Uniformity of Deep Levels in Semi-Insulating InP Obtained by Multiple-Step Wafer Annealing

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The uniformity of deep levels in semi-insulating InP wafers, which have been obtained by multiple-step wafer annealing under phosphorus vapor pressure, was studied using the thermally stimulated current (TSC) and photoluminescence (PL) methods. Only three traps related to Fe, T_0 (ionization energy $E_i = 0.19$ eV), T_1 (0.25 eV), and T_2 (0.33 eV), probably forming complex defects, were observed in the wafer and they exhibited a relatively uniform distribution. PL spectra relating to phosphorus vacancies observed in some regions of the wafer are correlated with a small TSC signal having an ionization energy of 0.43 eV.

Key words: Defects, InP, photoluminescence (PL), semi-insulating (SI)

INTRODUCTION

The realization of semi-insulating (SI) InP is important for device applications such as high-frequency devices and optoelectronic integrated circuits. Commercially available Fe-doped SI InP has a large concentration of Fe in a range of $(0.2–1.0) \times 10^{17}$ cm^{-3} and shows various disadvantages for its applications, such as the out-diffusion of Fe into the epitaxial layers,[1] the displacement of Fe by Mg or Zn dopant diffusing into Fe-doped InP substrate during metalorganic chemical vapor deposition (MOCVD) process,[2] and the slip-like defect formation after epitaxial growth.[3] Recently, it was found that a multiple-step wafer annealing (MWA) under phosphorus vapor pressure is very effective in improving the uniformity of electrical properties such as resistivity and mobility.[4] The InP obtained by the MWA technique is semi-insulating, even though the Fe concentration is very low in a range of $(1.0–2.5) \times 10^{15}$ cm^{-3}, note that the conventional, unannealed, InP with Fe concentration below 2.5×10^{15} cm^{-3}, is conductive. Since the MWA treatment can improve the uniformity of resistivity and mobility in the wafer, in addition to holding the semi-insulating property, the study of the distribution of the deep level defects in annealed SI InP wafers is important. In this paper, we demonstrate by using a thermally stimulated current (TSC) method, that the MWA technique can achieve a relatively uniform distribution of defects relating to residual Fe atoms. We also show that the phosphorus vacancy (V_p) concentration introduced in the MWA process is less than the detection limit of the photoluminescence (PL) measuring system used here except in some regions of the wafer.

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EXPERIMENTS

The starting materials were *annealed* SI InP wafers prepared by the MWA technique[4] and containing Fe to a concentration 1.5×10^{15} cm^{-3} as a residual impurity. Two inch diameter InP wafers were annealed at 950°C for 40 h under a phosphorus vapor pressure of 1 atm. Furthermore, a second annealing step was carried out at 807°C for 40 h under a phosphorus vapor pressure of 30 atm. The typical resistivity and mobility of wafers used in the present work were 3.2×10^7 Ωcm and 4280 cm^2/Vs, respectively, as given by the van der Pauw method. TSC measurements were carried out using the method described below. This method has been used for the identification of deep level defects in Fe-doped InP and neutron irradiated GaAs.[5]

Samples were cooled down to 80K and exposed to illumination through the front electrode with a light-emitting diode (with a peak wavelength of 940 nm and a light intensity of 2 mW/mm^2). The wavelength of 940 nm was optimum to obtain TSC spectra from annealed SI InP. The front side of the sample was

