PHYSICAL REVIEW B VOLUME 35, NUMBER 8 15 MARCH 1987-I

Electronically stimulated deep-center reactions in electron-irradiated InP: Comparison between experiment and recombination-enhancement theories

Alain Sibille

Centre National d'Etudes des Télécommunications, Laboratoire de Bagneux, 196 avenue Henri Ravera, 92220 Bagneux, France

(Received 18 November 1985; revised manuscript received 31 March 1986)

We present a detailed study of the recombination enhancement of several defect reactions involving the main deep centers in low-temperature electron-irradiated InP. A fairly good agreement is obtained with the Weeks-Tully-Kimerling theory for the activation energies of the enhanced process. On the other hand, a thorough investigation of a thermally and electronically stimulated defect transformation shows evidence that one major approximation (local vibrational equilibrium) fails, and that the recently proposed [H. Sumi, Phys. Rev. B **29**, 4616 (1984)] mechanism of coherent recombination on deep centers is responsible for altered reaction rates at high injection levels.

I. INTRODUCTION

Electron irradiation creates simple primary defects in semiconductors,[1] such as vacancies, interstitials, antisites, etc. Once the collision processes terminate ($\simeq 10^{-13}$ s), these defects can eventually react in various manners, such as Frenkel pair recombination, reconstruction or dissociation, long-range diffusion, and capture of vacancies or interstitials by impurities or native defects, etc. Such reactions can be stimulated thermally, because of the natural thermal energy stored in the lattice at a fixed temperature, or electronically. The latter case involves either conversion of the energy of an electron-hole pair into a vibrational one, through nonradiative recombination,[2] or through excitation of the defect into a spontaneously reacting antibonding state.[3] Such an electronic enhancement has been demonstrated in several semiconductors, both for irradiation defects[4,5] and for impurities[6] or impurity complexes.[7]

The study of electron-irradiation-induced defects in InP has really started only recently, mainly with the deep-level transient spectroscopy technique (DLTS). Briefly summarized, the introduction rates of electron traps in n-type InP are generally weak, and large variations are found depending on the sample origin and diode fabrication procedure.[8–12] In p-type InP, on the contrary, systematic hole traps $H2$—$H4$ (Ref. 13) are produced by the irradiation, in concentrations close to the maximum theoretical limit.[14] Furthermore, it has been shown[15,16] that these centers are descendants of primary V_P-P_i Frenkel pairs on the phosphorus sublattice. Two thermal reaction stages have been evidenced following 77 K irradiations, one below room temperature (RT) (stage I) resulting in secondary formation of these defects, the other above room temperature (stage II), leading to the final annealing out of defects.[16,17] We present here an investigation of the recombination enhancement of these defect reactions (REDR) under minority carrier injection in n^+-p diodes, in relation to the available theories.

The paper is organized as follows. Section II deals with experimental aspects and Sec. III presents experimental results on secondary deep-center formation by thermal or electronic stimulation, following an irradiation at 77 K. Section IV describes the thermal and recombination-enhanced annealing of the dominant deep centers, with emphasis on a defect transformation giving insight into unusual physical phenomena inherent to the recombination process. Section V recalls the available information on the microscopic nature of the observed reactions. The main conclusions of this work are summarized in Sec. VI. Finally, an appendix describes a theoretical approach to the phenomenon of coherent recombination-enhanced defect reactions, from a dynamic point of view.

II. EXPERIMENTAL ASPECTS

Most of the samples used in this work were grown by liquid-phase epitaxy (LPE) of an n^+ layer on a lightly-Zn-doped p-type InP substrate ($p \simeq 5\times10^{16}\ h^+\,\mathrm{cm}^{-3}$ where h^+ represents holes). Photolithographically defined and mesa-etched diodes were then obtained following Au-Ge-Ni and Au-Zn alloying of ohmic contacts. The thermal reactions of stage I were also studied in Schottky barriers on Zn-doped LPE layers or Czochralski bulk InP slices. All irradiations were performed with a Van de Graaff accelerator and low current densities ($< 1\ \mu\mathrm{A\,cm}^{-2}$ at 1 MeV), through a 15-μm Al window in the case of *in situ* irradiations at 77 K in the DLTS cryostat.

