free-hole concentration in the Zn-doped InP layer saturates at a mid 10^{18} cm⁻³ level and precipitates of Zn₃P₂ and Zn are responsible for the hole saturation⁴.

Implantation is a widely used fabrication technology that allows planar and area selective processes. It has especially been proven to be an effective way of achieving interdevice electrical isolation in GaAs and InP related materials.⁵ Ti implantation has been studied due to its thermal stability at high temperatures⁶ and larger solubility than other transition metals such as Fe or Co.⁷ Recently, Ti implantation has been used in forming the guard-ring of a planar long wavelength avalanche photodiode (APD).⁸

However, defects in an implanted InP layer cause limitations in the device performance and reliability because defects and their complexes act as deep electronic traps in the middle of the semiconductor band gap. It is, therefore, important to understand the conditions under which these defects are formed, how they behave, and how they can be controlled. In this work, we report the deep levels associated with phosphorus vacancies in the as-grown Zn-doped InP layers grown by MOCVD onto which Ti is implanted. The characterization is done using low temperature photolumi-

nescence (PL). In addition, Ti/P co-implantation is carried out to investigate the effect of stoichiometric balance on the deep level distribution.

Zn-doped InP layers with 1.0 μm thickness were grown on semi-insulating (100) InP(Fe) substrates using low pressure MOCVD. The source chemicals were trimethyl-indium (TMIn), phosphine (PH₃) and diethyl-zinc (DEZn). Palladium-purified H₂ was used as a carrier gas and the growth rate of InP was 3.4 μm/h at a growth temperature of 620 °C. Some samples were implanted with Ti at 80 keV with a dose of 1×10^{14} cm⁻². Others received Ti/P co-implantation with identical Ti implantation condition, but also with P implanted at 55 keV with doses of 1×10^{14} cm⁻², 5×10^{14} cm⁻² and 1×10^{15} cm⁻², respectively. The energy of the P implant is designed to make its profile coincide with that of Ti. All implantations were performed at room temperature with the substrates tilted at 7° with respect to the beam to avoid the effect of channeling. The annealing was done for 30 s at 650 °C, 700 °C and 800 °C, respectively. Low temperature PL measurements were made at 9 K using a closed cycle He refrigerator. The samples were excited with the 514.5 nm line from an Ar⁺ laser, where the excitation power was 10 mW. Hall measurements were performed at room temperature with alloyed contacts in the van der Pauw geometry.

Figure 1 shows the PL spectra of the as-grown layers with hole concentrations of 7.6×10^{17} and 1.5×10^{18} cm⁻³. The latter is a saturated level. The spectrum in Fig. 1(a) is for the 7.6×10^{17} cm⁻³ doping, and characterized by peaks centered at 1.408, 1.378, and 1.334 eV. The 1.408 eV peak is due to band edge transition, whereas the 1.378 eV peak is due to band to acceptor (B-A) transition involving Zn acceptors.⁹ The 1.334 eV peak is donor to acceptor (D-A) transition, which we confirmed by the blueshift dependency of the corresponding energy on the excitation power.¹⁰ In the spectra from samples with saturated Zn doping, additional peaks centered at 0.89, 0.94, 1.228 and 1.274 eV are seen as

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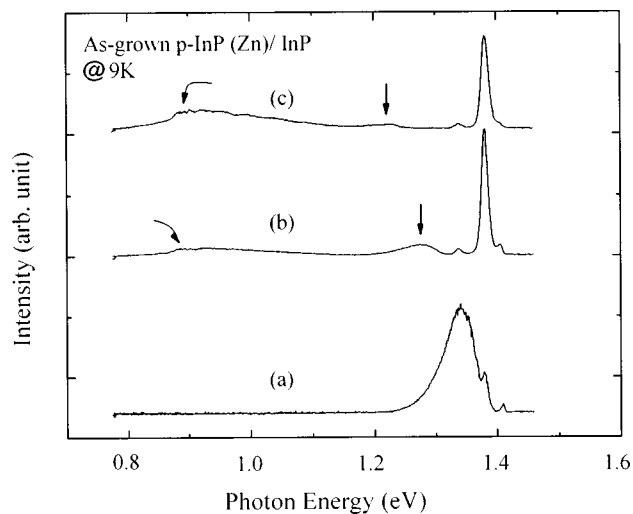


FIG. 1. PL spectra of as-grown p-InP layers are shown with different hole concentrations. Hole concentrations were (a) $7.6 \times 10^{17} \text{ cm}^{-3}$, (b) $1.5 \times 10^{18} \text{ cm}^{-3}$ at DEZn flow rate of 0.12 sccm and (c) $1.5 \times 10^{18} \text{ cm}^{-3}$ at DEZn flow rate of 0.22 sccm.

in Figs. 1(b) and 1(c). The hole concentration was saturated to $1.5 \times 10^{18} \text{ cm}^{-3}$, but different DEZn flow rates were used for (b) and (c). These peaks are not observed at the hole concentration of $7.6 \times 10^{17} \text{ cm}^{-3}$ and the ones below. The peaks centered at 1.228 and 1.274 eV also showed the excitation power dependency, thus indicating D-A transitions at each Zn doping. The small peak at 1.334 eV in Figs. 1(b) and 1(c) did not show the excitation power dependency unlike the large peak at the same position in Fig. 1(a). The former is the LO-phonon peak,¹¹ while the latter represents the D-A transition, which is overshadowed by the strengthened B-A transition at higher acceptor concentrations in Figs. 1(b) and 1(c).

