Evidence for two distinct defects contributing to the $H4$ deep-level transient spectroscopy peak in electron-irradiated InP

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Deep-level transient spectroscopy (DLTS) has been used to study the dominant deep-level $H4$ produced in InP by electron irradiation. The characteristics of the $H4$ peak in Zn-doped InP has been studied as a function of pulse duration (t_p) before and after annealing. Our results show that at least two traps contribute to the $H4$ peak: one is a fast trap (labeled $H4_F$) and the other is a slow trap (labeled $H4_S$). This is shown through several results concerning the activation energy, the capture cross section, the full width at half-maximum, and the peak temperature shift. It is shown that both traps are irradiation defects created in the P sublattice. [S0163-1829(98)04644-X]

I. INTRODUCTION

Due to the growing importance of InP in electronic and optoelectronic devices and in solar cells resistant to radiation damage[1,2] considerable work has been devoted to the investigation of the irradiation-induced defects in this material. The defects detected by the deep-level transient spectroscopy (DLTS) technique in p-type room-temperature irradiated samples are $H4$ and $H5$ hole traps. The origin of these defects has been under discussion for many years.[3,4] Anisotropic introduction rate measurements revealed that $H4$ originates in the P sublattice[5] while $H5$ originates in the In sublattice.[6] Annealing studies, pure thermal and recombination-enhanced, showed that these defects are not simple ones but rather are complexes resulting from the association of primary defects and impurities. The complex annealing behavior of these defects supports this interpretation.[7,8] The $H4$ annealing kinetics in Zn-doped material was found to be nonexponential[3,5,9,10] while in Cd-doped material it was found to be exponential.[11] Empty (of hole) defects anneal faster than the filled ones.[4] While almost all the defects (more than 90%) forming $H4$ anneal out thermally, a substantial part (about 25%) of them survive after injection-enhanced annealing.[12]

Defect transformation ($H4 \rightarrow H'4$) under thermal annealing or minority carrier injection was reported.[13] According to those authors $H4$ anneals by transformation into another hole trap ($H'4$), which gives rise to a DLTS peak at almost the same temperature as $H4$, but has a higher activation energy and a much lower hole capture cross section, and hence is not detectable using conventional DLTS equipment. A special electronic setup with very long filling pulses (4 s) was needed.

The aim of this paper is to report experimental evidence for the existence of at least two distinct traps contributing to the $H4$ DLTS peak and to determine their characteristics. The standard method for resolving superimposed DLTS peaks corresponding to traps differing in capture cross section is to use short filling pulse widths (t_p) in order to fill the fast traps only, the filled fraction n_T being given by the filling relation (in p-type material):

$$n_T = N_T[1 - \exp(-C_p t_p)], \qquad (1)$$

where N_T is the total trap concentration and C_p is the free hole capture rate. The change of the capacitance of a reverse-biased Schottky diode after the application of a filling (zero bias) pulse of duration t_p is given by

$$\Delta C(t_p) = \Delta C_{\max}[1 - \exp(-C_p t_p)], \qquad (2)$$

where $\Delta C_{\max}$ is the maximum change of the capacitance due to filling all the traps N_T. C_p depends on the peak temperature T_m through the relation

$$C_p = \sigma v p = \sigma_\infty v p \, \exp(-E_B / kT_m), \qquad (3)$$

where σ is the hole capture cross section, v the hole average thermal velocity, p the free hole concentration, E_B the capture barrier energy, and k the Boltzmann constant. Because T_m increases with the pulse frequency f one can fill the desired fraction n_T by applying pulses of convenient width t_p and frequency f. In order to detect slow traps, the product $C_p t_p$, which determines the refilled fraction, should be increased. Since C_p is approximately proportional to f, t_p and f should both be increased. However, in the double lock-in method there is a limitation: $t_p f < 1/4$.

In the next section we describe the experimental details and in Sec. III we report our results concerning $H4$. Sections IV and V are devoted to the discussion of the results and the conclusion.

