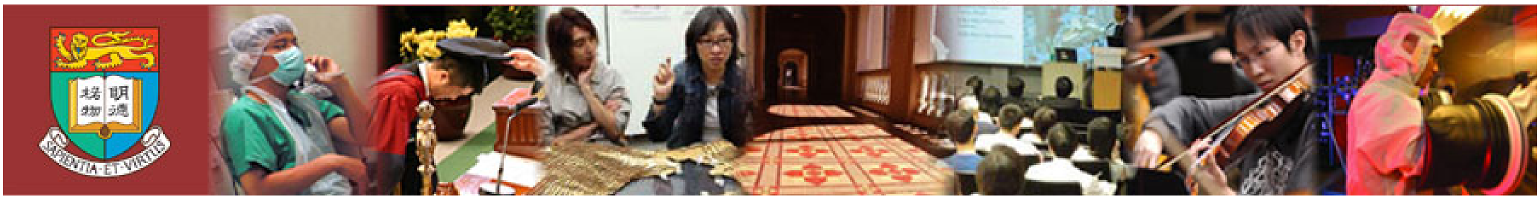

Title	**Formation of P In defect in annealed liquid-encapsulated Czochralski InP**
Author(s)	**Zhao, YW; Xu, XL; Gong, M; Fung, S; Beling, CD; Chen, XD; Sun, NF; Sun, TN; Liu, SL; Yang, GY; Guo, XB; Sun, YZ; Wang, L; Zheng, QY; Zhou, ZH; Chen, J**
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Formation of P_{In} defect in annealed liquid-encapsulated Czochralski InP

Y. W. Zhao, X. L. Xu, M. Gong, S. Fung, and C. D. Beling[a)]
Department of Physics, The University of Hong Kong, Hong Kong, People's Republic of China

X. D. Chen, N. F. Sun, T. N. Sun, S. L. Liu, and G. Y. Yang
Hebei Semiconductor Research Institute, P.O. Box 179, Shijiazhuang, Hebei, People's Republic of China

X. B. Guo, Y. Z. Sun, L. Wang, Q. Y. Zheng, Z. H. Zhou, and J. Chen
Tianjin Semiconductor Institute, P.O. Box 55, Tianjin, People's Republic of China

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Fourier transform infrared spectroscopy measurements have been carried out on liquid-encapsulated Czochralski-grown undoped InP wafers, which reproducibly become semi-insulating upon annealing in an ambient of phosphorus at 800–900 °C. The measurements reveal a high concentration of hydrogen complexes in the form $V_{\mathrm{In}}\mathrm{H}_4$ existing in the material before annealing in agreement with recent experimental studies. It is argued that the dominant and essential process producing the semi-insulating behavior is the compensation produced by an EL_2-like deep donor phosphorus antisite defect, which is formed by the dissociation of the hydrogen complexes during the process of annealing. The deep donor compensates acceptors, the majority of which are shallow residual acceptor impurities and deep hydrogen associated V_{In} and isolated V_{In} levels, produced at the first stage of the dissociation of the $V_{\mathrm{In}}\mathrm{H}_4$ complex. The high concentration of indium vacancies produced by the dissociation are the precursor of the EL_2-like phosphorus antisite. These results show the importance of hydrogen on the electrical properties of InP and indicate that this largely results from low formation energy of the complex $V_{\mathrm{In}}\mathrm{H}_4$ in comparison with that of an isolated V_{In}. © *1998 American Institute of Physics.* [S0003-6951(98)01117-6]

Undoped *n*-type high-purity liquid-encapsulated Czochralski (LEC) InP has been reported to become semi-insulating (SI) if it is annealed at 800–900 °C in vacuum or phosphorus ambient for about 90 h.[1–5] The reason for this transform in conductivity has been studied extensively in recent years.[2–5] In particular, it has been demonstrated by electrical measurements that the possible phosphorus in- and indium out-diffusion, which can lead to the formation of vacancy defects in a thin surface layer, cannot explain the bulk SI properties.[1,2] Moreover, the concentration of transition metal contaminants after annealing is always measured to be too low to compensate residual impurities and give the observed high resistivity of $10^7\ \Omega$ cm, so the metal contamination effects may also be excluded even though a deep-level activation energy close to Fe in InP of 0.64 eV has been found from electrical measurements.[1–5] Another result is that only LEC-grown InP can be annealed into a semi-insulating form but InP grown under the same stoichiometry by the horizontal gradient freeze method does not have this property.[2] These phenomena give a clear indication that both intrinsic defects and residual deep-level metals are not directly responsible for the compensation mechanism of thermally induced undoped SI InP. The compensation mechanism has, thus, remained unclear.

