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Traps in semi-insulating InP studied by thermally stimulated current spectroscopy

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Traps in Fe-doped semi-insulating InP samples have been studied by thermally stimulated current spectroscopy with IR ($h\nu < 1.12$ eV) excitation at 81 K. The possible involvement of native defects in determining the compensation mechanisms is suggested based on the observation of other than the usual 0.64 eV Fe-related activation energy for the dark current in one of the four samples supplied from different sources. A metastable behavior of traps in another sample was found and explained by a charge-controlled defect reaction model. Three out of the six traps observed are suggested to be electron traps and one among the other three traps is believed to be a hole trap.

Semi-insulating (SI) InP is a very promising material for high-frequency devices and optoelectronic integrated circuits (OEICs). It can be routinely obtained by doping with Fe, which acts as a deep acceptor. Recently, however, nominally undoped SI InP has been obtained by high-temperature annealing under high phosphorus overpressure.¹ Understanding the defects in this material is very important, since they act as traps and recombination centers, and it has even been inferred that the native phosphorus-antisite defect (P_{In}) may play an important role in the compensation mechanism of undoped SI InP.² We have previously used thermally stimulated current (TSC) spectroscopy to study the defects in undoped SI GaAs grown by different techniques, i.e., the liquid-encapsulated Czochralski (LEC) and vertical-gradient freeze (VGF) methods.³ It was found that the TSC technique with IR ($h\nu < 1.12$ eV) excitation at $T < 90$ K can be used not only to reveal the electron and hole traps, but also to monitor the quenching and enhancement processes of the various traps during IR photocurrent quenching. Many of the GaAs traps are believed to be associated with the transition of EL2, a main native defect (As_{Ga}-related defect) in undoped SI GaAs, from the normal state to its metastable state.⁴

In this letter, we report the application of the TSC technique to Fe-doped SI InP samples. The main results are: (1) the dark current (I_d) for most samples of $250\text{ K} < T < 380\text{ K}$ is controlled by a deep center with $E_T = 0.64$ eV; (2) unlike the undoped SI GaAs case, no IR photocurrent quenching can be observed; (3) at least six traps are revealed in the range $81\text{ K} < T < 250\text{ K}$; and (4) in one particular sample a metastable behavior of traps was observed.

The LEC-grown Fe-doped SI InP samples used in the study were provided from four different sources. Hall effect data at 300 K show that $\rho > 10^7\ \Omega\text{ cm}$ and $\mu \approx 2500\text{ cm}^2/\text{V s}$ for the samples. For TSC studies, both In and Au-Ge ohmic contacts were used. Alloying was performed in forming gas at 410 °C for 5 min for the In contacts and at 420 °C for 40 s for the Au-Ge contacts. The IR light source

was provided by a tungsten lamp (8 W) filtered through a Si wafer, thus allowing photon energies less than 1.12 eV. All the currents, i.e., the dark currents (I_d 's), the photocurrents (I_{ph} 's) at 81 K, and the I_{sc} 's were measured under a bias of 20 V. The I_d 's were recorded during slow cooling (0.1 K/s) at $250\text{ K} < T < 380\text{ K}$ and the I_{ph} 's at 81 K were measured immediately after the IR light illumination. To observe the effect of the illumination time on the TSC spectra, the tested sample was always quickly cooled down from 320 to 81 K in the dark and then exposed to IR light for various times from 1 s to 5 min. For consistency, the TSC thermal scan ($81\text{ K} < T < 250\text{ K}$) with a heating rate of 0.3 K/s was always started 30 s after the termination of the IR light. For comparative purposes, a 1.46 eV light from a GaAs laser diode (100 mW) and a white light (without using a Si filter) were used for the carrier excitation at 81 K.

