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Electrical conduction in annealed semi-insulating InP

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Variable-temperature current–voltage has been used to study the conduction properties of Fe-doped semi-insulating (SI) InP in the as-grown and annealed states. It is found that the trap-filling (TF) process disappears gradually with lengthening of annealing time. This phenomenon is explained by the decrease of the concentration of the empty Fe deep level (Fe^{3+}) that is caused by the thermally induced donor defect formation. The TF process cannot be observed in annealed undoped and long-time annealed Fe-doped SI InP material. The breakdown field of annealed undoped and Fe-doped SI InP is much lower than that of as-grown Fe-doped InP material. The breakdown field decreases with decreasing of temperature indicating an impact ionization process. This breakdown behavior is also in agreement with the fact that the concentration of the empty deep level in annealed InP is lowered. © *2000 American Institute of Physics.* [S0021-8979(00)04108-6]

I. INTRODUCTION

Semi-insulating (SI) InP is a key material for high-frequency devices and optoelectronic integrated circuits. It is thus important that SI InP has a high thermal stability and breakdown field. Many researches have shown that the breakdown field of SI InP can be as high as 10^5 kV/cm, which makes it suitable for microwave devices.

Electrical conduction of SI InP has often been studied by the current–voltage ($I-V$) method in the past years.[1–8] Its $I-V$ characteristic is qualitatively in agreement with the space-charge-limited process of Lampert and Mark's injection theory.[9] As voltage increases, there are three regions on the $I-V$ curves: Ohmic (linear), transition (quadratic), and trap-filled regimes.[3–8] The trap-filling process that depends on the concentration of empty deep levels controls the transition regime. After the empty trap is filled up, the material behaves as a trap-free insulator (trap-filled regime).[9]

Under high-electric-field conditions, field effects such as impact ionization, variation of capture cross section, velocity saturation, etc., have to be take into account in order to explain the $I-V$ characteristics.[8,10] These works have led to a deeper understanding of the trap-filling and breakdown behavior in SI Fe-doped InP.

In this article, we present the $I-V$ characteristics of annealed Fe-doped SI InP, including annealed undoped SI InP. It is found that the trap-filling (TF) process cannot be observed for long-time annealed Fe-doped and undoped SI InP. This result is consistent with previous works that have shown thermal donor formation in Fe-doped SI InP.[11–15] It is also observed that the breakdown field of annealed Fe-doped SI InP decreases significantly. Indeed, the breakdown field of annealed undoped SI InP is found to be as low as 2.8 kV/cm, giving a negative appreciation of this material.

II. EXPERIMENTS

Liquid-encapsulated Czochralski-grown Fe-doped SI InP wafers were used for the measurements. The electrical parameters of the samples were obtained by Hall-effect measurement. The annealing of the wafers was carried out in a sealed quartz tube that was cleaned and evacuated before use. Both sides of the samples are first lapped and then degreased by acetone and methanol. Then, the wafer is etched, rinsed in deionized water, dried, and put into a metal deposition chamber. Gold spots 1 mm in diameter were deposited on one side and 6 mm in diameter on the other side of the sample to make electrical contacts. It was found that the annealing process normally required to get Ohmic contacts was not necessary because no significant difference in the $I-V$ characteristics of the samples with and without alloy annealing could be found.

The $I-V$ measurement system consisted of a HP 3245A programmable voltage generator which drove a programmable EG&G ORTEC 556H high-voltage power supply, a Keithley 485 digital programmable electrometer, and an IBM XT computer. The temperature of the sample is controlled by a closed-cycle helium refrigerator (HS-4 HELIPLEX® refrigeration system).

III. RESULTS

The annealing condition, electrical parameters, and breakdown field of six samples are listed in Table I. The breakdown field is obtained from the breakdown voltage divided by the sample thickness. It is noted that the breakdown field of the annealed sample is much lower than that of the as-grown sample. As there are differences in sample thickness, the results are presented here in the form of current–electric-field ($I-E$) graphs instead of $I-V$ for proper comparison of different samples.