In this letter, Fourier transform infrared (FTIR) transmission spectroscopy results are described, which indicate a very high concentration of hydrogen complex $V_{\mathrm{In}}\mathrm{H}_4$ existing in all the undoped LEC InP wafers grown under different conditions (P rich, In rich, and stoichiometric) in one of our laboratories. Moreover, in a manner similar to that seen by other works,[2,5] all our SI samples possess shallow donor concentrations higher than that of the residual deep-level impurities such as Fe. The concentration of residual shallow acceptor impurities, which come from homemade indium,[6] is much higher than that of shallow donor impurities in our samples. These data, along with the high measured values of electron mobility in annealed InP lead us to conclude that the most likely reason for the annealed SI behavior of InP is that there is a heavy compensation of residual acceptor impurities and thermally induced acceptors by deep donor phosphorus antisite defects, which have their origin in the dissociation of hydrogen complex $V_{\mathrm{In}}\mathrm{H}_4$.

The samples studied in this work were *n*-type undoped 3 mm LEC InP wafers of carrier-concentration $2–5 \times 10^{15}\ \mathrm{cm}^{-3}$ that were produced using the phosphorus *in situ* injection method.[6] The cleaned undoped InP wafer samples, along with some red phosphorus to give a phosphorus gas pressure of more than 60 mbar at 950 °C, were placed into a quartz tube and then pumped to a vacuum of 10^{-2} mm Hg and sealed. These samples were annealed at 950 °C for 90–100 h and then cooled slowly to room temperature. The resistivity and carrier mobility of the samples were measured by a Bio-Rad Hall measurement system. The FTIR transmission measurements were carried out in vacuum using a NIC-170 spectrometer on the samples before and after annealing. The impurity content in the sample is measured by spark source mass spectrometry. Annealed SI samples were characterized using photocurrent spectroscopy.

The FTIR transmission spectrum is shown in Fig. 1. There is a strong absorption peak at $2315\ \mathrm{cm}^{-1}$, which has been shown to be due to the local vibration mode (LVM) of

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[a)] Electronic mail: cdbeling@hkucc.hku.hk

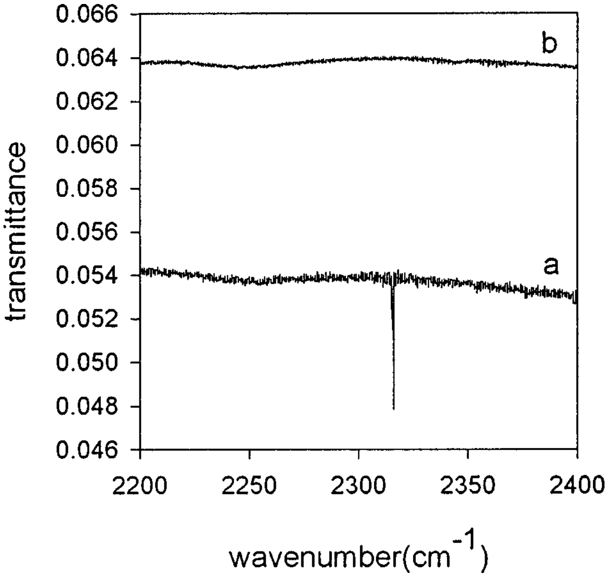

FIG. 1. Transmission spectrum of undoped LEC InP at 17 K. (a) before annealing; and (b) after annealing. The absorption peak at 2315 cm^{-1} is the LVM of the hydrogen indium complex $V_{\mathrm{In}}\mathrm{H}_4$.

hydrogen indium vacancy complex $V_{\mathrm{In}}\mathrm{H}_4$.[7,8] This absorption peak can also be seen clearly at room temperature, which implies a high concentration of $V_{\mathrm{In}}\mathrm{H}_4$ in the sample for this kind of defect. As shown in Fig. 1, the 2315 cm^{-1} peak disappears completely after annealing. Due to the lack of calibration data for this complex, its concentration can only be estimated by using the calibration value 2.0×10^{16} cm^{-3} per unit integrated absorption of the zinc hydrogen complex in InP.[8] This method has been used by Clerjaud *et al.*[9] for the study of the unintentional hydrogen concentration in LEC InP and shown to give a lower limit value. The integrated absorption at 2315 cm^{-1} in Fig. 1 is about 0.6 cm^{-2}, and so a concentration of at least 1.2×10^{16} cm^{-3} of $V_{\mathrm{In}}\mathrm{H}_4$ can be deduced. This value is in reasonable agreement with the result of Clerjaud and co-workers[9,10] in which the total hydrogen concentration in as-grown LEC InP was found to be 10^{16} cm^{-3} (and possibly, 5×10^{16} cm^{-3} or more). Moreover, the absorption of $V_{\mathrm{In}}\mathrm{H}_4$ is much more intensive than that of other complexes,[8,9] indicating a significantly higher $V_{\mathrm{In}}\mathrm{H}_4$ concentration.

