Mechanisms of the semi-insulating conversion of InP by anelastic spectroscopy

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Elastic energy absorption measurements versus temperature on semiconducting, semi-insulating (SI), and Fe-doped InP are reported. A thermally activated relaxation process is found only in the SI state, which is identified with the hopping of H atoms trapped at In vacancies. It is proposed that the presence of In vacancies in InP prepared by the liquid encapsulated Czochralski method is due to the lowering of their energy by the saturation of the P dangling bonds with H atoms dissolved from the capping liquid containing H_2O. The conversion of iron-free InP to the SI state following high temperature treatments would be due to H loss with the transformation of the H-saturated In vacancies, V_{In}-H_4 donors, into neutral and acceptor V_{In}-H_n complexes with $n<4$. Such complexes would produce the observed anelastic relaxation process and may also act as deep acceptors that neutralize unwanted donor impurities.

I. INTRODUCTION

Semi-insulating (SI) InP is usually obtained by adding Fe before growing the crystal by the liquid encapsulated Czochralski (LEC) method. SI InP:Fe offers remarkable perspectives as a substrate in optical fiber communication systems, and in high frequency electronic devices. Essential prerequisites are both high electrical resistivity and carrier mobility, in addition to a high material homogeneity. Generally, the semiconducting as-grown InP is quite inhomogeneous, as it exhibits growth striations, dislocations decorated by microdefects, microprecipitates embedded in the crystal lattice, and sometimes inclusions.[1] In particular, since the Fe concentrations necessary to reach the semi-insulating state are close to the Fe solubility limit, domains of Fe precipitates are inevitably formed. Post-growth thermal treatments of the ingots at about 900 °C produce beneficial effects concerning defect annealing besides a resistivity increase, but cause inhomogeneities across the crystal diameter[2] and do not improve the Fe homogeneity.[3] Therefore, the thermal treatments have to be carried out on the wafers cut from the as-grown ingots; in this way the wafer homogeneity results improved[4] and the striations and other types of lattice imperfections may be annealed.

It is diffusely believed that in the SI state of InP:Fe, the electrons supplied to the crystal by the unwanted residual impurities (shallow donors) are trapped by Fe, which acts as a deep acceptor and provides compensation. However, the SI state is reached only if the Fe concentration (typically in the range of 10^{16} cm^{-3}) is remarkably higher than the residual donor impurity content; as a confirmation, it was reported that the impurity content in SI InP:Fe is lower than the free carrier concentration,[5] indicating that sources of donors other than the impurities considered above must be active; they were identified later as $V_{In}(HP)_4$ complexes,[6,7] and labeled here as V_{In}-H_4. Lastly, it should be mentioned that the achievement of the SI state by Fe doping may present further disadvantages due to the nonuniformity of the electrical properties along the crystal growth axis caused by Fe segregation.[8]

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The semi-insulating state is also reached by thermally treating undoped InP for several hours or days at about 950 °C under phosphorus atmospheres ranging from tenths to tens of bars,[9–11] after which the resistivity can be increased above 10^5 Ω cm. However, for the conversion to occur it is necessary that the carrier concentrations be below the limit of 4×10^{15} cm^{-3} (Ref. 10); thermal treatments of materials having higher residual carrier concentrations due to higher impurity contents in the starting material usually display only a slight reduction in the concentration of free carriers after annealing,[12] and the same effect is also produced in SI InP:Fe.[2]

Several mechanisms have been proposed for the SI conversion, and many of them hypothesize that the thermal treatment may activate some kinds of deep acceptors in such a concentration to compensate the shallow donors related to impurities. Among the possible deep acceptors, the Fe atom both in Fe-doped and in undoped InP (therefore present as residual impurity) has been considered. However, also the hydrogen-related defects are receiving great attention, as H is always present[13] and may form complexes with native defects and impurities.

Generally, the studies of the properties of SI InP are conducted on the material doped with Fe, whilst a systematic analysis of the comparative properties of SI InP:Fe and undoped InP is missing. The purpose of the present work is to carry out, through measurements of the complex modulus (elastic energy loss and dynamic modulus), a comparative study of the defects in InP in the semiconducting and the semi-insulating state obtained both by the doping with Fe and by the thermal treatment.

