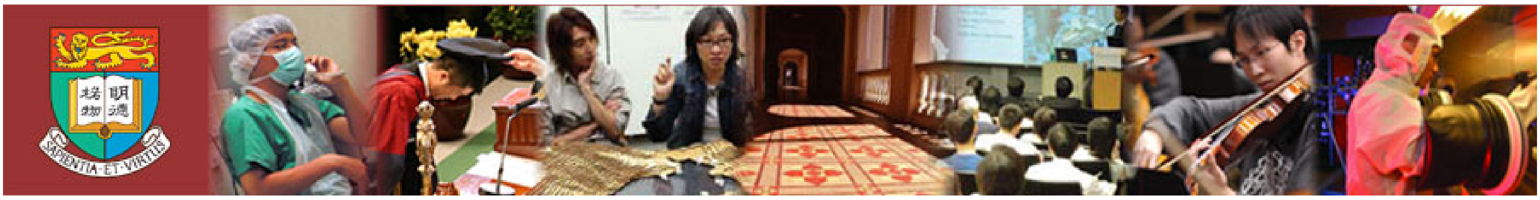

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Effects of annealing on the electrical properties of Fe-doped InP

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Fe-doped liquid encapsulated Czochralski InP has been annealed between 500 and 900 °C for different durations. The electrical property of annealed InP has been studied by temperature-dependent Hall measurement. Defects in annealed Fe-doped InP have been detected by room-temperature transient photocurrent spectroscopy. Upon annealing, the change of electrical property in this material is indicative of the formation of a high concentration of defects. The formation process of these thermally induced defects is discussed. [S0021-8979(99)02914-X]

I. INTRODUCTION

Fe-doped semi-insulating (SI) InP has been used as substrate material for electronic devices for a long time.[1,2] High thermal stability of SI InP is necessary during the epitaxy growth process of a device structure. However, the resistivity of Fe-doped SI liquid encapsulated Czochralski (LEC) InP was found to decrease rapidly with increasing annealing temperature.[3–6] Thermal donor defects with a concentration of $10^{16}\,cm^{-3}$ were also found in rapidly annealed SI InP.[7,8] Different annealing temperatures and durations have been found to give rise to different defects.[4] These results indicate that thermally induced defects are closely related to the change of resistivity of annealed SI InP.

Recently, it has been reported that the resistivity and mobility of Fe-doped SI InP can be increased by annealing for a longer time.[9] This result is different from previous reports and indicates that the donor concentration is increased after annealing. The concentration of Fe has also been found to influence the electrical property of as-grown and annealed SI InP.[6] A possible reason for the apparent discrepancy of these phenomena is that defects in these samples are different in as-grown and annealed state. Thus, the thermal stability of Fe-doped SI InP also depends on growth conditions in some way. In view of these experimental results, it is necessary to study the formation process of any defects by controlling the annealing conditions. The relationship of defect formation and the change of the electrical properties of the material certainly requires further investigation.

In this article, we investigate the electrical properties of Fe-doped InP before and after annealing. The annealing conditions are controlled by changing either the temperature or duration. The change of electrical parameters is found to correlate with the change of defect concentration at a different annealing stage. The defects and the change of their concentrations in Fe-doped SI InP have been detected by room-temperature photocurrent spectroscopy. The origin of defect formation and formation process are discussed.

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II. EXPERIMENTAL

All samples used are Fe-doped high-resistivity ($\rho \sim 10^4\,\Omega\,cm$) or SI($\rho \geqslant 10^6\,\Omega\,cm$) InP wafers grown by the LEC method in one of our laboratories. The annealing of samples was carried out in a sealed quartz tube with phosphorus ambient to prevent the wafer from disassociating. The electrical parameters of Fe-doped InP were characterized by a Hall-effect measurement system using Van Der Pauw configuration samples. Temperature-dependent Hall (TDH) measurements were carried out on high-resistivity samples in the temperature range of 300–430 K. Excitation light in the photon energy range of 0.3–1.6 eV was used for the measurement of transient photocurrent spectroscopy at room temperature. The setup of this system has been described elsewhere.[10] This measurement is similar to the conventional photoconductivity method involving interalia, the phase lock-in amplification technique. Instead of observing a steady-state photocurrent, the transient photocurrent is recorded. It detects the change of current caused by photoexcitation of carriers from deep levels in the gap, respectively, to the band edge. Thus, the photoexcited transient current peak observed gives reasonably accurate position for the trap level in the gap. Furthermore, the concentration change of one trap can also be inferred by the change of its peak intensity. Infrared-absorption spectra were taken by a Bruck ISF 120 infrared-absorption spectrometer at 20 K.