Figure 1 shows the $I-E$ curves of an as-grown Fe-doped SI InP sample (purchased from MCP) for temperatures 200–300 K. The $I-E$ characteristics are consistent with previous works on SI Fe-doped InP.[3–8] Such electrical transport behavior can be described by the space-charge-limited current theory of Lampert and Mark,[9] which may be summarized as follows. For single-carrier injection into a SI material having

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TABLE I. Preparation conditions and room-temperature electrical parameters of SI InP.

Sample	Annealing Conditions	Thickness (mm)	Mobility (cm^2/vs)	Electron concentration	Breakdown field (kV/cm)
A-SI-01	As grown Fe doped	0.4	2900	1.9×10^8	>28
B-SI-01	700 °C 40 h Fe doped	0.3	2200	2.2×10^8	26
A-SI-02	As grown Fe doped	0.45	2300	3.62×10^7	>30
D-SI-02	700 °C, 12 h Fe doped	0.45	1700	1.95×10^8	~10
F-SI-02	900 °C, 50 h Fe doped	0.45	111	2.34×10^{11}	~5.4
A-N-01	900 °C, 80 h Undoped	0.5	2700	8.37×10^7	~2.8

a single trap, the current density j in the Ohmic and space-charge-limited regimes are expressed by[9]

$$j=n_0 q\mu V/d, \tag{1}$$

$$j=\tfrac{9}{8}\theta\epsilon\mu V^2/d^3. \tag{2}$$

The transition between linear and quadratic regimes begins at a voltage V_Ω given by

$$V_\Omega=\tfrac{8}{9}qn_0 d^2/\theta\epsilon, \tag{3}$$

while the trap-filling-limited voltage V_{TFL} is described by

$$V_{\mathrm{TFL}}=\frac{qp_t d^2}{2\epsilon}, \tag{4}$$

where d is the sample thickness, p_t is the concentration of empty deep traps, and $\theta=n/(n+n_t)$, where n_t is the concentration of electron occupied traps, other symbols having their usual meanings. It can be seen that the value of V_{TFL} depends on the concentration of empty traps, while the current in the transition regime (quadratic) is controlled by the ionized trap concentration. For the as-grown Fe-doped SI InP, the concentration of Fe^{2+} $(=n_t)$ and Fe^{3+} $(=p_t)$ can be known from Eqs. (2) and (4) by the measured current–voltage data. Here, we avoid this quantitative evaluation since it has been found that the concentration of Fe^{3+} calculated from Eq. (4) is usually lower than that measured by other methods.[8,10,16,17] However, the change of the $I-E$ characteristics is still an indication of the change of trap occupancy. The kinks in the curves above 260 K that occur around 20 kV/cm are indications of the end of trap-filling processes and the material starts to behave like a trap-free insulator.[9] The onset of the kink results from the beginning of trap filling, while the end of the kink indicates the completion of trap filling. For curves below 260 K, much higher fields are needed to observe this process since more shallow donors freeze out and the concentration of Fe^{3+} increases in the material at low temperature.

In Fig. 2, the $I-E$ curves at different temperatures of a Fe-doped InP sample before and after annealing are shown. It can be seen that there are obvious changes of the transport characteristics of annealed InP. There are no distinct regions

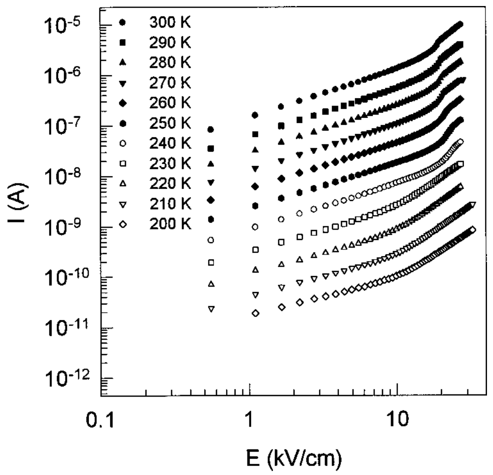

FIG. 1. $I-E$ curves of an as-grown Fe-doped SI InP sample between 200 and 300 K.