II. EXPERIMENT

The thermal treatments (TT's) finalized to the conversion from the semiconducting to the SI state were carried out on wafers at about 950 °C under a phosphorous vapor pressure of ~0.2 bar for times of the order of hours. The crystals were grown by the LEC method at Venezia Tecnologie, and the samples were three rectangular bars (about 43×5 ×0.4 mm^3) of normal purity and high purity. They were characterized as follows: sample 1 was an undoped highly pure sample subjected to the TT for conversion and presented the SI state. Sample 2 was of normal purity and doped with 10^{16} cm^{-3} Fe impurities; therefore it was semi-insulating without need of TT's. Sample 3 was highly pure but not subjected to the thermal treatment for the conversion, and hence non semi-insulating.

The elastic energy loss and resonant frequency measurements were carried out between 1.9 and 650 K. The samples were horizontally suspended on two nodal lines by thin wires and three flexural vibration modes were electrostatically excited in the frequency range between 1 and 16 kHz. The vibration amplitude was detected through the variation of the sample-electrode capacitance by a frequency modulation technique, and the elastic energy absorption was measured from the rate of the free decay of the vibration.

The elastic energy loss coefficient, or reciprocal of the mechanical Q of the sample, is related to the imaginary part of the complex Young's modulus E^* as[14]

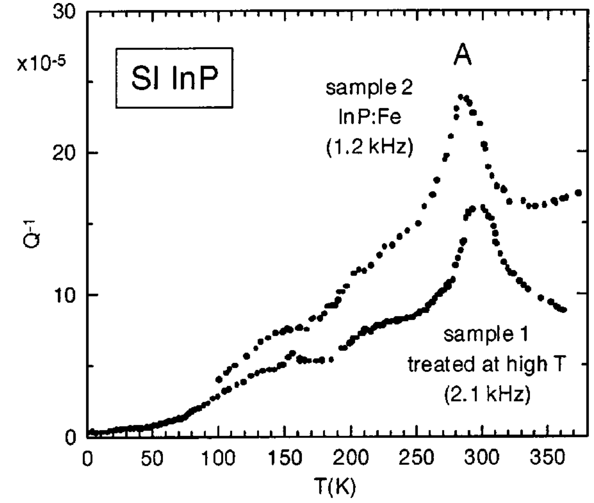

FIG. 1. Elastic energy loss versus temperature of semi-insulating InP. Sample 1: highly pure and subjected to the thermal treatment for conversion to the SI state; sample 2: doped with 10^{16} cm^{-3} Fe.

$$Q^{-1}=\mathrm{Im}\left(\frac{\delta E}{E}\right)=E\frac{v_0 c}{k_B T}(\Delta\lambda)^2\frac{\omega\tau}{1+(\omega\tau)^2}, \qquad (1)$$

where the last expression is the contribution of a molar concentration c of defects diffusing or reorienting with a characteristic time τ between states or sites that are made inequivalent by the vibration stress σ; $\Delta\lambda$ is the appropriate component of the change of the elastic dipole tensor after a defect reorientation, and the elastic dipole tensor λ is defined as the strain caused by a unit concentration of the defects; v_0 is the cell volume and $\omega=2\pi f$ is the angular vibration frequency. The above contribution to the absorption is peaked at the temperature at which $\omega\tau=1$; since τ is temperature dependent and usually follows an Arrhenius law, $\tau(T)=\tau_0\exp(E/k_BT)$, the peak shifts to higher temperature if measured at higher ω. The present samples had the $\langle 110\rangle$ axis parallel to the length, so that the appropriate modulus is[14] $E^{-1}_{[110]}=\frac{1}{2}(s_{11}+s_{12}+\frac{1}{2}s_{44})$. For trigonal defects $\delta E^{-1}_{[110]}=\frac{1}{2}\delta s_{44}=(cv_0/kT)\frac{2}{9}(\lambda_1-\lambda_2)^2$ while for $\langle 110\rangle$ orthorhombic defects $\delta E^{-1}_{[110]}=\frac{1}{6}\delta(s_{11}-s_{12})+\frac{1}{2}\delta s_{44}=(cv_0/kT)\frac{1}{6}[\frac{1}{12}(\lambda_1+\lambda_2-2\lambda_3)^2+(\lambda_1-\lambda_2)^2]$. Young's modulus is related to the frequency of the first flexural mode by $E=\rho(0.975fl^2/t)^2$, where ρ, l, and t are the sample density, length, and thickness, respectively; for our samples it is $E_{[110]}=1.40\times10^{11}$ Pa.