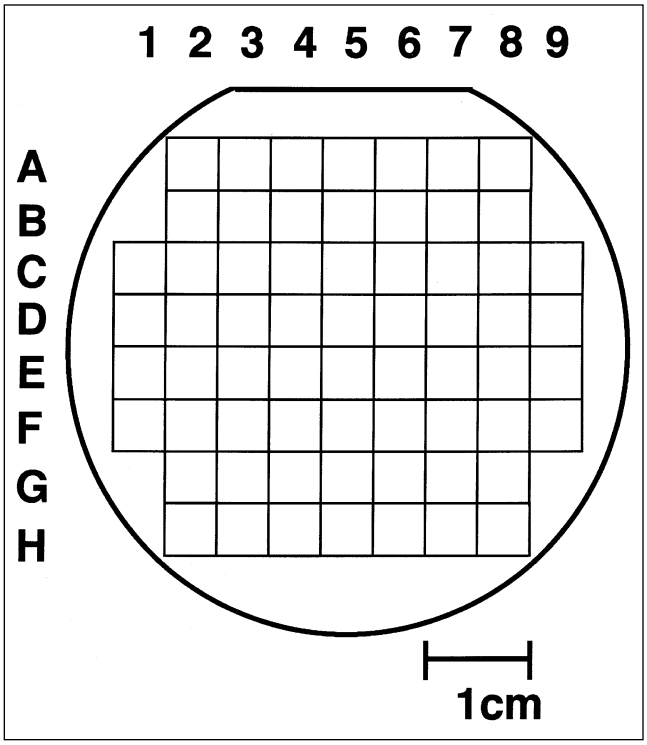


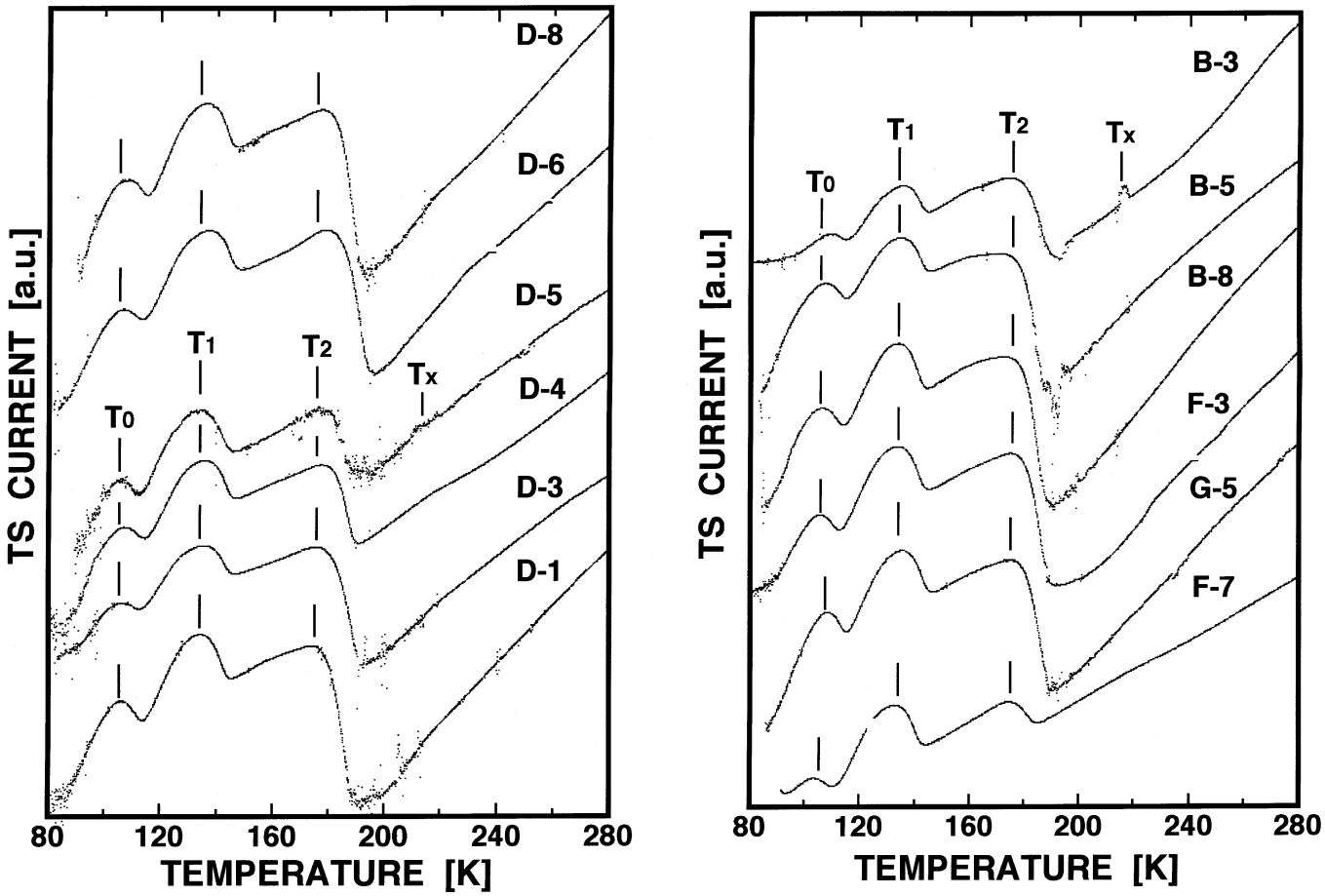
Fig. 1. Typical portions measured by the TSC and PL methods. Each piece ($5 \times 5 \times 0.5$ mm^3) was cut from a wafer obtained by the MWA technique.

