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Compensation ratio-dependent concentration of a $V_{In}H_4$ complex in *n*-type liquid encapsulated Czochralski InP

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The concentration of hydrogen–indium vacancy complex $V_{In}H_4$ in liquid encapsulated Czochralski undoped and Fe-doped *n*-type InP has been studied by low-temperature infrared absorption spectroscopy. The $V_{In}H_4$ complex is found to be a dominant intrinsic shallow donor defect with concentrations up to ~10^{16} cm^{-3} in as-grown liquid encapsulated Czochralski InP. The concentration of the $V_{In}H_4$ complex is found to increase with the compensation ratio in good agreement with the proposed defect formation model of Walukiewicz [W. Walukiewicz, Phys. Rev. B **37**, 4760 (1998); Appl. Phys. Lett. **54**, 2094 (1989)], which predicts a Fermi-level-dependent concentration of amphoteric defects. © *1998 American Institute of Physics.* [S0003-6951(98)04435-0]

Hydrogen in liquid encapsulated Czochralski (LEC) InP is an unintentional contaminant which mainly comes from the wet boron oxide used as the encapsulant in the growth process.[1–7] The total hydrogen concentration in as-grown LEC InP has been shown to be ~10^{16} cm^{-3}.[5] Generally, hydrogen in InP can form a complex with an indium vacancy or an acceptor impurity giving rise to passivation effects.[6] Indeed, the level of hydrogen in LEC InP suggests other significant influences of hydrogen complexes on the properties of InP materials.[4] Since the influence of hydrogen complexes has only recently been recognized there is much work still to be done in understanding their behavior on the microscopic level.

Fourier-transform infrared absorption (FTIR) spectroscopy, which evidences hydrogen-related local vibration modes (LVMs), is one of the main techniques allowing the study of hydrogen in InP. In particular, the technique has revealed a fully hydrogenated indium vacancy complex $V_{In}H_4$ in as-grown undoped and Fe-doped LEC InP with a LVM of around 2316 cm^{-1} at low temperature.[7] A recent theoretical calculation has confirmed this LVM signature to be that of $V_{In}H_4$ and has shown the complex to be a shallow donor in as-grown LEC InP.[8] The latter property implies that the existence of this defect can significantly change the electrical properties of InP. Moreover, the weak bonding of $V_{In}H_4$ suggests that both undoped and Fe-doped LEC InP may be thermally unstable. Upon high-temperature annealing, $V_{In}H_4$ is thus expected to dissociate either completely leaving an isolated indium vacancy, or partially giving hydrogen-related defects.[8] Confirmation of such dissociation, which subsequently leaves the material in a semi-insulating form, has recently been given.[9] It is clear from these observations that in order to control the quality of LEC InP, it is necessary that the concentration of $V_{In}H_4$ and the factors controlling it be well characterized. In this letter, we report on an infrared absorption investigation of the $V_{In}H_4$ abundance in undoped and Fe-doped as-grown LEC InP. The results indicate that $V_{In}H_4$ is a common defect in LEC InP and that a positive correlation exists between its concentration and the compensation ratio.

The electron concentration and mobility for undoped LEC InP were measured by a commercial Bio-Rad HL5500 Hall-effect measurement instrument. The compensation ratio θ of the undoped InP samples was then obtained from the computation technique of Walukiewicz *et al.*[10] Electron concentration and mobility data taken at both 300 and 77 K were examined to given the most reliable compensation ratio result. The infrared measurements were performed at low temperature (20–30 K) with a Digilab 80 E-V vacuum Fourier-transform spectrometer equipped with a Ge:Cu detector. The integrated absorption intensity at 2316 cm^{-1} was obtained from the spectra and used as an indication of the concentration of $V_{In}H_4$.