III. RESULTS

Figure 1 shows the elastic energy dissipation curves from 1.9 to 370 K of the undoped SI sample 1 and sample 2. An intense peak (peak A) is present at about 290 K in both samples, whereas the dissipation curves in the low temperature side indicate that two additional peaks (around 130 and 220 K) may be present but confused with the background; however, due to their small height, they will not be considered here. It is surprising that the two samples, having in common only the SI state but not the purity and the thermal history, present the same type of spectrum, and differ only

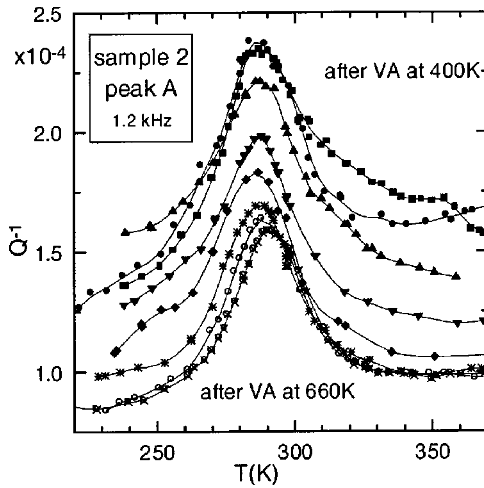

FIG. 2. Peak A of sample 2 during a series vacuum annealings for about 30 min at temperatures subsequently increased from 400 and 660 K at steps of 40 K.

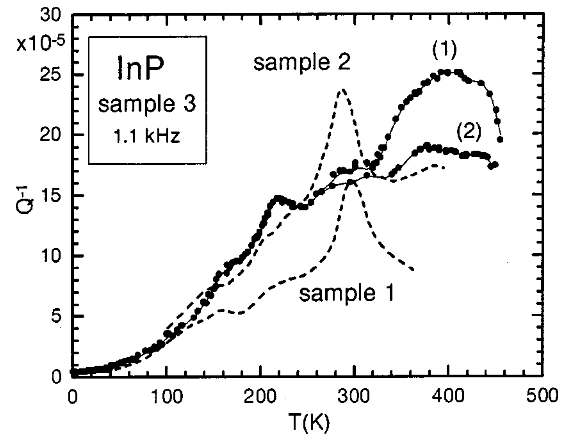

FIG. 4. Elastic energy absorption of semiconducting sample 3 ($f=2$ kHz) during two subsequent measurements (curves 1 and 2). For comparison, the dissipation curves of the SI sample 1 (2.1 kHz) and sample 2 (1.2 kHz) are also shown.

for the height of the background dissipation.

In order to test the thermal stability of the anelastic relaxation spectrum, sample 2 was annealed in vacuum for about 30 min at temperatures subsequently increased from 400 to 660 K at steps of 40 K; after each step the relaxation spectrum was measured, and the results are reported in Fig. 2. With increasing annealing temperature the background dissipation progressively decreases down to a saturation value that is attained after the treatment at 620 K (7th annealing). Instead, the height of the peak remains practically unaffected and is also stable versus thermal cycling, as the curves are retraced on heating and cooling. After this series on annealings, it was checked that the sample remained in the semi-insulating state.

The energy-loss curves, measured at three vibration modes (between 1 and 16 kHz), showed that the peak A is thermally activated, since it shifts towards higher temperatures with increasing frequency. Figure 3 presents the experimental data of sample 2 after the 7th vacuum annealing at 620 K at 1.2 and 15.6 kHz, after subtraction of the background; the data are satisfactorily fitted by Debye curves

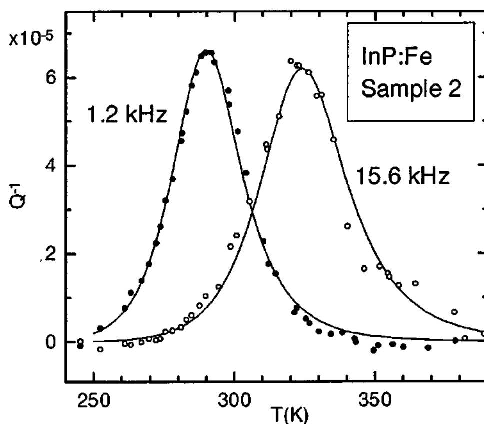

FIG. 3. Peak A in sample 2 after the 7th vacuum annealing at 620 K, after subtraction of the background. The continuous lines are single time Debye curves with $E=0.67$ eV and $\tau_0^{-1}=3\times10^{14}$ s^{-1}.

(continuous lines) with a single relaxation time following the classical Arrhenius law. The activation energy of the relaxation process and the preexponential factor of the relaxation rate obtained from the fit are $E=0.67$ eV and $\tau_0^{-1}=3\times10^{14}$ s^{-1}.