In Table I some reported annealing results of InP are listed and compared with the results of this work. All our undoped InP samples can be annealed to be semi-insulating. Table I also reveals an important fact, namely, that for all the samples not only the concentration of Fe is far below that of the residual shallow donors (mainly Si and S), but the concentration of residual shallow acceptor impurities (mainly Mg, Zn, Ag, and Ca) is much higher than that of residual donor impurities in our samples. This leads us to conclude that the Fe impurity cannot be responsible for the semi-insulating property and that some other deep donor level must be responsible for the compensation mechanism.

The disappearance of the LVM spectral line of $V_{\mathrm{In}}\mathrm{H}_4$ implies that this hydrogen vacancy complex has decomposed upon annealing. This complex has proved to be a shallow donor.[7] The dissociation of $V_{\mathrm{In}}\mathrm{H}_4$ is, thus, in agreement with the experimental fact that in InP that does not become semi-insulating, some shallow intrinsic donor is being annihilated on annealing at level $\sim5\times10^{15}$ cm^{-3}.[2,4] The $V_{\mathrm{In}}\mathrm{H}_4$ is expected to dissociate into $V_{\mathrm{In}}\mathrm{H}_3$, $V_{\mathrm{In}}\mathrm{H}_2$, $V_{\mathrm{In}}\mathrm{H}$, and V_{In} during the annealing and then through the recombination of V_{In} with mobile phosphorus to form the antisite defect P_{In} according to the following reactions:

$$4V_{\mathrm{In}}{\mathrm{H}_4}^{+}+10e\rightarrow V_{\mathrm{In}}\mathrm{H}_3+V_{\mathrm{In}}{\mathrm{H}_2}^{-}+V_{\mathrm{In}}\mathrm{H}^{2-}+{V_{\mathrm{In}}}^{3-}+10H^0\uparrow, \tag{1}$$

$${V_{\mathrm{In}}}^{3-}+\mathrm{P}_i+\mathrm{P}_{\mathrm{p}}+6h\rightarrow {\mathrm{P}_{\mathrm{In}}}^{2+}+{V_{\mathrm{p}}}^{+}. \tag{2}$$

These reactions, while not attempting a detailed breakdown of the reaction scheme, show the general decomposition of the $V_{\mathrm{In}}\mathrm{H}_4$ complex with direction as shown, and it is noted that the deficit of hydrogen and ${V_{\mathrm{In}}}^{3-}$ in Eq. (2) leads to stronger driving of this reaction. $V_{\mathrm{In}}\mathrm{H}_3$ has been shown to be electrically inactive while the partially hydrogenated vacancies, $V_{\mathrm{In}}\mathrm{H}_2$ and $V_{\mathrm{In}}\mathrm{H}$ act as acceptors, forming $V_{\mathrm{In}}{\mathrm{H}_2}^{-}$ and $V_{\mathrm{In}}\mathrm{H}^{2-}$, respectively, with acceptor levels in the lower gap region.[8] The indium vacancy ${V_{\mathrm{In}}}^{3-}$ also forms a deep acceptor in the gap. Both ${\mathrm{P}_{\mathrm{In}}}^{2+}$ and ${V_{\mathrm{p}}}^{+}$ are expected to form donor levels with energy levels at about 0.7 and 0.44 eV, respectively, as predicted by theoretical calculation[11] and as confirmed by experimental measurement.[12] It is the former deep level, namely, the phosphorus antisite P_{In} which we believe is largely responsible for the compensation of the InP, and the semi-insulating properties that result. This defect is the exact analogue of the EL2, arsenic antisite defect that is responsible for the compensation found in semi-insulating GaAs.

To clarify the existance of an annealing induced deep donor in our undoped InP, we carried out room-temperature photocurrent spectroscopy on an annealed SI sample. The results are shown in Fig. 2 compared to those in a control Fe-doped SI sample annealed at different temperatures. A

TABLE I. Electrical parameters and impurity content of undoped InP after annealing. A, Ref. 3, B, Ref. 2, C, Ref. 4, D, Ref. 5, and E, this work.

Source No.	Resistivity (Ω cm)	Mobility (cm^2/V s)	Impurity detected ($\times10^{14}$ cm^{-3})							Activation energy (eV)
			Fe	S	Si	Mg	Zn	Ag	Ca	
A	1.3×10^7	4340	N.D.							0.64
B	1.0×10^7	>4000	3.3[a]	6.3	57		0.88			0.67
C	4.4×10^7	3940								0.64
D	5.6×10^6	1350	$<10^{14}$ cm^{-3}					~480[b]		0.64
E	$2\text{–}3\times10^7$	$\geqslant2760$	25	24	12	80	62	18	34	0.66

[a] N.D., not detected. Only Fe^{2+} can be detected.