The peaks at 0.89 and 0.94 eV did not show the excitation power dependency, but their intensities increased with the flow rate of DEZn, as shown in Figs. 1(b) and 1(c). As mentioned above, the hole concentration saturates at $1.5 \times 10^{18} \text{ cm}^{-3}$ and for increased DEZn flow rates. The excess Zn may be consumed in local precipitation of Zn_3P_2 , which is energetically more stable than InP at growth temperature.¹² Local strain energy from the precipitate in the zincblende structure may be lowered by P vacancy formation. We will show below that these peaks are indeed related to P vacancy.

We have implanted Ti into the Zn-doped InP samples corresponding to the PL spectrum of Fig. 1(b) and observed the changes in the peaks of interest. The implanted samples were subsequently annealed using rapid thermal annealing (RTA). Figure 2(a) shows the PL spectrum of a typical Ti implanted sample annealed at 800 °C where the peaks centered at 0.89 and 0.94 eV enhanced. Implants may cause damage in the form of vacancies and interstitials due to the difference in the amount of recoil of each atom,¹³ causing stoichiometric imbalance. It is, therefore, reasonable to consider that the peaks are related to such defects.

We continued our study by co-implanting P with Ti. Figures 2(b), 2(c) and 2(d) show the spectra obtained from

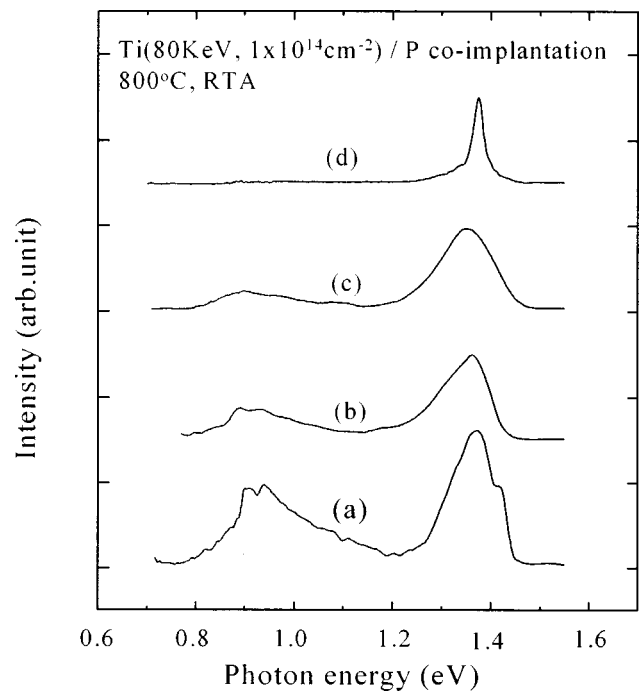


FIG. 2. PL spectra of Ti implanted and Ti/P co-implanted, originally *p*-type InP layers are shown as a function of phosphorus co-implant dose at an annealing temperature of 800 °C. Annealing was done for 30 s in flowing N_2 . Ti implantation was at 80 keV with a dose of $1 \times 10^{14} \text{ cm}^{-2}$. Phosphorus co-implantation was with doses of (a) no phosphorus, (b) $1 \times 10^{14} \text{ cm}^{-2}$, (c) $5 \times 10^{14} \text{ cm}^{-2}$ and (d) $1 \times 10^{15} \text{ cm}^{-2}$ at 55 keV.

samples which received different doses of P co-implant. We can readily see that the intensities of these deep level peaks reduce with increasing P dose, and at the P coimplant dose of $1 \times 10^{15} \text{ cm}^{-2}$, the deep level peaks completely disappeared from the spectrum [Fig. 2(d)]. The Zn related transitions such as B-A and D-A, dominate the PL spectra. Thus, these deep level peaks at 0.89 and 0.94 eV must be phosphorus vacancy related. These peaks appear when such vacancies are formed by introducing excess Zn or implant damage, but can be reduced in size by introducing additional P. Below we show how the P co-implant affects the donor activation of implanted Ti and how the deep level PL peaks are correlated with the amount of activation.