The spectrum of the semiconducting sample 3 is reported in Fig. 4 together with those of samples 1 and 2 (continuous lines) for comparison. Sample 3 displays (curve 1), superimposed on a high background, a small peak at 220 K and a well developed peak at 400 K that decreases during its measurement and disappears after a vacuum annealing of about 30 min at 450 K (curve 2). It is remarkable that the peak A, found in the SI samples, is absent here, or at least nonemergent from the background. The lack of peak A in the non-SI samples was confirmed also in undoped InP samples cut from the same ingot and from a different ingot (results not shown).

In order to study the stability of the anelastic spectrum in the non-SI sample 3, a series of vacuum annealings of 30 min each at increasing temperatures was conducted, as for sample 2. The results are displayed in Fig. 5 and show that (i) the dissipation around 400 K is not a stable peak as a function of temperature; indeed, it starts decreasing on heating above 350 K, even keeping the sample temperature constant (result not reported here) and practically disappears after a vacuum annealing at 500 K; (ii) the small peak around 220 K increases after the first vacuum annealing (450 K), but is depressed after the subsequent treatments at higher temperatures; (iii) the overall dissipation steadily decreases down to saturation values with the subsequent isochronal annealings at progressively higher temperatures.

Figure 6 compares the dissipation curves of SI InP:Fe (sample 2) and of non-SI InP (sample 3) after the last annealing treatments at 650 K; only the peak at 300 K in the SI sample persists after the high temperature treatments. In order to test whether peak A is suppressed by heating above 660 K, the isochronal annealings on sample 2 were continued up to 847 K, and Fig. 7 shows that the species giving rise to peak A is stable up to that temperature. At this temperature a few droplets appeared on the sample surface, indicating onset of surface degradation due to P loss and conse-

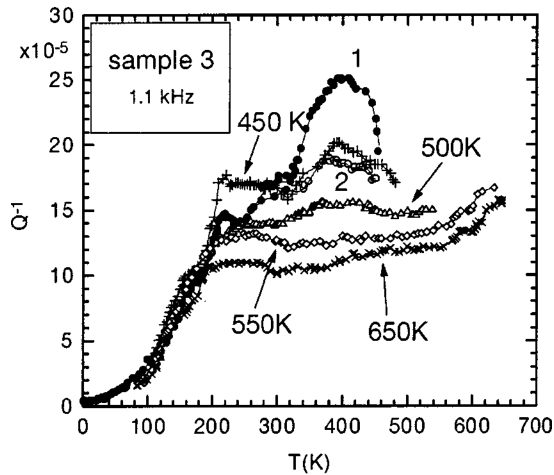

FIG. 5. Evolution of the anelastic spectrum of semiconducting InP (sample 3) measured in vacuum: as prepared (curve 1); 2nd heating run (curve 2); after subsequent annealings in vacuum for 30 min at the temperatures indicated in the figure.

quent formation of In clusters.[15] However, the sample bulk was very little affected, as deduced by the small relative variation of the resonance frequency ($<3.5\times10^{-3}$); the vibration frequency is directly related to the elastic modulus, which is very sensitive to the formation of second phases. In conclusion, peak A is stable up to the sample decomposition in vacuum.

To better interpret the annealing behavior observed, two samples cut from the same wafers of sample 2 (Fe-doped) and sample 3 (non-SI) were subjected to vacuum effusion experiments with a rate of 3–4 K/min, monitored with a residual gas analyzer. It was found that H out-diffusion starts above 560 °C, i.e., at about the same temperature at which the sample decomposition starts, as indicated by the appearance of some peaks in the effusion spectrum corresponding to the masses of PH_n and P_2H_n, besides H_2.

IV. DISCUSSION

A. The vacancy-H complexes

Optical absorption experiments on InP:Fe have revealed several local vibrational modes (LVM's), regardless of

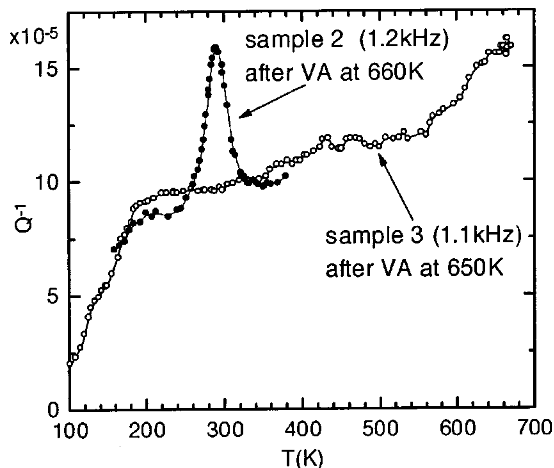

FIG. 6. Elastic energy loss of SI InP:Fe (sample 2) and of non-SI InP (sample 3) after the last vacuum annealings at 660 and 650 K, respectively.