connected to the positive terminal of an electrometer (Keithley 617) and the back side to the ground terminal of the same electrometer via a bias power supply. The sample was exposed for 10 min at 80K with a biasing voltage of +1 V. TSC spectra of samples were measured with +20 V applied to the front electrode. The sample temperature was raised to 280K at a constant rate of 0.2 Ks^{-1} in the dark. The PL measurement system[6] used here has been previously employed for the identification of cation antisite defects in semi-insulating GaAs. The 514.5 nm line of a 100 mW Ar^+ laser was used as the excitation source. Figure 1 shows the typical portions measured by the TSC and PL methods. Prior to chemical etching of the wafer for TSC measurements, PL spectra were taken in three regions of each piece ($5 \times 5 \times 0.5$ mm^3) cut from the wafer.

RESULTS AND DISCUSSIONS

Figures 2a and 2b show TSC spectra taken for various pieces from an *annealed* SI InP wafer. In the TSC spectrum of *annealed* SI samples, three peaks can be resolved, labeled as T_0 (ionization energy E_1 = 0.19 eV), T_1 (0.25 eV), and T_2(0.33 eV). According to the approximate relationship[7] $E_i = kT_m \ln(T_m^4/\beta)$, where E_i is the ionization energy (trap depth), k Boltzmann's constant, T_m the TSC peak temperature, and β the heating rate for the thermal scan, the ionization energy for each trap was calculated. E_i values estimated by the present TSC study contain an uncertainty of ±0.01 eV. The T_0 and T_1 traps are close to the TSC peaks, P_2 and P_4, respectively, which have been observed in Fe-doped SI samples,[8,9] but the T_2 trap cannot be associated with the P_6 trap observed in Fe-doped SI InP, because the peak temperature of the T_2 trap is about 10K higher than that of the P_6 trap. Similar TSC peaks associated with the T_1 and T_2 traps have been observed in SI InP[10] annealed under a phosphorus vapor pressure of about 5 atm, while T_0(E_i = 0.18 eV), T_1(0.23 eV), T_2(0.32 eV), and T_3 (0.40 eV) peaks have also been observed in SI InP[10] annealed under a phosphorus vapor pressure of about 0.06 atm. The discrepancy in the appearance of deep levels between the present work and other reported works may be attributed to a difference of preparation among the annealed SI InP wafers. Samples prepared by a single step annealing sometimes showed an inhomogeneous distribution of deep level defects, involving the PL spectra relating to V_p, as discussed later. The T_0, T_1, and T_2 traps might be related to residual Fe atoms such as Fe-X complex defects, where X may be attributed to residual impurities such as Zn. Since the trap T_2 was not observed in the conventional Fe-doped InP,[8] which was annealed below 700°C for 30 min, this trap should be due to a complex defect consisting of Fe and annealed-introduced defects in MWA crystals, which were annealed at two desired temperatures for 80 h. Note that the trap level of an isolated Fe impurity has been reported to be 0.61 eV by a photoinduced current transient spectroscopy (PICTS) method.[11]