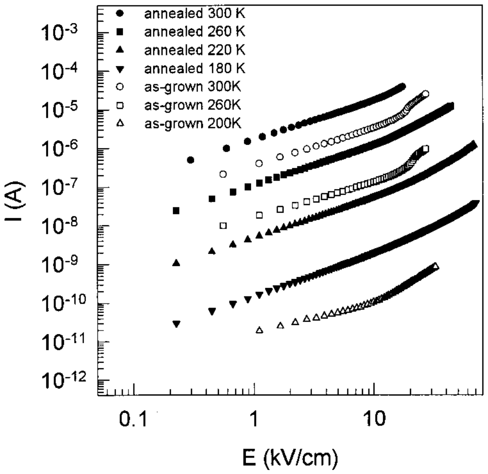

FIG. 2. $I-E$ curves over the range 180–300 K of Fe-doped SI InP before (open symbols) and after (closed symbols) annealing. The annealing conditions are 700 °C for 40 h.

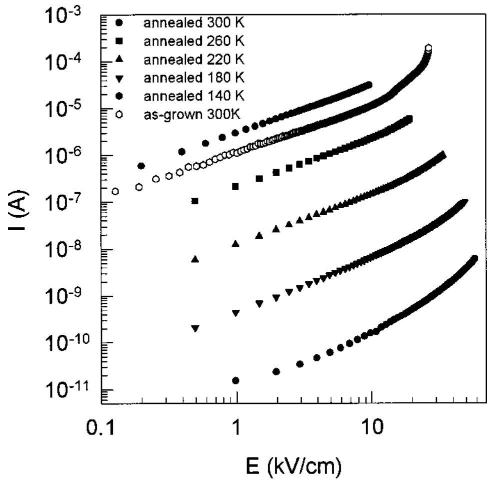

FIG. 3. $I-E$ curves of an Fe-doped SI InP before (open symbols) and after (closed symbols) annealing. This sample comes from a different source from that in Fig. 2 and is annealed at 700 °C for 12 h.

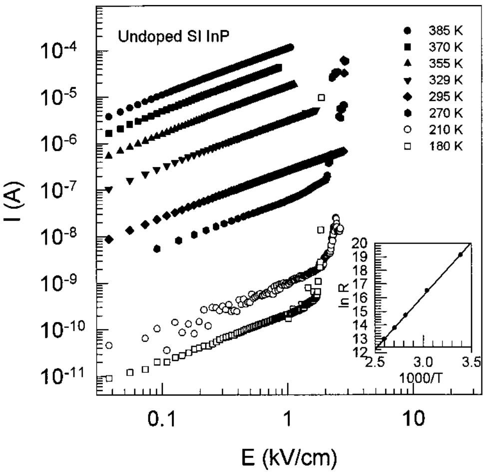

FIG. 4. $I-E$ curves of an annealed undoped SI InP sample at different temperatures. This sample is obtained by annealing undoped InP at 900 °C for 80 h. The inset is the plot of $\ln R$ vs $1/kT$ over the temperature range 300–430 K.

related with the trap-filling process even at low temperature. This can be quantified by the decreasing of θ of the annealed sample compared with that of the as-grown sample. The value of θ, taking into account the different V_{Ω} and sample thickness, is about 84% of that of the as-grown sample. This means that the concentration of Fe^{2+} in the annealed sample increases by ~20%, n being nearly the same as that for as-grown and annealed SI InP. Thus, the concentration of Fe^{2+} is apparently higher than that of the sample before annealing. It is also found for this Fe-doped InP that breakdown happens easily and causes a catastrophic failure.

Figure 3 gives the $I-E-T$ results of a Fe-doped InP sample before and after annealing. This sample is obtained from a different source to the one discussed above and having results shown in Fig. 2. The change of $I-E$ characteristics of Fe-doped InP after annealing is obvious and the situation is nearly the same as those in Fig. 2. Thus, we believe that the effect of annealing on the empty trap concentration is quite general, and does not result from any specific sample property.