We took Hall measurements from the Ti/P co-implanted, heavily Zn-doped InP samples as a function of annealing temperature. Figure 3 shows the sheet resistance (R_s) of the samples implanted and annealed at 650–800 °C using three P doses. The original *p*-type samples were all found to have converted to *n* type. Our sheet resistance data, summarized in Fig. 3 as functions of P co-implant dose and annealing temperature, show that the sheet resistance decreases with increasing P co-implant dose and temperature. Ti acts as a donor if it occupies column III (In) sublattice and forms a deep level at 0.63 eV below E_c in InP.¹⁴ The co-implanted P that replaces the vacancy helps restore stoichiometric balance and enhances the donor activation of Ti. We have used Be/P co-implantation in InP where the Be activation was significantly improved by the co-implanted P.¹⁵ The stoichiometric and damage effects of P were used to explain the latter.

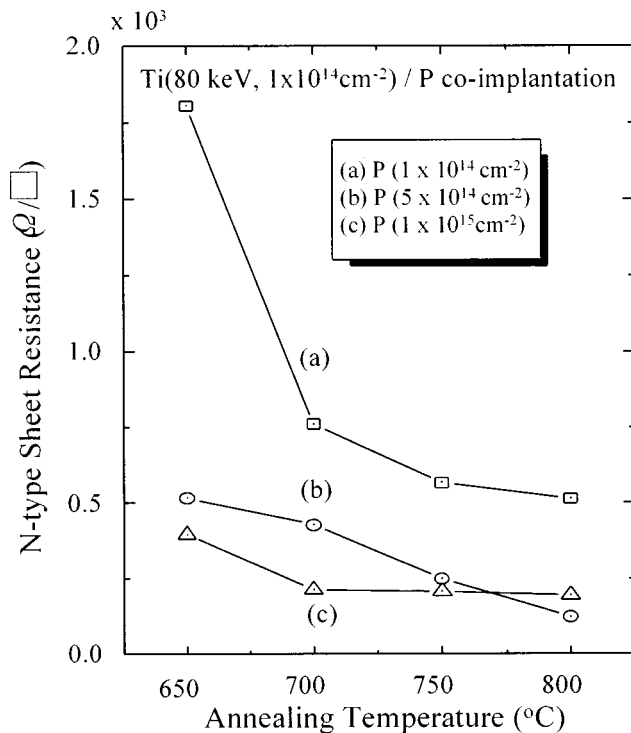


FIG. 3. The sheet resistance (R_s) of the InP layers after the Ti/P co-implantation is shown as function of phosphorus co-implant dose and anneal temperature. The sheet resistance decreases at higher P co-implant dose and higher anneal temperature.

In Fig. 4, we plotted the deep level PL maximum intensity as a function of sheet resistance where the two are shown to be highly correlated. At higher doses of co-implanted P, the size of the deep level peaks reduces, and the dopant activation increases. There may be an optimum co-implant dose over which the dopant activation decreases, as we have observed in the Be/P case.¹⁵ Higher anneal temperatures also helped achieve higher activation and lower sheet resistance.

In conclusion, we have investigated the deep levels in as-grown and implanted InP layers using low temperature PL. The PL spectra centered at 0.89 and 0.94 eV showed characteristic emission associated with deep levels of phosphorus vacancies in the heavily Zn-doped and Ti implanted layers. These peaks disappeared at a P co-implant dose after thermal annealing at 800 °C. These results indicate that two peaks centered at 0.89 eV and 0.94 eV from phosphorus vacancies are very likely to be formed by heavy Zn doping or by implant damage. The increased donor activation of Ti

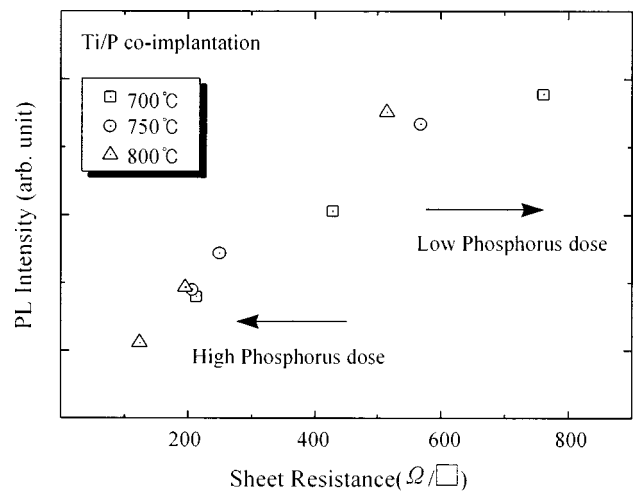


FIG. 4. The maximum PL intensity for the deep levels centered at 0.89 and 0.94 eV is plotted against the sheet resistance listed in Fig. 3. The lower sheet resistance and higher donor activation of Ti can be indicated by the smaller amount of the PL intensity for the deep levels.

for higher P co-implant dose is also shown to be highly correlated with co-implanted P dose and the PL intensity of the deep level peaks mentioned above.

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