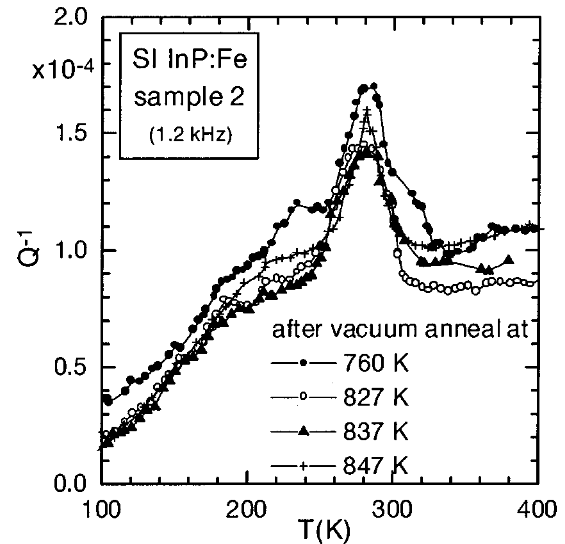

FIG. 7. Peak A in sample 2 after annealings of 30 min in vacuum at the increasing temperatures indicated in the legend; these measurements follow those of Fig. 2.

whether the material was as-grown,[6,16] plasma hydrogenated,[7,17] or ion implanted:[18–20] these lines occur in the range included between 2200 and 2300 cm^{-1} of the spectral region. However, if the same material is implanted with deuterons[20] instead of protons, the corresponding LVM's are shifted to lower energies ($\sim1600\ cm^{-1}$), and the ratio between the energies is close to $(m_D/m_H)^{1/2}$. This observation provided evidence that the lines are due to hydrogen-related defects, and they have been attributed to PH stretching modes.[6,7,16–20]

Four of the reported lines are particularly important, as they have been reproducibly observed, and there seems to be an agreement on their attribution; such peaks occur at 2202 cm^{-1} (peak 1), 2273 cm^{-1} (peak 2), 2286 cm^{-1} (peak 3), and 2316 cm^{-1} (peak 4). The main line is peak 4 (Ref. 7), but peak 1 is of comparable intensity if the samples are ion implanted;[20] instead, peaks 2 and 3 are rather weak.

Peak 1 is originated by a H complex with trigonal symmetry with a P-H bond oriented along the $\langle 111\rangle$ direction;[7,17] the low energy of its stretching mode is indicative of a long bond length. Therefore it has been attributed to an In vacancy having the P dangling bonds saturated by a H atom occupying a bond center (BC) site between V_{In} and P; this complex will be labeled as V_{In}-H.

Peak 4 appears in the high energy region of the P-H stretching mode, indicating a shorter bond length. Optical absorbance measurements in undoped InP samples co-charged with H and D have convincingly demonstrated that the complex giving rise to this peak is constituted by more than one H atom.[6] In addition, the stress splitting of this line indicates a cubic symmetry for the corresponding cluster.[7] The various authors agree that the complex consists of an In vacancy decorated by four H atoms in BC occupancy, V_{In}-H_4; in this configuration, the repulsion between the four H atoms shortens the P-H bond lengths and gives rise the observed high energy LVM's. The four H atoms, each bonded to one of the four P atoms around V_{In}, contribute four electrons to the trivalent vacancy and leave one electron available.[6] The V_{In}-H_4 complex is therefore a shallow donor,

and could be responsible for the discrepancy between the donor content estimated from the concentrations of the impurities and from the Fe^+ content that is necessary to passivate them.[6]

Peak 3 was studied by local vibrational mode experiments and was attributed to the Zn residual impurities;[7,21] the complex is believed to be formed by the Zn atom occupying an In site having one H atom as a nearest neighbor bonded to P. Peak 2 is of uncertain origin, but may be due to a cluster similar to that of peak 3 with Mn.[17]

B. Peak A

In InP, the omnipresence of hydrogen[13] (certainly due to the LEC preparation method), the fact that LVM lines due to isolated H have not been reported, the ability of H to form complexes,[6,7,16–20] and the high mobility of H strongly indicate that the atomic defect giving rise to peak A may be a H-related complex. Undoubtedly, the presence of the thermally activated process with maximum near 300 K proves that the InP samples in the SI state contain a species that is highly mobile at room temperature ($\sim 10^3$ jumps per second) and that this species is rather abundant, considering the height of the corresponding peak. In addition, the value of the preexponential factor is typical of point defect relaxations and indicates that this imperfection involves an atomic complex.