Figures 4 and 5 show the $I-E-T$ curves of annealed undoped and Fe-doped SI InP, whose annealing times are much longer. Compared with the above-mentioned three samples, the $I-E$ curves are linear, indicating that there are no trap-filling processes even though breakdown begins. To exclude the heating effect at room temperature, the sample is also measured at lower temperatures down to 180 K. Figure 6 shows the breakdown voltage against temperature for the undoped SI InP sample. The breakdown voltage almost decreases linearly with decreasing temperature. When the sample temperature decreases, the breakdown voltage also decreases. This characteristic is of avalanche breakdown in which impact ionization dominates.[18] Again, it is found that breakdown always damages the sample.

Resistance R of the samples is obtained from $I-E$ measurements in 300–430 K. The plots of $\ln R$ vs $1/kT$ are straight lines with a slope around 0.6 eV (insets in Figs. 4 and 5). This indicates that the relation $R \propto \exp(E_a/kT)$ is valid for all these samples. The activation energy of 0.6 eV is in agreement with the ionization energy of Fe in InP.[19,20]

IV. DISCUSSION

In as-grown Fe-doped SI InP, the donors N_D and acceptors N_A are mainly residual shallow donors (e.g., Si, S) and acceptor impurities (e.g., Zn, Cd). It has been long understood that the deep Fe acceptor (Fe^{2+}) compensating the net shallow donor concentration ($N_D - N_A$) causes the SI property of Fe-doped InP.[19,21] Thus, in general the concentration of Fe^{2+} equals the net shallow donor concentration. Introduction of a new shallow donor may thus be seen as introducing electrons, which then trap onto the neutral Fe^{3+}, thus increasing the concentration of negative Fe^{2+} centers. It has been found that intrinsic donor defects are formed when Fe-doped InP is annealed at high temperature.[11–14] Our recent work has confirmed the formation of donor defects.[15] Indeed, the resistivity of annealed SI InP is found to decrease due to

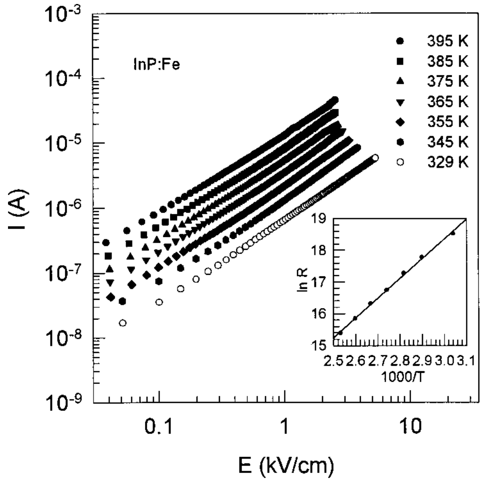

FIG. 5. $I-E$ curves of an annealed Fe-doped SI InP at different temperatures. The sample is annealed at 900 °C for 50 h. The inset is the plot of $\ln R$ vs $1/kT$ over the temperature range 300–430 K.

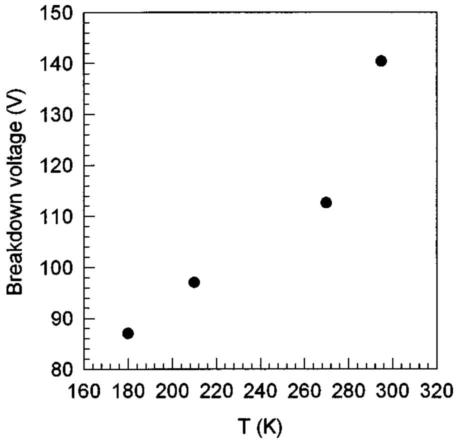

FIG. 6. Breakdown voltage against temperature for annealed undoped SI InP.

the formation of such defects.[11,13,14] As expected, the resistivity change also depends on the concentration of neutral Fe^{3+} in the as-grown Fe-doped InP.[11] Direct measurement of the Fe^{2+} concentration in as-grown and annealed Fe-doped InP indeed confirms this speculation.[13]