[b] Estimated from the compensation ratio.

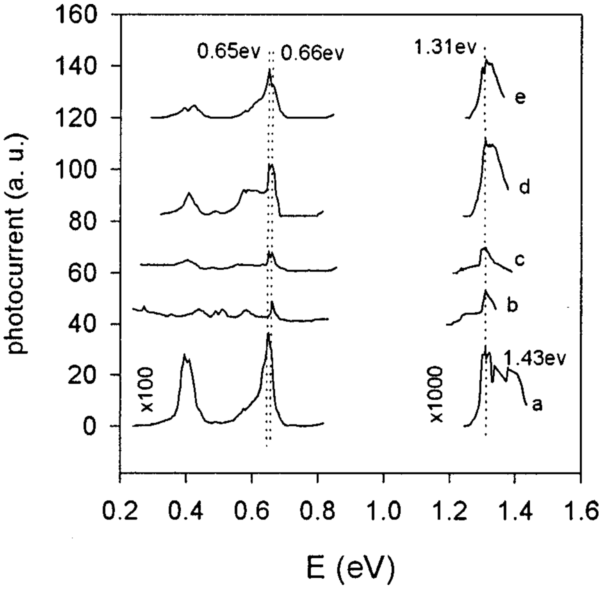

FIG. 2. Room-temperature photocurrent spectra of undoped SI InP (a) and Fe-doped SI LEC InP annealed at different conditions: (b) before annealing; (c) 600 °C, 30 min; (d) 700 °C, 30 min; and (e) 700 °C, 12 h. The 0.65, 1.31, and 1.43 eV peaks correspond to transitions from a midgap donor level to conduction minima Γ_6^c, L_6^c (band to band), and X_6^c, respectively.

strong peak at 0.65 eV and weak peak at 0.66 eV are found in the undoped SI InP. In the Fe-doped SI InP, which has a very high concentration of $V_{\text{In}}\text{H}_4$ (estimated to be $2-3 \times 10^{16}$ cm^{-3}), only the Fe-related 0.66 eV peak can be detected before annealing, whereas two peaks at 0.65 and 0.66 eV are found for 30 min annealing at temperatures of 600 and 700 °C. Further annealing of the Fe-doped sample at 700 °C for 12 h results in increasing of the intensity of the 0.65 eV peak relative to that of the 0.66 eV peak and a corresponding drop in resistivity from 7.68×10^7 to 8.15×10^4 Ω cm. It can be concluded from these results that the 0.65 eV level is to be associated with P_{In}. The resistivity decrease of the annealed Fe-doped InP is caused primarily by the increasing of the intrinsic shallow donor concentration.[13] FTIR absorption steps around 0.7 and 1.43 eV are found, which correspond to the transitions from a midgap level to two of the conduction minima Γ_6^c and X_6^c, respectively.

Further evidence that Fe cannot be the cause of SI behavior comes from the fact that residual Fe in undoped SI InP has been found to be all in the Fe^{2+} state since Fe^{3+} cannot be detected by electron spin resonance and caloremetric absorption spectroscopy.[14] This situation is similar to that found in GaAs when both EL_2 and Cr are present and only Cr^{2+} can be detected, which is caused by the compensation of EL_2.[15]

The process that we have described above naturally gives rise to a set of energy levels. Such levels have also been measured in photocapacitance studies[16] of annealed undoped InP, which is still low enough in resistance for such measurements and photoinduce current transient spectroscopy after the heat treatment of undoped LEC InP.[17] These levels, which presented previous workers with difficulty in interpretation, are now attributed to the hydrogen associated V_{In} centers and intrinsic defects with levels in reasonable agreement with those predicted by theoretical calculation.[7,11]

The phosphorus antisite defect was detected with a high concentration only in annealed high-resistivity undoped LEC InP by Kennedy *et al.* through the use of optical detected magnetic resonance in 1986.[18] The P_{In} defect has also been reported in low-temperature molecular beam epitaxy grown InP. In this material the defect appears to give rise to a donor level in the conduction band.[19–21] However, the high concentration of defects such as phosphorus precipitates and their interaction in this kind of material is not yet clear and its conduction properties and defect levels cannot be definitely correlated with P_{In}.

In summary, a concentration of 1.2×10^{16} cm^{-3} of a hydrogen complex of the form $V_{\text{In}}\text{H}_4$ has been found in our LEC-grown bulk InP crystals, which can be annealed to be semi-insulating easily and reproducibly. These experimental results have led us to conclude that the dissociation of the hydrogen complex $V_{\text{In}}\text{H}_4$ leads to the production of a high concentration of deep donor antisite defect P_{In}, which is the center that compensates the InP giving rise to the observed semi-insulating property.

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