II. EXPERIMENTAL DETAILS

The samples used in this work are the same as those that have been the subject of a previous study.[6] These are a series of identical Schottky diodes of Zn-doped InP grown by liquid-phase epitaxy on Zn-doped p^+-type InP substrates. Ohmic contacts were realized on the p^+-side by Au-Zn evaporation and Schottky barriers were made by Ti-Au evaporation on the epitaxial side. The hole concentration at room temperature, determined from capacitance-voltage measurements, was approximately 1.2×10^{17} cm^{-3}. Irradiations were performed at room temperature using an electron Van de Graaff accelerator, in the electron energy range 0.3–

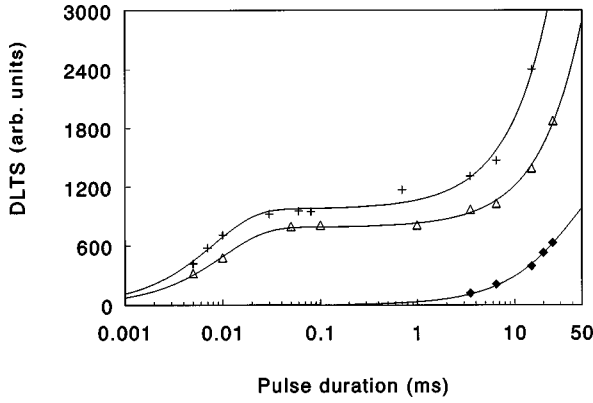FIG. 1. $H4$ peak height vs filling pulse width (logarithmic scale) before $(+)$ and after annealing at 110 °C with 2.5 V reverse bias for 10 min $(\triangle)$ and for 60 min $(\blacklozenge)$.

1.6 MeV. Electron doses were chosen in such a way that the concentration of free holes after irradiation did not differ by more than 10% from the initial value. The electron current densities did not exceed 0.5 μA cm^{-2} to insure that the sample temperature did not rise more than 10 °C during irradiation. C-V curves and DLTS spectra were recorded after irradiation and after successive isothermal annealings with and without the application of 2.5 V reverse bias. In recording the DLTS spectra the temperature-raising rate was chosen to be as low as 3 °C/min and a special sample holder of large thermal capacity was used to insure thermal homogeneity between the sample and the thermocouple. This was found to be essential for detecting small temperature shifts of DLTS peaks.

The refilling (zero bias) pulse amplitude ΔV was chosen as low as 1 V in order to stay in the linear part of the peak height S versus ΔV for any t_p to minimize the internal electric-field effect.[14] DLTS spectra were recorded using a Boonton S4910 capacitance meter and PAR-5204 lock-in analyzer for a series of the filling pulse width t_p ranging from 5×10^{-6} to 5×10^{-2} s. For every filling pulse duration a series of pulse frequencies f ranging from 1 up to $0.1/t_p$ Hz were used. For every recorded $H4$ peak the following quantities were carefully measured: its height S, its full width at half-maximum (FWHM), ΔT, and the temperature of its maximum T_m.

III. RESULTS

Figure 1 shows the $H4$ peak height S versus pulse duration t_p on a logarithmic scale, measured before and after thermal annealing at 110 °C with 2.5 V reverse bias applied on the sample (empty traps). These results fit very well the curves plotted using the following relation, which is the sum of two filling relations (2) taken with appropriate parameters S_{m1}, S_{m2}, C_{p1}, and C_{p2}:

$$S(t_p) = S_{m1}[1 - \exp(-C_{p1}t_p)] + S_{m2}[1 - \exp(-C_{p2}t_p)]. \tag{4}$$