III. RESULTS AND DISCUSSION

A. Electrical property of annealed Fe-doped SI InP

The annealing results of Fe-doped LEC InP are summarized in Table I. Generally, electrical properties such as resistivity and mobility can be increased by short-time annealing. High-resistivity material can be changed to semi-insulating by the annealing of 50 h. The annealing temperature for such change has to be below 700 °C. This phenomenon is in agreement with the results of Shimakura *et al.*[3] and Kalboussi *et al.*[4] The annealing results of our samples at 800 and 900 °C for 50 h are different from the

TABLE I. Annealing results of Fe-doped LEC InP.

Sample No.	Annealing temperature (°C)	Annealing time (h)	Before annealing			After annealing		
			n (cm^{-3})	μ (cm^2/vs)	ρ (Ω cm)	n (cm^{-3})	μ (cm^2/vs)	ρ(Ω cm)
H-01	700	50	6.53×10^9	237	4.03×10^6	4.78×10^{11}	40.3	3.24×10^5
H-02	700	50	3.68×10^{11}	182	9.34×10^4	3.04×10^8	736	2.79×10^7
H-03	600	50	1.37×10^9	51.8	8.76×10^6	6.64×10^8	611	1.54×10^7
H-04	500	0.5		2200	2.0×10^7	3.62×10^7	2250	7.68×10^7
	600	0.5				1.40×10^8	2350	6.41×10^7
	700	0.5				1.95×10^8	1700	1.88×10^7
	700	12				3.85×10^{10}	1990	8.15×10^4
	800	50				2.34×10^{11}	111	2.45×10^5
	900	50				1.60×10^{10}	8.8	4.40×10^7

recently reported result of Avella *et al.* which indicated that both the mobility and resisitivity of SI InP were increased.[9] The extremely low mobility of those annealed samples indicates mixed conduction in the material. From mixed conductivity analysis,[11] these samples change into *p* type after long time annealing at 800 and 900 °C.

B. Defects in as-grown and annealed SI InP

Figure 1 shows the result of Hall measurements of an annealed Fe-doped InP sample carried out at 300–430 K. It can be seen from the slope of the plot $\ln(nT^{-3/2})$ vs $(kT)^{-1}$ that there are two dominant traps at 0.64 and 0.43 eV. The 0.64 eV trap can be attributed to the Fe acceptor level according to the TDH and photoconductivity measurement results in Fe-doped SI material.[12,13] However, the 0.43 eV trap is most likely to be a thermally induced intrinsic defect with high a concentration because TDH generally gives one Fe related level energy before annealing.[13] This is in agreement with the results of Bardeleben *et al.*[7,8] in which two thermal donor defects with energy levels at 0.4 and 0.14 eV in annealed Fe-doped InP were detected. The 0.14 eV level can also be seen on the right side of the curve in Fig. 1. These defects could well be involved in the compensation of annealed SI InP.

In Fig. 2, transient photocurrent spectroscopy results of Fe-doped SI InP are given. As shown in Fig. 2(a), there are two peaks at 0.45 and 0.66 eV in all of our Fe-doped SI InP samples before annealing. It would seem reasonable to associate these peaks to the Fe acceptor because both are regularly detected in all our Fe-doped SI InP samples. The 0.66 eV level has been proved to be Fe^{2+}/Fe^{3+} acceptor level by absorption spectroscopy method.[12,14,15] It corresponds to the electron transition process $Fe^{2+}\rightarrow Fe^{3+}+e$. The 0.45 eV peak has also been detected by optical absorption[14] and photoconductivity in Fe-doped SI InP.[16] This absorption peak has been assigned to electron-lattice interaction in the Fe^{2+} $^5T_2$ excited state by Look.[16,17] For our measurement, the appearance of two peaks can be the characteristic of Fe-doped SI InP since both of them can be detected regularly. Thus, the appearance of these two peaks is an indication of the presence of high concentration Fe in the sample.

As shown in Fig. 2, peaks with energy at 0.49, 0.56, 0.59, and 0.81 eV can also be detected in some as-grown SI InP samples. These peaks can be attributed to be defects formed in the growth process. Defects in as-grown Fe-doped SI InP have been reported by Fang *et al.* through the use of thermally stimulated current spectroscopy.[18] Those defects are generally considered to be native defects or complexes with impurities. It indicates that there are some defects involved in the compensation in as-grown SI InP. Defects in as-grown Fe-doped InP must be related with growth conditions because not every sample has this result.