The Arrhenius plots of the I_d 's for four samples are shown in Fig. 1. Three samples (Nos. 1, 2, and 3) present a consistent activation energy, i.e., $E_T = 0.64 \pm 0.01$ eV, whereas sample No. 4 gives activation energies of 0.59 eV for $T > 300\text{ K}$ and 0.44 eV for $T < 300\text{ K}$. The 0.64 eV center is widely believed to be due to Fe. However, the deep center causing the semi-insulating nature of undoped InP, was determined from the temperature dependence of the carrier concentration to be 0.64 eV, too.¹ The 0.59 and 0.44 eV centers were reported by several authors and attributed to the P-interstitial or In-vacancy, and the P-vacancy in *n*-type LEC InP, respectively.⁵ In the study of defects in nominally undoped SI GaAs, we have found that two different deep centers dominate the dark conductivity, depending on the crystal stoichiometry; i.e., an 0.74 eV center due to EL2 dominates As-rich LEC SI GaAs and an 0.43 eV center controls a number of VGF SI GaAs samples. The fact that there exists more than just the usual 0.64 eV Fe-associated activation energy in some SI InP samples implies the possible involvement of native defects in the compensation mechanism. The photocurrent responses at 81 K have been measured and no IR photocurrent quenching was observed. An interesting observation is

FIG. 1. Arrhenius plots of I_{dark} , showing three different activation energies.

that regardless of the small difference in net photocurrents at 300 K, which vary between 24 and 42 nA for the four samples, Sample No. 1 shows an I_{ph} nearly two orders of magnitude higher at 81 K as compared to the others.

The TSC spectra with 5 min IR light illumination for four samples have been measured and at least six TSC peaks are revealed in the range 81 to 250 K. The TSC peaks above 250 K cannot be observed due to masking by the increasing I_d 's. According to the approximate relationship $E_T = kT_m \ln(T_m^4/\beta)$, where E_T is the trap depth, k the Boltzmann's constant, T_m the TSC peak temperature, and β the heating rate for the thermal scan,⁶ the T_m 's at a rate of 0.3 K/s and the E_T 's for the traps are: T_b (168 K) 0.32 eV, T_c (147 K) 0.27 eV, T_d (130 K) 0.23 eV, T_e (125 K) 0.22 eV, T_f (99 K) 0.17 eV, and T_g (88 K) 0.15 eV.

In Sample No. 1, four traps (T_b , T_c , T_e , and T_f) were found, but not trap T_d . In contrast to the other three samples, when this sample was illuminated with increasing time from 1 s to 5 min, three TSC peaks (T_c , T_e , and T_f) were decreased in amplitude and the other one (T_b), increased, as shown in Fig. 2(a). In Fig. 2(b) is shown the illumination-time dependence of the TSC spectra using a neighbor sample, but with Au-Ge contacts. These data clearly demonstrate a different variation of the TSC peaks: two of them (T_c and T_e) are decreased and the other two (T_b and T_f), increased. This kind of metastable behavior can be repeated by warming the sample up to 320 K and then quickly cooling down to 81 K in the dark. Although effects due to the illumination time can be observed on samples with both types of contacts, there are some differences in the TSC spectral structure: (1) the TSC peaks in the sample with Au-Ge contacts are much lower than those in the sample with In contacts; and (2) the relative peak heights of T_e and T_f over T_b and T_c is largely reduced in the former sample. Similar differences were observed in undoped SI GaAs samples, using unannealed Au or Au-Ge contacts on the top and annealed (450 °C, 5 min). In contacts on the two ends, and were attributed to differences in the contact properties (Schottky contact versus ohmic contact) and the detected region (near surface versus bulk).³ It is possible that the annealing of 40 s at 420 °C is not long

(a)

(b)

FIG. 2. TSC spectra as a function of the IR light illumination times at 81 K, showing a metastable behavior of traps in sample No. 1 with (a) In contacts and (b) Au-Ge contacts.

enough for Au-Ge on SI InP to form a good ohmic contact.