Five undoped *n*-type InP samples with electron concentrations in the range of $2–12 \times 10^{15}$ cm^{-3} and compensation ratios varying from 0.2 to 0.8 were selected for the infrared absorption measurements. Two Fe-doped semi-insulating (SI) *n*-type InP wafers were also measured for the concentration of $V_{In}H_4$. All the samples were cut from the seed to the end portion of InP single-crystal ingots and were of 14 $\times 10$ mm^2 square dimensions and of 2.5 mm thickness with both side polished. All the samples used were grown under the same conditions (stoichiometry, boron oxide quality, etc.) using the *in situ* synthesis LEC technique in one of our laboratories.[11]

Infrared transmission spectra of four undoped and one
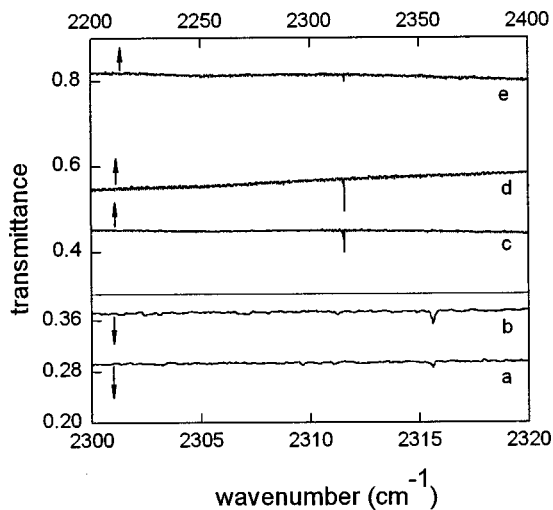

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FIG. 1. Infrared transmission spectra of as-grown *n*-type LEC InP of different compensation ratios. (a) Undoped $\theta=0.3$; (b) undoped $\theta=0.5$; (c) undoped $\theta=0.8$; (d) Fe-doped SI; $\theta=1.0$ and (e) undoped $\theta=0.2$. The spectra of (a) and (b) are measured at lower resolution and are thus shown on a different scale.
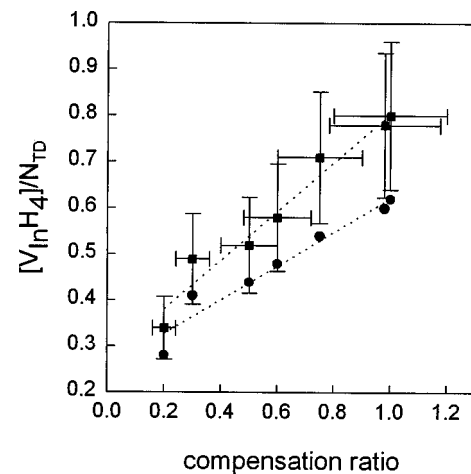

FIG. 2. Percentage of $V_{In}H_4$ concentration in total donor concentration of InP with different compensation degrees. The data in the filled rectangle are obtained by Eq. (1) and those in the filled circle are of infrared absorption results. For clarity, the compensation ratio of Fe-doped SI InP is taken as unity.

Fe-doped SI InP samples are shown in Fig. 1. It is noted that the $V_{In}H_4$ complex is found in all the samples and this indicates that it is a common defect in as-grown LEC InP. Moreover, an important feature may be noted, namely, that the absorption peak of $V_{In}H_4$ is strong in both the Fe-doped sample and the undoped InP samples with large compensation ratios. Indeed, the 2316 cm^{-1} peak of the Fe-doped samples and the undoped samples with large compensation ratios, is large enough to be measured at room temperature. As the calibration data of $V_{In}H_4$ in InP is not known, accurate evaluation of the concentration of this complex cannot be obtained from these spectra. However, it is usually accepted that the calibration data of a Zn–H complex is approximately valid for this complex.[5,12] This calibration value was shown to give a lower limit concentration of $V_{In}H_4$.[5] Thus, an approximate evaluation of the $V_{In}H_4$ concentration in LEC InP can be obtained from these spectra.