This strongly suggests that S is the sum of two signals S_1 and S_2 arising from two different defects: a fast one ($H4_F$) giving rise to a signal that saturates at approximately $t_p = 0.05$ ms and a slow one ($H4_S$) giving rise to a signal, the
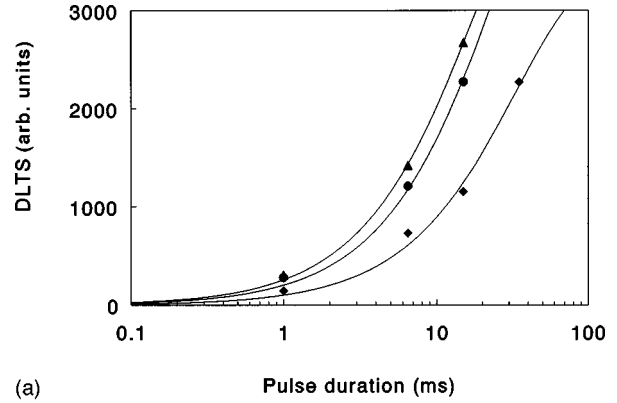
(a)
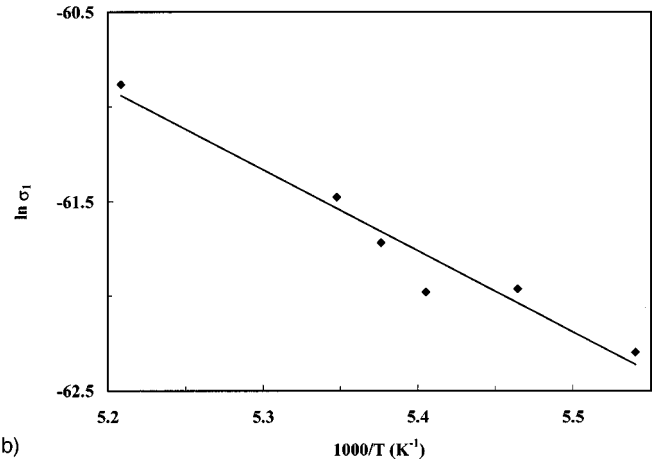
(b)

FIG. 2. (a) $H4$ peak height vs filling pulse width (logarithmic scale) in annealed samples plotted at 5.55 Hz ($\blacktriangle$), 3.33 Hz ($\bullet$), 1.40 Hz ($\blacklozenge$). The experimental results fit very well the curves representing the filling relation (2). (b) The plot of $\sigma_1(T)$ vs $1/T$.

onset of which is approximately $t_p = 0.5$ ms and that does not saturate even for $t_p > 50$ ms. It can also be seen from Fig. 1 that the thermal annealing leads to a reduction of the $H4$ signal for the whole range of t_p. An annealing of approximately 100 min leads to a practically undetectable signal in the small t_p range ($t_p \lesssim 0.5$ ms) while approximately 20% of the initial signal persists in the large t_p range ($t_p \gtrsim 10$ ms). The persisting signal remains unchanged even after several hours of annealing at higher temperature (up to 150 °C). To determine the main characteristics of these two defects, we shall present our results deduced from the recorded series of DLTS spectra for two categories of irradiated samples: completely annealed and unannealed samples. By ''completely annealed'' we mean that the fast defect has completely annealed out.

a. Completely annealed samples. These samples still give, even after annealing for several hours at 150 °C, a nonnegligible $H4$ peak when filling pulses of relatively large duration ($t_p \gtrsim 1$ ms) are applied. The peak height increases with t_p in accordance with the filling relation (2) [Fig. 2(a)]. The hole capture cross section σ_1 has been determined at various temperatures using relations (2) and (3) (corrected for double lock-in detection[15]). It was found [Fig. 2(a)] that it is impossible in practice to fill all the traps in order to determine N_T. The saturation of the DLTS signal $\Delta C_{\max}$ was
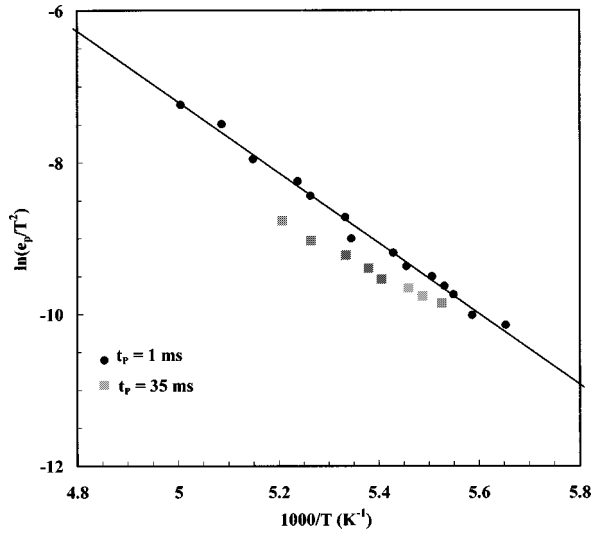
FIG. 3. $H4_S$ signature (in annealed samples) recorded at $t_p = 1$ and 35 ms.