A very small TSC signal, labeled as T_x, with an ionization energy of 0.43 eV, was observed at the B-3 and D-5 portions in the wafer (see Figs. 2a and 2b). We believe that the T_x signal can be distinguished from the background level. A broad TSC peak with an ionization energy of 0.42 eV has been observed clearly in Fe-doped SI InP[8] annealed at temperatures above 600°C and has been identified as a P_8 trap. Also, however, a broad T_3 peak with an ionization energy of 0.40 eV has been observed in SI lnP annealed under relatively low phosphorus vapor pressures.[10] We cannot confirm at present whether the T_x trap is identical to the T_3 (or P_8) trap, because the T_x trap observed here is the weak peak, while the T_3 peak is relatively broad and its energy level is 0.02 eV lower than that of the T_x peak. Figure 3 shows the PL spectra of a portion in the wafer where the T_x peak with E_i = 0.43 eV is observed, together with spectra of other portions in the wafer. The PL spectra were recorded at 15K. Emission peaks,[8,12] respectively, labeled No. 1 and No. 2, around 875.0 nm (1.417 eV) and 899.5 nm (1.378 eV) are associated with the band edge (BE) emission, and the band-neutral Zn acceptor ($BA°_{Zn}$) and donor-neutral Zn acceptor ($D°\text{-}A°_{Zn}$) pair emissions, respectively. Emission peak No. 3, at 912.0 nm (1.359 eV), is attributed to an exciton bound to a deep donor related to a V_P complex. Emission peak No. 4, at 918.5 nm (1.350 eV), is associated with a V_P donor-acceptor pair transition. Although emission peak No. 5, at 924.5 nm (1.341 eV), was unidentified in the previous work,[12] we speculate that this emission is associated with divacancies related to phosphorus, because



a b

Fig. 2. (a) Thermally stimulated current spectra taken for various pieces in the D-th row. D-5 represents a portion in the D-th row, the 5-th column. (b) Thermally stimulated current spectra taken for various pieces except the D-th row.

- It has always been observed together with the emissions No. 3 and No. 4 in undoped-conductive InP annealed at temperatures higher than 700°C, suggesting that by high-temperature annealing, not only phosphorus single vacancies are formed but also divacancies and clusters are generated,[12]
- Its emission peak intensity is lower than that of emission No. 3, and
- An ionization level (0/+) of V_P in InP has been calculated[13] to be 1.37 eV from the top of the valence band and other ionization levels of V_P are located in the conduction band.

The electronic structure[14] of divacancy in InP suggests the following energy states. In the absence of lattice distortion, the symmetry point group of the divacancy is C_{3v}. The broken-bond-like orbitals from either the three P atoms adjacent to the In vacant site or three In atoms adjacent to the P vacant sites can be symmetrized to form a_1 and e symmetric combinations. A strong interaction between the two a_1 states is expected to occur and to give rise to a binding and an anti-binding σ-like defect states. In the charge states $(V_{In}\text{-}V_P)^{1-}$ and $(V_{In}\text{-}V_P)^{2-}$,the energy levels of the lower a_1 level (binding state) are located at $E_v + 0.02$ and $E_v + 0.05$ eV, respectively. Therefore, the emission peak No. 5 (924.5 nm; 1.341 eV) is associated with $(V_{In}\text{-}V_P)^{-1}$ or $(V_{In}\text{-}V_P)^{2-}$. The remaining emission peaks, No. 6 (931.0 nm; 1.332 eV), No. 7 (940.5 nm; 1.318 eV), No. 8 (947.5 nm; 1.308 eV), and No. 9 (954.0 nm; 1.300 eV), are associated with phonon replicas ($\hbar\omega_{LO}$) of the emissions No. 2, No. 3, No. 4, and No. 5, respectively. Therefore, we strongly suggest that the PL spectrum assigned to V_p, observed at around 930 nm, is associated with a deep level, T_x, having an ionization energy of 0.43 eV and appearing as a weak TSC signal. Although we cannot explain exactly why these defects are unique to those positions of the wafer, the V_P defects may occur easily in the vicinity of structural defects such as dislocation loops induced by high temperature annealing.