It is remarkable that the process is characterized by a single relaxation time: in fact, the absence of peak broadening indicates that the mobile species relaxes with only one type of elementary jump, and that there is no interaction among the relaxing units. Single-time Debye processes are not common, and one was also discovered in Si:B charged with hydrogen.[22] In that system the H atom hops among the four equivalent BC sites coordinated with substitutional B, overcoming an energy barrier ($E=0.22$ eV) that is lower than that presently reported. The absence of broadening of the peak due to the reorientation of the H-B pair led to the conclusion that the interaction between H-related defects may be negligible at dopant concentrations as high as 10^{19} atoms/cm^3. The relaxational dynamics of H within the H-B pairs in Si has also been measured by the decay of the stress-induced ir dichroism[23] for relaxation times between 10^3 and 10^6 s. By joining the data for the two types of experiments,[24–26] relaxation rates spanning 11 orders of magnitude were obtained in the temperature range 60–120 K; a weak deviation from the Arrhenius dependence was observed at low temperature, which was interpolated[24] with a polaronlike model.

Similarly to the case of B-H in Si, it would be natural to think of the reorientation of H around Fe as a source of anelastic relaxation in the Fe-doped InP sample. Indeed, measurements of the local vibrational modes show that in InP:Fe, H resides between the Fe atom (which substitutes In) and a nearest neighbor P atom, mainly bonded to P. However, the fact that both undoped and Fe-doped InP display the same peak (see, for instance, Fig. 1, where the small temperature shift between the two peaks is due to the different frequencies) demonstrates that Fe does not play any role in the mechanism causing peak A.

We discuss now the possibility that peak A is due to $V_{\rm In}$-H_n complexes ($n=0-4$). For $n=0$ and $n=4$ the complexes have in principle the same cubic symmetry of the crystal, so that there would not be any differentiation between complexes under stress, unless a Jahn-Teller-type lowering of the defect symmetry occurs. Indeed, it has been proposed that in certain ionization states the $V_{\rm In}$ is distorted.[27] In this case, different distortions would be distinguished by stress and would cause anelastic relaxation, but the reorientation between them would be expected to occur with a faster rate than in the cases where atomic hopping is involved and produce a peak at much lower temperature:[14] the barrier of 0.67 eV seems too high for the reorientation of a Jahn-Teller-like distortion.

Instead, the reorientation of the $V_{\rm In}$-H_n complexes with $n=1$, 2, and 3 is expected to appear as a slower single-time relaxation process. In fact, in all three cases the complexes can reorient among equivalent configurations through a single elementary jump of an H atom between the four different P dangling bonds around the vacancy. For $n=1$ there are four equivalent BC sites for H, each coordinated with one of the four P bonds, and the defect has trigonal symmetry. For $n=3$, one of the four BC sites is unoccupied, so that the complex reorientation is due to the jump of the H vacancy instead of the H atom, and the symmetry is again trigonal. For $n=2$ the H atoms can occupy six equivalent pairs of BC sites along the $\langle 110\rangle$ directions. The corresponding elastic dipole has the principal axes along two $\langle 110\rangle$ and one $\langle 100\rangle$ directions and its symmetry is $\langle 110\rangle$ orthorhombic.

The three complexes may have different energy barriers for reorientation, producing distinct relaxation peaks. In this case, peak A would be due to the dominant complex, and the other two complexes would produce peaks at different temperatures, e.g., the two small peaks at 130 and 220 K. However it is also possible that all the complexes have nearly the same energy barrier for reorientation; in fact, the LVM energies of the various complexes differ by only 5% (Refs. 6 and 7), and this can be taken as an indication that the potential ''felt'' by H and therefore the barriers between different minima are little affected by the presence of neighboring H atoms. In this case all the three complexes would contribute to peak A, and indeed the present data are compatible with a spread of activation energies of the order of 5%. At present it is not possible to decide between the two cases, and further measurements on crystals with different orientations are needed.