As discussed above, the annealing of Fe-doped InP results in the formation of donor defects, causing the concentration of Fe^{2+} to increase. This fact on its own gives sufficient explanation of the results of $I-E$ measurements reported in this work, since the TF process is dependent on the availability of empty Fe^{3+} traps. It is understood that the TF process (kink in the $I-E$ characteristic) becomes less obvious or even disappears in annealed Fe-doped InP as a direct result of a decreasing of Fe^{3+} trap concentration. The increase of the concentration of Fe^{2+} in annealed InP deduced from the $I-E$ data is quantitative proof of this process.

For the long-time annealed samples (Figs. 4 and 5), the concentration of thermally induced donor defects can be very high. This causes the ionization of most of the Fe^{3+} acceptor and mixed conduction appears in the material (see Table I). Here, the annealed undoped SI InP (Fig. 4) is a special case. The compensation in this SI InP is believed to be caused by a low concentration contamination or residual of the Fe compensating net donor.[22,23] The contribution of deep intrinsic defects detected in this material is also important.[24,25] In any case, the compensation in annealed undoped SI InP must be very light compared to the as-grown Fe-doped SI InP. It has indeed been found that the Fe was all in the Fe^{2+} state since Fe^{3+} cannot be detected in annealed undoped SI InP.[26]

The $I-E$ curves of long-time annealed InP are linear, indicating that there is no TF process. This implies that there is a negligible concentration of empty deep traps in the material. In other words, nearly all the Fe acceptors are occupied by electrons. The phenomenon also agrees well with the Hall-effect measurements of the long-time annealed sample F-SI-02 (see Table I), which indicates that it is in a state of mixed conduction. In this annealed mixed conduction state of Fe-doped InP, it is reasonable to think that the concentrations of acceptors and donors are close to each other. Thus, most Fe must be in the Fe^{2+} state. For annealed undoped SI InP, this result agrees very well with the fact that no Fe^{3+} can be found in the material.[26]

The breakdown field of SI InP has been found to depend on the Fe concentration in the material.[8] The higher the Fe concentration, the higher the breakdown field.[8] A recent work from Corvini and Bowers[10] has shown that avalanche breakdown occurs mainly from impact ionization for a thicker SI InP sample with large trap densities. The breakdown of our annealed SI InP indeed exhibits an impact ionization characteristic, i.e., a breakdown field that decreases with decreasing temperature. It has been shown that the current breakdown of SI InP occurs at a critical electric field E_C that is given by[8]

$$\frac{\chi(E_C)}{C_n(E_C)}=\frac{p_t}{n_t}, \tag{5}$$

where $\chi(E_C)$ and $C_n(E_C)$ are the impact ionization coefficient and the electron capture coefficient, respectively. The impact ionization coefficient can be expressed as[10]

$$\chi(E)=\chi_0 \exp(-E_0/E). \tag{6}$$

From Eqs. (5) and (6), it is clear that a low ratio of p_t/n_t will lead to a lower breakdown electric field. Thus, the decrease of the breakdown field in annealed SI InP implies a decrease of the ratio p_t/n_t. For Fe-doped InP, this corresponds to a decrease of Fe^{3+} and a simultaneous increase of Fe^{2+}. This analysis is again consistent with the result that donor defects have been formed in the annealing process. The two phenomena, the low breakdown field and the disappearance of the TF process, in long-time annealed Fe-doped and undoped SI InP can thus be ascribed to the same underlying cause.

V. SUMMARY

The $I-E$ characteristics of annealed SI InP show obvious changes compared to those of as-grown Fe-doped InP. The regime of trap filling becomes obscure when the annealing time of the sample increases. The $I-E$ curves of annealed undoped and long-time annealed Fe-doped SI InP exhibit close to Ohmic behavior. The breakdown fields of annealed SI InP, including annealed undoped SI InP, are much lower than those of as-grown Fe-doped InP. These changes are ascribed to the formation of donor defects in the annealing process which cause more Fe acceptors to ionize and there to be less empty deep traps in the material.

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