CONCLUSIONS

In conclusion, we have investigated the uniformity of deep levels in *annealed* SI InP wafer obtained by multiple-step wafer annealing under a phosphorus vapor pressure. Two TSC peaks were observed, T_0 (E_i = 0.19 eV) and T_1 (0.25 eV), which were correlated with complex defects related to Fe, and probably also involved residual impurities such as Zn. The T_2 trap (0.33 eV) was assigned to complex defects consisting

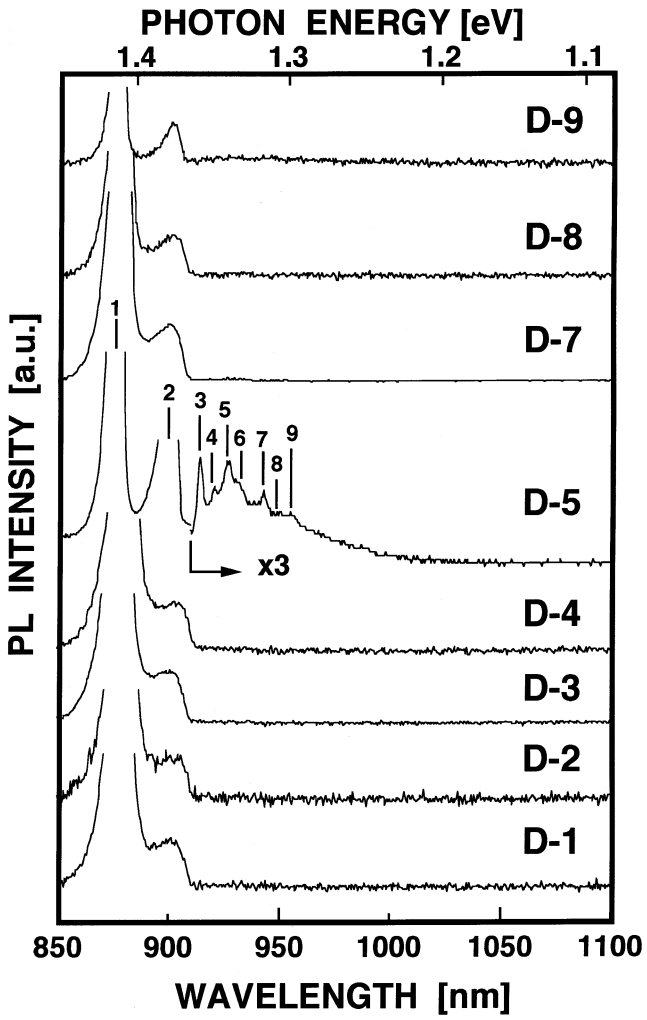


Fig. 3. PL spectra taken for various pieces in the D-th row. PL spectra in another row are similar. For example, the PL spectrum of B-3 piece is similar to that of D-5.

of Fe and defects introduced in the MWA process. The T_0 and T_1 traps were close to the P_2 and P_4 traps observed in conventional Fe-doped SI InP, respectively, but the T_2 trap would not be identified as the P_6 trap. On the other hand, the small TSC signal, T_x (0.43 eV), observed in some regions of the wafer was associated with a V_P related defect.

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