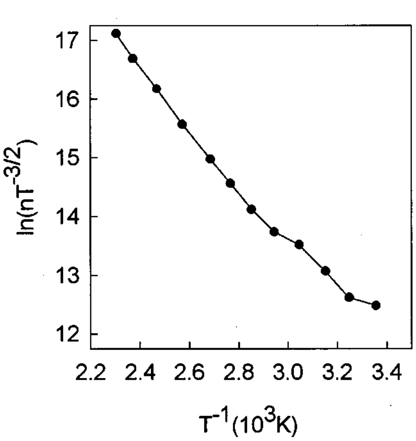

FIG. 1. Temperature-dependent carrier concentration of annealed Fe-doped InP.

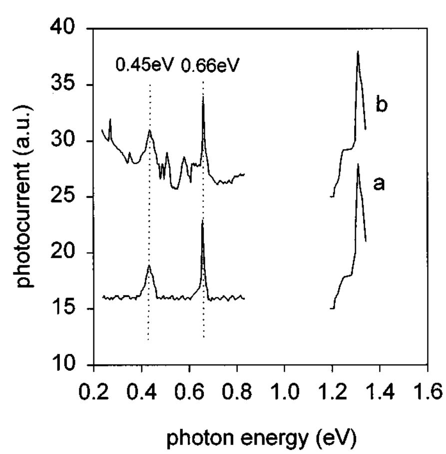

FIG. 2. Typical room-temperature transient photocurrent spectra of Fe-doped SI InP. The peaks at 0.45 and 0.66 eV are related to the Fe acceptor. Some structures attributed to native defects can be seen in spectrum (b).

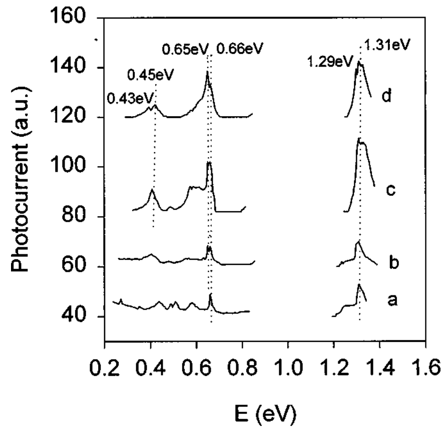

FIG. 3. Room-temperature transient photocurrent spectra of Fe-doped SI InP annealed at different temperatures: (a) as-grown; (b) 600 °C, 30 min; (c) 700 °C, 30 min; (d) 700 °C, 12 h.

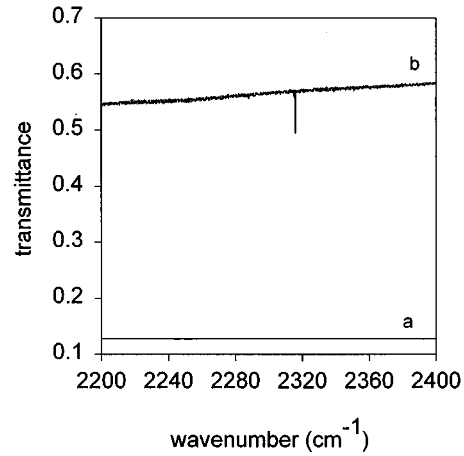

FIG. 4. Infrared transmission spectra of Fe-doped SI InP taken at 20 K. The $V_{In}H_4$ absorption peak can be seen before annealing (b) and disappears after annealing (a).

To detect defects in annealed Fe-doped InP, a room-temperature transient photocurrent spectroscopy investigation has been carried out on Fe-doped InP annealed at different temperatures. Results of this measurement are shown in Fig. 3. As shown in Fig. 3, new peaks begin to appear when the sample is annealed at 600 °C for 30 min. This situation is nearly the same for samples annealed at 700 °C, for 30 min. A new peak at 0.65 eV can be seen in the two spectra. After this sample is annealed at 700 °C for 12 h, the 0.65 eV peak is much stronger than that of the Fe-related 0.66 eV peak. In addition, strong 0.43 peak and 1.29 eV peaks are formed and can be distinguished clearly in this case. Moreover, the resisitivity of this annealed sample decreased to $8.15\times 10^4\ \Omega$ cm. These phenomena indicate that thermally induced defects change the electrical property of Fe-SI InP significantly when the annealing temperature is higher than 700 °C.

As the 0.65 eV peak only appears after annealing, and its intensity relative to the Fe related 0.66 eV peak also increases after the sample is annealed for a longer time, it cannot be attributed to the Fe acceptor level related electron capture and excitation process. Furthermore, the photoionization cross section of electron is larger than that for hole in the energy range of 0.6–0.8 eV.[19] Thus, electron excitation should dominate in this photoexcitation region. Another interesting phenomenon is that the 1.29 eV peak appears along with the existence of a strong 0.65 eV for 700 °C, 12 h annealed sample. This 1.29 eV peak can only be attributed to the electron transition from the 0.65 eV mid-gap level to one of the conduction-band minima *X*. The transition from the Fe acceptor level to the *X* point seems to superimpose with the band-to-band transition as shown in the spectroscopy of as-grown Fe-doped InP. Based upon this analysis, the 0.65 eV peak should be related to a thermally induced mid-gap defect.