obtained by computer fitting. Figure 2(b) shows the plot of $\ln \sigma_1(T)$ versus $1/T$ from which we have deduced the following relation for σ_1:

$$\sigma_1(T) = 8 \times 10^{-19} \exp(-0.19 \ \text{eV}/kT) \ \text{cm}^2 \qquad (5)$$

The signature, $\ln(e_p/T^2)$ versus $1/T$, is plotted in Fig. 3 according to

$$e_p = \gamma \sigma T_m^2 \exp(-\Delta E/kT_m), \qquad (6)$$

where e_p is the hole emission rate and γ is a constant depending on the carrier effective mass and the degeneracy factor. The apparent activation energy ΔE_1 determined from the signature was found to be decreasing with t_p from 0.42 to less than 0.3 eV when t_p increases from 1 to 50 ms as can be seen from Fig. 4. We will discuss this in the next section. Figures 5(a) and 5(b) show that increasing t_p leads to an increase in the peak temperature T_{m1} and to a decrease in the FWHM, ΔT_1, of $H4$. The FWHM of a DLTS peak can be deduced from the derivative of Eq. (6) with respect to T.[16] Figure 6 shows that the measured values of ΔT_1 at $t_p = 35$ ms fit fairly well the theoretical curve plotted for ΔE
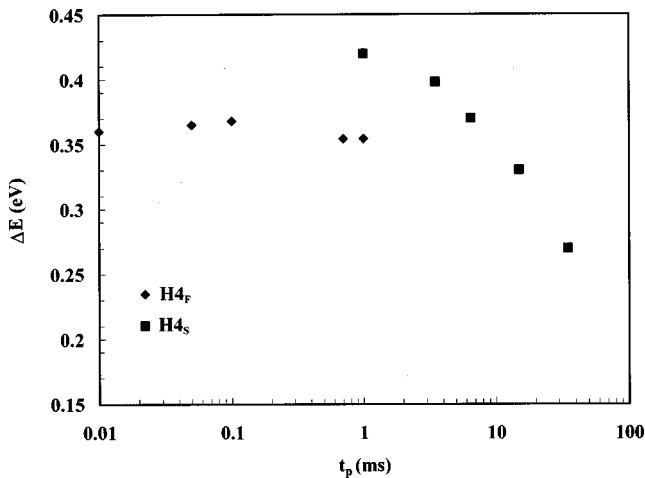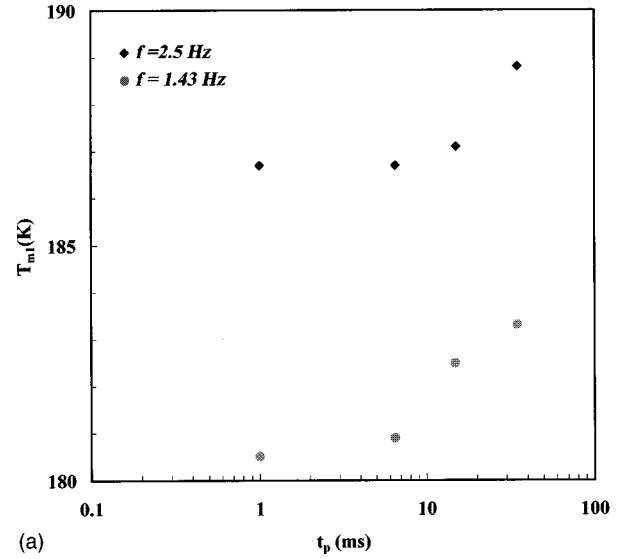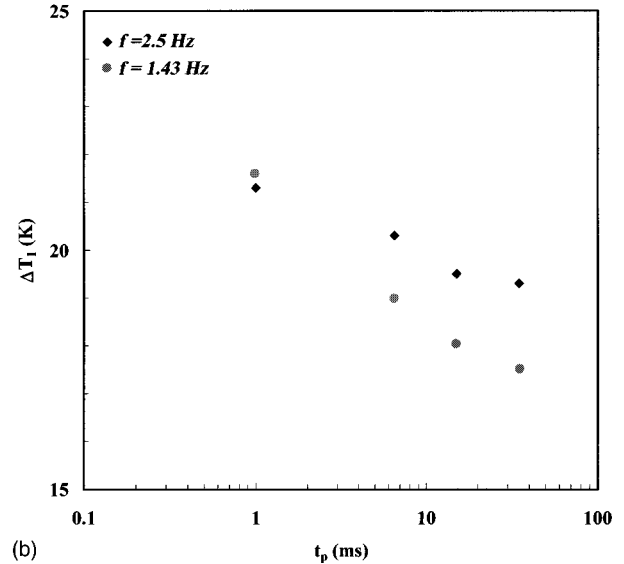

FIG. 4. Activation energy of $H4_F$ and $H4_S$ as a function of t_p.