By using the calibration value of the Zn–H complex, the concentration of the $V_{In}H_4$ complex in each sample can be known from the integrated absorption of the spectrum. The absolute concentration of $V_{In}H_4$ in these samples is deduced to be in the range of $4-18\times10^{15}$ cm^{-3} from the spectra. The total donor (TD) concentration N_{TD} can be estimated from the compensation ratio value and the electron concentration allowing the ratio $[V_{In}H_4]/N_{TD}$ to be calculated. In Fig. 2 (filled circles), we plot $[V_{In}H_4]/N_{TD}$, thus obtained against the compensation ratio ($\theta=N_A/N_{TD}$) for the samples studied. It is noted that the content of $V_{In}H_4$ has a strong positive correlation with the sample's compensation ratio.

Also shown in Fig. 2 (filled squares) are the estimated concentration ratios $[V_{In}H_4]/N_{TD}$ based on the assumption of this complex being a dominant shallow donor (in comparison with other native defects). Under this assumption the charge neutrality condition gives

$$[V_{In}H_4]=\frac{n}{1-\theta}-N_D,\qquad(1)$$

where N_D, the shallow donor impurity concentration, is de-

termined by spark source mass spectrometry and *n*, the electron concentration by Hall measurements. The fact that the concentration dependence on θ as determined from Eq. (1) closely follows $[V_{In}H_4]$ as obtained through the IR absorption data, is convincing evidence that $V_{In}H_4$ is a dominant shallow donor.

With $V_{In}H_4$ acting as a shallow donor, it is not unexpected to find that this native defect is capable of changing the electrical properties such as electron concentration, mobility, etc., of InP. One consequence is that InP having a high concentration of $V_{In}H_4$, should require a high concentration of the deep acceptor Fe to bring it into semi-insulating form. However, Fe being itself an acceptor impurity will induce, through the above-observed correlation, a high value of $V_{In}H_4$. This explains why high concentrations of intrinsic donors are always found in Fe-doped SI InP,[12] and why the Fe^{2+} concentration is observed to correlate with the $V_{In}H_4$ concentration.[13]

In undoped as-grown LEC InP, a very high concentration of the intrinsic donor has been regularly found.[14] Although other donor defects, such as the phosphorus vacancy, and the phosphorus antisite and interstitial, are also possible native centers in as-grown LEC InP, these deep donors are always found in concentrations around the detection limit of deep-level transient spectroscopy (DLTS)[15] and cannot be detected by optical detected magnetic resonance (ODMR).[16] Moreover, a recent positron annihilation study of as-grown *n*-type LEC InP has revealed the phosphorus vacancy to be present in very low concentrations.[17] With the recognition of $V_{In}H_4$ as a dominant intrinsic shallow donor these observations are now understood.

The emphasis of the present work has been that of reporting an experimentally observed correlation between the concentration of the $V_{In}H_4$ and the compensation ratio, with no attempt to explain why such a correlation should exist. We point out, however, that the concentration change of the $V_{In}H_4$ complex in InP with different compensation degrees can be explained by the amphoteric native defect model proposed by Walukiewicz.[18,19] In this model, the concept of the Fermi-level stabilization (FS) energy E_{FS} has been applied to

understand a variety of defect-related phenomena. Since E_{FS} is usually constant for InP with both acceptor and donor defects, the increase of acceptor concentration will enhance the formation of donor defects.[20]

In summary, infrared absorption measurements of the hydrogen indium vacancy complex $V_{In}H_4$ coupled with Hall measurements have confirmed this complex to be a common intrinsic shallow donor defect in conventional as-grown LEC InP present in the concentration range of 10^{15}–10^{16} cm^{-3}. An important correlation between the concentration of $V_{In}H_4$ and the compensation ratio has been discovered, which explains why the concentration of the intrinsic donor is high in Fe-doped SI InP and undoped InP with a large compensation ratio. This phenomenon is in agreement with the proposed model of the Fermi-level-dependent concentration of amphoteric defects.

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