The spectra in Fig. 3 also show that the formation of the 0.43 eV defect level depends on annealing temperature and time. It can be seen from Fig. 3 that for only 12 h, the 700 °C annealed sample at this level be clearly detected by the spectroscopy. This fact indicates that this level is preferentially formed for high temperature and long-time heat treatment processes. A similar thermal donor defect with high concentration has also been detected in annealed Fe-doped SI InP by electron paramagnetic resonance[7,8] In annealed undoped InP, a trap level at 0.4 eV has proved to be a dominant defect.[20,21] Thus, it seems that this trap is a common thermally induced defect in annealed InP.

C. Formation process of native defects

The formation process of these thermal defects has not been well understood so far. Recently, it is found that the hydrogen indium vacancy complex $V_{In}H_4$ is a common defect in as-grown LEC InP.[22,23] This defect decomposes and gives rise to the formation of other defects upon high-temperature annealing. The formation of phosphorus antisite related defect was also found to correlate with this decomposition during the annealing process.[24] The decomposition of $V_{In}H_4$ giving rise to the formation of various defects can generally be expressed as follows:[24]

$$4V_{In}H_4+6e\rightarrow V_{In}H_3+V_{In}H_2^{2-}+V_{In}H^{1-}+V_{In}^{3-}+10H^0\uparrow, \quad (1)$$

$$P+V_{In}^{3-}\rightarrow P_{In}^{2+}+V_P^{+}+6e. \quad (2)$$

These two equations, may indeed shed some light into the origin of the defects of InP formed in our annealing process. First, the existence of $V_{In}H_4$ in SI InP before annealing and its disappearance after annealing can be evidenced by infrared-absorption spectroscopy shown in Fig. 4. From this spectroscopy data, the concentration of $V_{In}H_4$ in these samples can also be deduced by the use of the calibration data of the Zn–H complex. This is found to be in the range of 10^{15}–$10^{16}\ cm^{-3}$ in these Fe-doped SI InP.[25] Then from Eqs. (1) and (2), both acceptor and donor defects can be formed when the sample is annealed at high temperature.

As high concentration of Fe exists in these samples, there is no large change of resisitivity for short-time annealed SI InP. However, our recent annealing results of undoped *n*-type InP indicate one interesting phenomenon. When the sample is annealed at 700 °C for a short time (1–10 h), it changes into *p*-type semiconducting. Further annealing for a longer time(20–80 h) gradually changes conduction into *n* type again. The resisitivity also increases up to $10^4\ \Omega$ cm with increasing annealing time. We think that this conductivity conversion is related to the decomposition of $V_{In}H_4$ and the subsequent formation of donor defects. For short-time annealing, acceptor defects such V_{In}, $V_{In}H_2$, and $V_{In}H$ are easily produced and cause the sample to change conduction type. Then for long-time annealing, native donor defects associated with antisite and vacancy are formed, as shown in Eq. (2). Since the $V_{In}H_4$ concentration in Fe-doped InP is usually high, it is believed that this process also happens in annealed Fe-doped InP. From the results shown in Table I and Fig. 3, the resisitivity of the 700 °C, 12 h annealed Fe-doped SI sample indeed decreases to $10^4\ \Omega$ cm because of the formation of a 0.43 eV native donor. This result is in full agreement with the work of Bardeleben *et al.*[7,8] Thus, the electrical deterioration of annealed Fe-doped SI InP can be largely ascribed to the formation of a high concentration of native donors. It is hardly surprising that the concentration of the thermally induced donors is of the order of $10^{16}\ cm^{-3}$ (Refs. 7 and 8) and because the concentration of $V_{In}H_4$ is around this range.

The fact that the electrical property of annealed InP can be changed in a very short annealing time further supports the above supposition. Since the bonding of the hydrogen complex is weak, the hydrogen atoms will diffuse quickly in the semiconductor and easily escape from the material.[26] Upon high-temperature annealing, the bond of the hydrogen complex will be broken and leave either an indium vacancy or another complex as shown in Eq. (1). This phenomenon also indicates the influence of hydrogen on LEC InP materials which was expected previously.[27,28]

IV. CONCLUSIONS

Fe-doped SI InP has been annealed in different conditions. The electrical property of this material can be changed significantly in most cases. The change, which arises from the formation of a high concentration of thermally induced native donors, tends to destroy the electrical property of material. The formation of thermally induced native donor defects in SI InP is largely originated from the thermal decomposition of the hydrogen indium vacancy complex.

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