FIG. 5. $H4$ peak temperature (a) and FWHM (b) as a function of t_p in the annealed samples measured at two different pulse frequencies.

$= 0.4$ eV, while at $t_p = 1$ ms the measured values are higher. This will be discussed in the following section.

b. Unannealed samples. Having determined C_{p1} for the slow defect, one can make the first term in relation (4) negligible by choosing the appropriate t_p and f. The condition to fill the fast defect alone could be set as $C_{p1}t_p < 0.01$. Then only less than 1% of the slow defects is filled. The deduced capture cross section for this fast defect σ_2 is

$$\sigma_2(T) = 1.9 \times 10^{-18} \exp(-0.05 \ \text{eV}/kT) \ \text{cm}^2, \qquad (7)$$

which is five orders of magnitude greater than σ_1 at 150 K.

The apparent activation energy ΔE_2 determined from the signature was found to be 0.36 ± 0.01 eV and it does not vary appreciably with t_p (Fig. 4).

Figures 7(a) and 7(b) show that the FWHM increases with t_p starting at t_p at approximately 1 ms, which corresponds to the onset of $H4_S$, and that the peak temperature T_m starts to increase at the same t_p. The measured values of ΔT_2 are
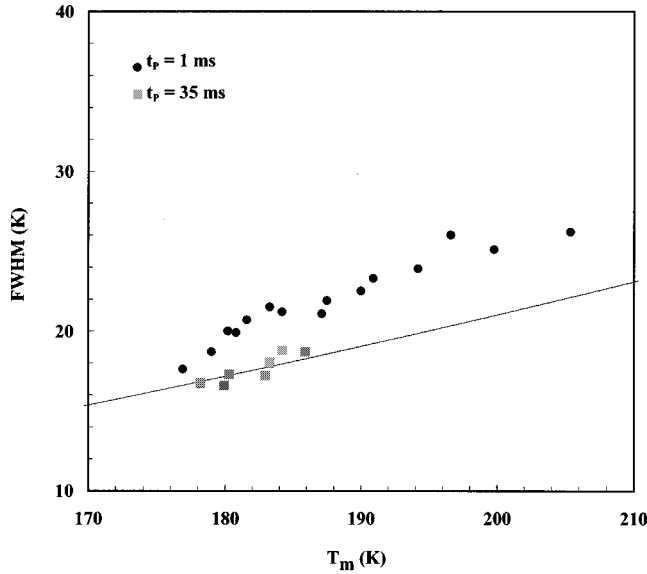
FIG. 6. FWHM of $H4_S$ vs peak temperature recorded at $t_p=1$ and 35 ms and the theoretical curve ΔT vs T_m for $\Delta E=0.40$ eV.

compared with the theoretical curve plotted for $\Delta E = 0.35$ eV in Fig. 8. A very good agreement is observed for $t_p=0.05$ ms in the high-temperature range, while in the low-temperature range and for $t_p=15$ ms the peak is noticeably broadened. This will be discussed in the following section.

IV. DISCUSSION

We have been able to resolve the $H4$ peak in two components due to the great difference in their capture cross sections and annealing rates. This allowed us to determine the main characteristics of the two defects. The nonexponential annealing behavior of $H4$ in Zn-doped material[5,8] may be accounted for if we take into consideration that the measured $H4$ contains two components, one of which anneals at temperature T with annealing rate K while the annealing rate of the other at this temperature is extremely low:

$$S=S_1+S_2 \exp[-K(T)t], \qquad (8)$$

where S_1 is the stable component arising from the slow defect, S_2 is from the fast one, and t is the annealing time. The fact that the nonexponential annealing is observed in Zn-doped and not in Cd-doped material suggests that the slow, stable defect is related to a Zn impurity-defect complex. Further investigation on Cd-doped InP should be carried out to confirm the absence of the slow defect in it.