Finally, we note that the concentration of defects producing peak A estimated from the peak intensity is fully consistent with the concentration of H and $V_{\rm In}$-H_n complexes that are generally present in InP crystals grown by LEC,[28] i.e., of the order of 10^{16} cm^{-3}. In fact, the peak intensity in Eq. (1) is

$$Q^{-1}_{\rm max}=c\,\frac{v_0 E}{2k_{\rm B}T}\Delta\lambda^2, \tag{2}$$

and substituting the measured $E=1.40\times 10^{11}$ Pa and assuming that[14] $0.1\leqslant\Delta\lambda\leqslant 1$, the volume concentration of defects turns out of the order of $c/v_0\sim 6\times 10^{16\pm 1}$ cm^{-3}.

C. The background dissipation and the peak at 400 K

The high background dissipation of both the SI (Fig. 2) and the semiconducting (Fig. 5) samples might be due to the

thermoelastic effect or to the movement of dislocations. The thermoelastic effect is due to the periodic heat transfer through the sample induced by the alternating vibration stress;[14] the corresponding relaxation rate τ^{-1} in Eq. (1) is directly proportional to the thermal conductivity, which is generally a slowly varying function of temperature, so that a very broad peak results. The observed lowering of dissipation after the high temperature treatments should be mainly explained in terms of a change of the charge carrier concentration and mobility, which in turn affects the thermal conductivity. During the present experiments, however, no relevant changes of the electrical conductivity were observed. Therefore, it is unlikely that the main contribution to the background dissipation in the as-grown samples was of thermoelastic origin.

Dislocations are formed during the crystal growth and subsequent cooling, and their stress-induced movement may produce a broad background dissipation. The decrease of such a dissipation after the high temperature treatments can be caused by the migration of defects onto the dislocation lines, resulting in the pinning of the dislocations.[29] The migrating defects should be rather mobile, since the lowering of dissipation starts already a few tens of kelvins above room temperature; they can be oxygen or hydrogen atoms. It should be noted that a few at ppm impurities are sufficient to saturate the whole dislocation network.

The presence of the peak at 400 K in the semiconducting sample 3 and its disappearance during its measurement, which occurs at a temperature at which there is certainly no H loss, indicates that the sample is not in thermal equilibrium. The species giving rise to the process is again rather mobile; therefore, the peak is likely due to a H-related defect, but it is not possible at present to make any attribution.

D. Interpretation of peak A and proposition of a model for the semi-insulating state

From the above results it appears that peak A is present only in the SI state of both Fe-free and Fe-doped InP, suggesting that there is a common mechanism of conversion to the SI state, which is also responsible for the anelastic relaxation process. The SI conversion in InP:Fe is attributed to the removal of the shallow donors by the deep acceptor Fe atoms. Similarly, during the high temperature treatments in P atmospheres necessary to reach the SI state in undoped InP, the activation of some sort of deep acceptors able to compensate the shallow donors introduced by impurities has been unanimously invoked. However, there is no agreement at present on the nature of such acceptors and consequently on the SI conversion mechanism. Bliss *et al.*[6] reported that the 2316 cm^{-1} line attributed to V_{In}-H_4 disappears after the TT finalized to the SI conversion, and in addition they observed that Fe and Cu were introduced during their TT's. On this basis they concluded, in accordance with Hirt *et al.*,[12] that the high resistivity values are due to the contamination by Fe and Cu deep acceptors during the annealing process and to the concomitant out-diffusion of the V_{In}-H_4 complexes acting as intrinsic donors. We exclude that Fe plays such a role in our undoped SI samples, since according to the chemical analysis sample 1 contained less than 1 atomic part per billion, and the TT for the SI conversion was carried out under controlled purity conditions.

For the model we presently propose we assume that hydrogen and vacancies are abundant, even though not intentionally introduced. As discussed in the following paragraph, we suppose that the as-grown material mainly contains V_{In}-H_4 complexes, whereas lower order complexes are also present if H is trapped by other defects, like Fe. This assumption is corroborated by several observations[7,18] of the LVM's at 2316 cm^{-1} (V_{In}-H_4) in as-grown InP and of the 2202 cm^{-1} (V_{In}-H) line in Fe-doped[18] and proton-implanted[20] InP. We believe that the disappearance of the V_{In}-H_4 line[19] consequent to the TT at 950 °C for the SI conversion is due to the out-diffusion of H, rather than of the whole V_{In}-H_4 complex, since we expect that V_{In} is less mobile than H. Evidence of H out-diffusion during high temperature treatments is provided by Zappettini *et al.*[2]. As a consequence of the H loss from the sample, transformation of V_{In}-H_4 complexes into complexes with $n<4$ takes place. Indeed, after thermal annealings above 600 °C new lines appear at lower energy,[7] attributed to V_{In}-H_n with $n<4$.