Several methods can be used to provide information on the trap type: for example, (1) comparison of TSC spectra under positive and negative bias using a sample with a Schottky contact on the top; and (2) Hall effect measurements during the TSC thermal scan. Here we present another method, i.e., comparison of TSC spectra excited with different light sources. Figure 3 shows the TSC spectra excited with IR light ($h\nu < 1.12$ eV), 1.46 eV light, and white light using the sample with Au-Ge contacts. It can be seen that T_c , T_e , and T_f clearly increase if either white light or 1.46 eV light is used for the excitation at 81 K. From the spectral shapes of the photoionization cross sections for electrons and holes, σ_n and σ_p , due to Fe in InP at 77 K,⁷ we know that the hole excitation will dominate the electron excitation when the photon energy ($h\nu$) is in the range from 0.78 to 1.12 eV and vice-versa when $h\nu$ is above 1.27 eV. From these arguments, T_c , T_e , and T_f can be reasonably assigned to electron traps and T_b to a hole trap.

For conventional Fe-doped SI InP, Fe concentrations are in the range of 10^{16} cm^{-3} for compensating the Si donors (10^{16} cm^{-3}) from horizontal Bridgman polycrystalline starting material. The relative Fe concentrations in

FIG. 3. TSC spectra excited with different light sources at 81 K, showing three electron traps (T_f , T_e , and T_b) and a hole trap (T_h).

the four samples studied were determined by secondary-ion mass spectroscopy (SIMS) to be 3.5, 2.5, 5.0, and 6.2 ppm for samples No. 1, 2, 3, and 4, respectively. Based on the SIMS data, it seems that the big difference in I_{ph} , the TSC spectra, and the metastable behavior between sample No. 1 and the other three samples cannot be explained in terms of the difference in Fe content. However, the native defects in the samples, such as P_{In} , V_{In} , V_p and their complexes with each other and with impurities, could be very different, depending on the various crystal-growth conditions. Levinson *et al.* studied a configurationally bistable defect (MFe center) in lightly Fe-doped *n*-type InP by thermally stimulated capacitance and DLTS.⁸ Depending on the charge state, the authors found that the defect has two atomic configurations, *A* and *B*, with the transformation *B*→*A* taking place during the trap filling pulse (or bias off) by electron capture, and the transformation *A*→*B* taking place between pulses (or bias on) by electron emission or by hole capture. A defect complex, consisting of a multiply charged native defect and an ionized shallow donor, and a kind of electrostatic and lattice-strain-driven defect complex rearrangement mechanism were proposed to explain the transformations. The thermal activation energies of the related electron traps observed in their DLTS spectra were determined to be 0.41 eV for A_1 and A_2 in configuration *A*, and 0.24 and 0.35 eV for B_1 and B_2 , respectively, in configuration *B*. Suppose a similar defect complex exists in our Fe-doped SI InP sample No. 1: then the metastable behavior of the traps observed in the illumination-time-dependent TSC spectra can be explained as follows. At the

initial stage of IR illumination, hole excitation due to $Fe^{3+} \rightarrow Fe^{2+} + h$ is dominant because $p(h\nu) > n(h\nu)$ in the IR spectral range, as mentioned above. The capture of holes by the supposed defect complex will cause it to be in configuration *B*, resulting in higher T_c (0.27 eV) and T_e (0.22 eV), two electron traps similar to B_2 and B_1 . More electrons will be excited by longer IR illumination through the transition $Fe^{2+} \rightarrow Fe^{3+} + e$ and captured by the defect complex, which leads to its configurational transformation from *B* to *A*, resulting in a decrease of T_c and T_e and an increase of hole trap T_b . Warming the sample up to > 300 K will cause electron emission from T_c and T_e , resulting in a transformation of the defect complex back into configuration *B* as observed in the repeated TSC run. Note that we did not observe the electron traps A_1 and A_2 due to the masking effects of increasing I_d and Levinson *et al.* did not report the presence of hole trap T_b . Obviously, this is a very phenomenological explanation and further studies, especially concerning the behavior of native-defect-related traps in nominally undoped SI InP, are needed.

In conclusion, traps in SI InP from four different sources have been studied by TSC. Six traps have been observed and characterized. It was found that there exists more than just the usual 0.64 eV Fe-associated activation energy for I_d in some SI-InP samples which suggests the possible involvement of native defects in determining the compensation. A metastable behavior was found in sample No. 1 and was explained by a charge-controlled defect reaction model. Through the use of different excitation light sources, three of the six observed centers are assigned as electron traps and the other one is suggested to be a hole trap.

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