The comparison of the amplitudes of $H4_S$ before and after heat treatment (that anneals out $H4_F$) did not reveal any increase of $H4_S$ as a result of a possible transformation $H4_F \rightarrow H4_S$. This suggests that both defects are created during irradiation. The increase of the FWHM and of T_m with $t_p>1$ ms observed in unannealed samples [Figs. 7(a) and 7(b) and Fig. 8] is easily explained by considering the fast and the slow components of $H4$. The increase of FWHM observed in the low-temperature part of Fig. 8 is probably resulting from the effect of the internal electric field on the emission rate, which is more important at lower temperature.[17] The decrease of the FWHM with t_p observed
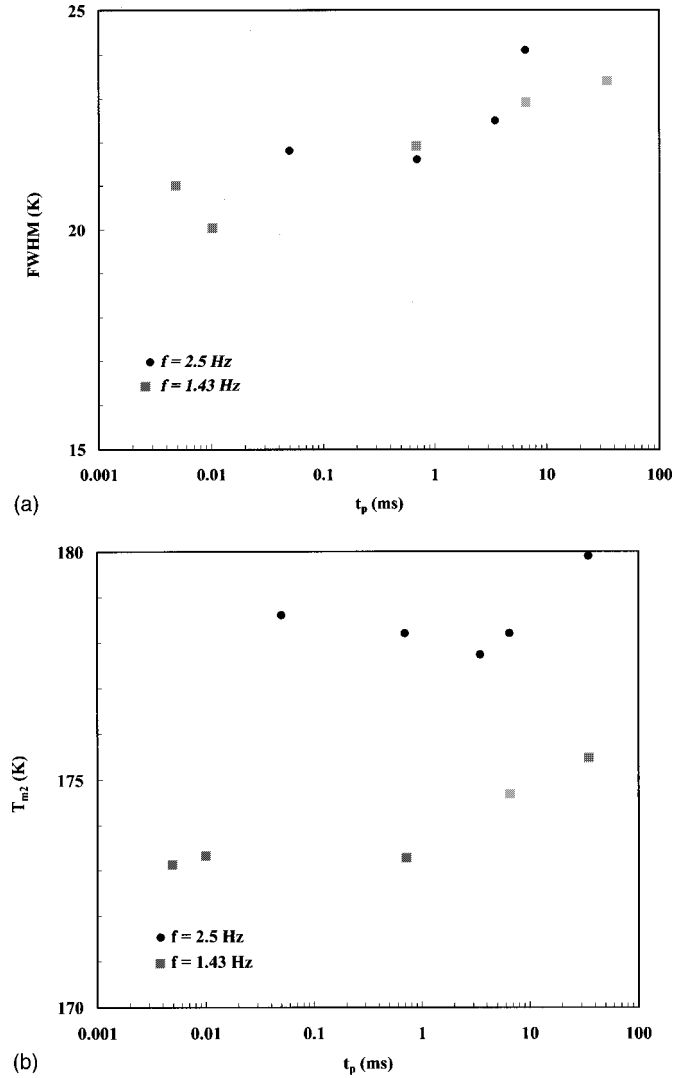

FIG. 7. FWHM (a) and peak temperature (b) of $H4$ vs t_p in unannealed samples measured at two different pulse frequencies.

in annealed samples [Fig. 5(b)] could be a result of the presence of a saturated trap with slightly lower T_m and lower concentration. Increasing t_p increases the contribution of $H4_S$ and it finally becomes dominant, while the concentration of the saturated defect remains constant. This is confirmed by the increase of T_m with t_p as seen in Fig. 5(a). In Fig. 6 too, the FWHM values measured at $t_p=1$ ms in annealed samples are higher than those measured at $t_p=35$ ms.