Considering that V_{In} is a triple acceptor,[6,27,30] we expect that the V_{In}-H_3 complex is neutral, as the H atoms supply the three electrons. Similarly, V_{In}-H_2 and V_{In}-H are expected to be acceptor complexes, and we hypothesize that they are deep acceptors. The dissociation of the V_{In}-H_4 complexes during high temperature annealing reduces the number of shallow donors, and at the same time the newly formed V_{In}-H_n $(n=0-2)$ deep acceptors remove the free carriers introduced by impurities and render the material semi-insulating.

The proposed model is congruent with the observation that peak A (attributed to V_{In}-H_n with $n=1-3$) in undoped InP appears only after the TT at 950 °C, which transforms the complexes with $n=4$ into lower order complexes; therefore, the existence of the peak should be closely related to the SI state. Accordingly, we expect that peak A is absent in as-grown undoped samples, as experimentally observed (Fig. 4).

The occurrence of the peak also in the Fe-doped sample, which did not undergo the TT, can again be explained by the presence of lower order vacancy-H complexes. Indeed, the V_{In}-H_1 line in as-grown samples of InP:Fe has been reported by several authors[6,7,18] (depending on the growth conditions or the location of the samples in the crystal). At least two mechanisms might then be possible: (i) partial trapping of H in Fe-H pairs, with consequent trasformation of V_{In}-H_4 centers into lower order complexes. A support to this possibility is the presence of a line at 2273 cm^{-1} in H-implanted samples, which was tentatively attributed to the PH-Fe cluster;[20] (ii) possible influence of Fe on the formation energies of the various V_{In}-H_n complexes. This mechanism hypothesizes that a lowering of the Fermi level due to Fe may perturb the relative energies of the V_{In}-H_n complexes, making the formation of the $n=1$, 2, and 3 complexes competitive with that of V_{In}-H_4.

E. Formation of V-H_n complexes

It remains to be explained why InP prepared by the LEC method contains a substantial concentration of V-H_n com-

plexes, as indicated by the corresponding LVM. In fact, the equilibrium concentration of vacancies in crystals are very small even near the melting temperature, and for the case of InP it seems natural that vacancies of the more volatile P, V_P, are predominant over the V_{In}. However, the formation energy of V_{In} can be lowered if the P dangling bonds are saturated by H atoms, and could even become negative; then, in the presence of H the formation of In vacancies saturated by H would be possible or even energetically favorable. During the LEC crystal growth, hydrogen would be supplied by the capping liquid, which contains H_2O;[31] H could dissolve in the liquid InP forming P-H bonds and then be incorporated in the crystal as V_{In}-H_4.

That the P-H bonds are much more stable than the In-H bonds is demonstrated by the lack of In-H LVM's in InP even after the irradiation with H, which produces both P and In vacancies and self-interstitials. Within the proposed picture, the high stability of the P-H bond is consistent with the stability of peak A against vacuum annealings up to the sample decomposition (Fig. 4) and with the relatively high barrier for the hopping of H between different P bonds in the V_{In} (0.67 eV, compared to 0.22 eV for the reorientation of the B-H complex in Si).

The formation of superabundant vacancies is already observed in metal hydrides at high temperatures,[32] when the binding energy of H to the metal vacancies can substantially lower the V-H_n formation energy. By exposing the metal to a high H pressure at high temperature, it is possible to let very high concentrations of H-saturated vacancies to migrate into the bulk (even tens of percent).

V. CONCLUSION

Anelastic spectroscopy experiments on InP crystals grown by the liquid encapsulated Czochralski method have revealed the presence of defects whose reorientation rate is thermally activated over a barrier of 0.67 eV. The corresponding anelastic relaxation process is observed only in the semi-insulating InP samples, irrespective of whether the semi-insulating state is obtained by doping with Fe or by annealing near 900 °C. It is proposed that these defects are In vacancies with the P dangling bonds partially saturated by H, whereas vacancies completely filled with four H atoms do not cause anelastic relaxation. A possible mechanism for the formation of the V_{In}-H_4 complexes and for the reversion to the semi-insulating state after annealing near 900 °C is proposed, based on the stability of the P-H bonds. The formation of such bonds with H dissolved from the capping liquid during the crystal growth would make the formation of V_{In}-H_4 complexes favorable. Such complexes would be donors that contribute to make the crystal a semiconductor. The subsequent treatment at 900 °C would partially outgas H from the sample and remove it from the V_{In}-H_4 complexes, transforming them into neutral or deep acceptor defects.

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