The decrease of the apparent activation energy ΔE_1 with t_p measured in annealed samples (Fig. 4), is due to the fact that when we increase t_p, T_m increases too [see Fig. 5(a)]. This explains the shift of the experimental points for $t_p=35$ ms towards higher T_m relative to those at $t_p=1$ ms as seen in Fig. 3. However, when the pulse duration is large the measurements can be performed at lower frequencies only, i.e., at lower T_m in a relatively small range of $1/T$ and therefore the deduced value of the activation energy is not accurate. We have noticed (Fig. 3) a slight decrease in the signature slope at the low-temperature end of it. This is probably due to the effect of the internal electric field, which is more important for low T_m in highly doped diodes. The calculated
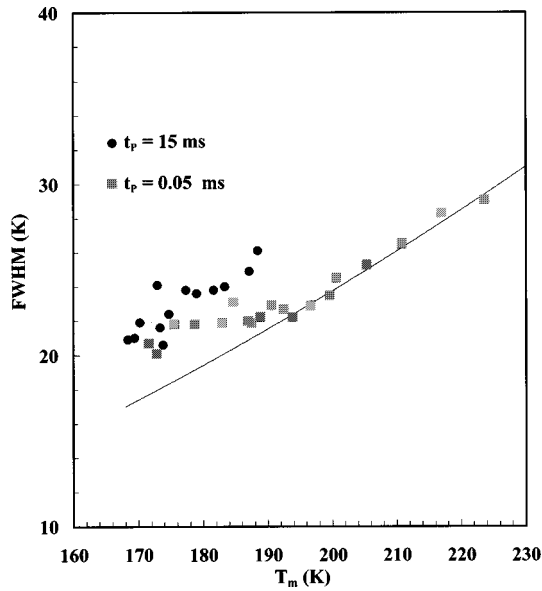
FIG. 8. FWHM of $H4$ vs peak temperature recorded at t_p $=0.05$ and 35 ms and theoretical curve ΔT vs T_m for ΔE $=0.35$ eV.

value of this field in our diodes is about 1.5×10^7 V/m. This makes the value of the activation energy deduced from the low-temperature part of the signature even lower.

In much of previous work, the $H4$ peak was considered as corresponding to only one kind of defect. In view of our present results in which we have clearly shown that at least two distinct kinds of defects contribute to this peak, it is necessary to revise these studies. In particular, the introduction rate of $H4$ as a function of incident electron energy was measured in Ref. 6 for two opposite directions of irradiation: [111]P and [111]In. It was concluded that the defects giving rise to $H4$ originate in the phosphorus sublattice. The measurement of the peak height in Ref. 6 was performed after irradiation (before any annealing) using filling pulses of 5 ms width. This means that the measured peak corresponds to $H4_F + H4_S$. Figure 9(a) shows the same results after deduction of $H4_S$. The results of the measurements performed on the residual peak recorded after annealing (for 1 h at 150 °C), which corresponds to $H4_S$, are shown in Fig. 9(b). In this figure the introduction rate η was corrected to take in account that the 5-ms pulse fills only about 20% of these defects. From the lower-energy part of these figures, where η[111]P$> \eta$[111]In, one concludes that both $H4_F$ and $H4_S$ originate in the P sublattice. The interesting feature of these figures is that, when increasing the electron energy, both η[111]P and η[111]In tend to increase slightly for $H4_F$, while for $H4_S$ they tend to decrease, contrary to the saturated behavior predicted by the McKinley-Feshbach model[18] for a primary electron-atom collision. This indicates a possible role of secondary atom-atom collision in creating these defects.[5,6,19,20] However, any attempt to identify the defects responsible for $H4_F$ and $H4_S$ should take into consideration the following facts: (i) $H4_F$ is found in both Cd- and Zn-doped material while $H4_S$ is found in Zn-doped material only. (ii) Both $H4_F$ and $H4_S$ are produced during room-temperature electron irradiation (see Fig. 1) and no indication of transformation from one to another during annealing
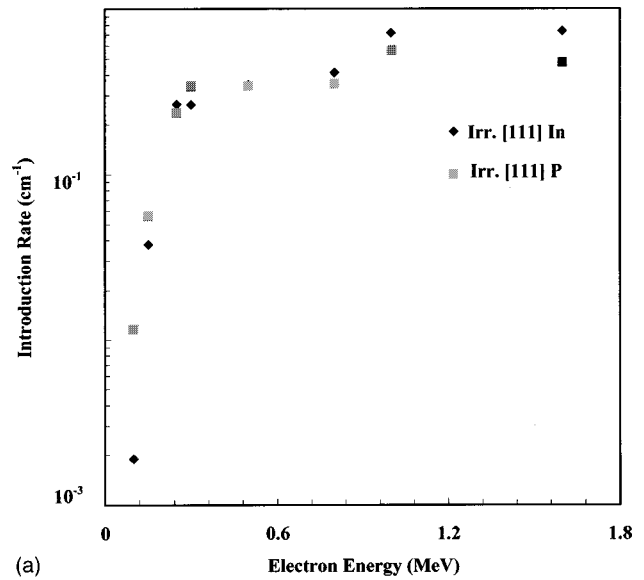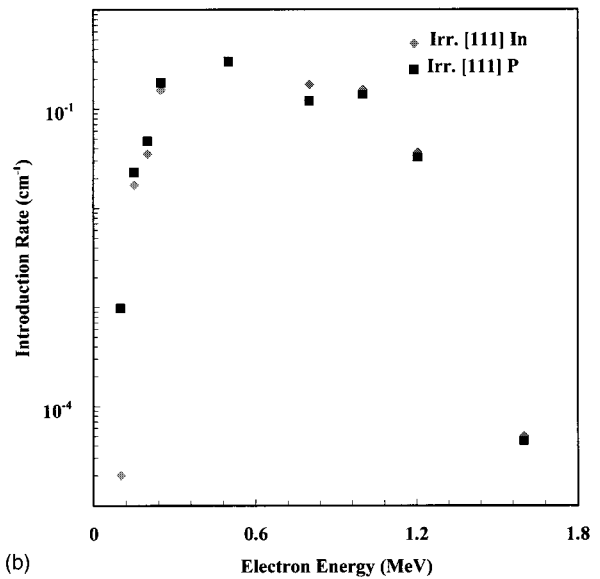
FIG. 9. Introduction rate η vs electron energy for $H4_F$ (a) and $H4_S$ (b) for irradiation along the ^{111}In and [111]P directions.

could be found. (iii) Both $H4_F$ and $H4_S$ originate in the P sublattice [Figs. 9(a) and 9(b)]. (iv) While the secondary collisions seem to have the effect of slightly increasing the $H4_F$ introduction rate at high incident electron energy, the opposite is observed for $H4_S$. (v) $H4_F$ has a much higher annealing rate than $H4_S$ and it anneals out in a first-order kinetics. Its annealing rate depends critically on its charge state and it can be annealed by minority carrier injection. (vi) $H4_S$ has a much smaller hole capture cross section (at 150 K) and smaller capture barrier energy than $H4_S$ [Eqs. (5) and (7)].

An identification consistent with the experimental facts (i)–(v) for $H4_F$ could be either the phosphorus vacancy (V_p) or the vacancy-interstitial Frenkel pair (V_p-P_i). This is in accordance with what was proposed by a number of investigators.[2,7,8] $H4_S$ could be tentatively identified with a V_p-Zn association. In fact, the observed decrease of the introduction rate with electron energy reflects the diminution of the probability to form a V_p adjacent to Zn atom in favor

of forming divacancies (V_p-V_p) or other complexes by secondary collisions between the displaced P atom and the second-neighbor P or even the first-neighbor In atom. This is due to the increase with the electron energy of both the mean recoil angle and the mean energy transferred to the displaced atom.[21]

Evidently more theoretical work should be done to account for the specific characteristics found for $H4_F$ and $H4_S$. From the experimental point of view, it would be interesting to see if the $H4_S$ introduction rate increases with Zn concentration.

V. CONCLUSION

We have proposed a simple model consisting of two distinct hole traps, created during irradiation, that contribute to the $H4$ DLTS peak: a fast one ($H4_F$) that has a larger capture cross section and lower activation energy (ΔE_2 =0.36 eV) anneals out at 110 °C, and a slow one ($H4_S$) with a much smaller capture cross section and higher activation energy (ΔE_1=0.42 eV) that is stable even at higher temperatures. A third defect of a much lower concentration contributing also to the same peak could be present. This model explains all the experimental results and, in particular, it explains the nonexponential annealing behavior of $H4$ in Zn-doped material as well as the peak temperature shift upon annealing and the variation of the FWHM with the filling pulse duration t_p. Moreover, an analysis of the results concerning anisotropic defect introduction rates enabled us to show that both defects ($H4_F$ and $H4_S$) belong to the phosphorus sublattice.

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