III. SECONDARY MECHANISM OF DEFECT FORMATION AFTER 77 K IRRADIATION (STAGE I)

Following 77-K *in situ* irradiation, the usual dominant hole trap $H4$ is found in a subsequent DLTS temperature scan from 77 to 200 K (Figs. 1 and 2), in addition to a weak $H2$ bump detected near 150 K. Heating at 300 K results in a very noticeable increase of $H4$ concentration and the appearance of $H3$ [stage I (Ref. 16)]. Since deep-center formation occurs in the absence of irradiation, we qualify these reactions as secondary. Recombination enhancement can be very efficiently obtained: If, following a 77-K irradiation, minority carriers (electrons) are injected in the diodes below stage I the amplitude of $H4$ is indeed increased (Fig. 2), together with a new dramatic in-

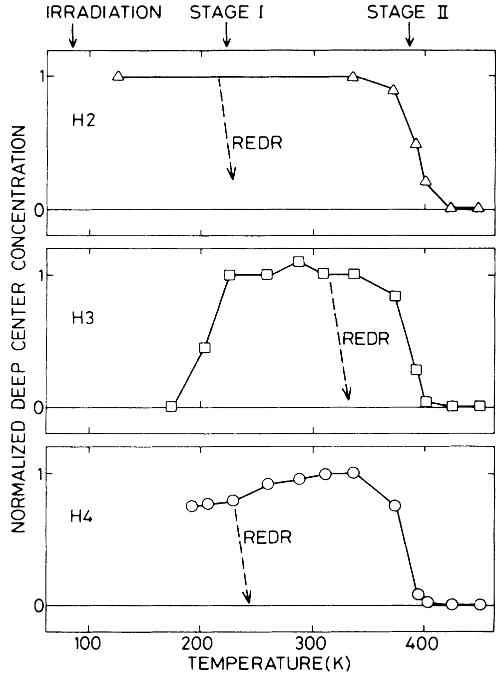

FIG. 1. Isochronal annealing treatments ($\simeq$100 s) of $H2$,$H3$,$H4$ deep centers (charge state empty of hole) following 1-MeV irradiation at 77 K. The annealing of $H3$,$H4$ is, in fact, not perfectly exponential (Ref. 17). For clarity, typical temperatures of stage-II reactions under recombination enhancement are also indicated; they are, however, strongly current density dependent.

crease of $H2$; this latter phenomenon was unobserved by pure heating above stage I.

These experiments indirectly give evidence of the existence of an unobserved defect HX in samples irradiated at 77 K, undergoing a secondary transformation either in $H2$, $H3$, or $H4$ according to the applied treatment, thermal ($HX \rightarrow H3$,$H4$) or REDR ($HX \rightarrow H2$,$H4$). Since no influence of applied reverse bias was observed on stage-I thermal growth of $H4$ the energy level of HX must be either very close to the valence band, or above midgap.

This transformation is in fact a complex phenomenon that was not quantitatively investigated in all of its aspects. The evidence for this is that the REDR growth of $H4$ is nonexponential, as revealed by time-resolved experiments, contrary to that of $H2$ (see both short, $\simeq$ 1 ms, and long, $\simeq$100 ms, time constants in Fig. 3). Furthermore, under strong electron injection, it was observed that $H4$ was not formed in the REDR transformation; in counterpart, the amplitude of $H2$ was particularly large (up to 28% of $H4$ in the final DLTS spectrum stable at 300 K), as expected from elementary conservation laws. A systematic study of the dependence on the various parameters (temperature, current density) could help to clarify the transformation dynamics. However, since HX was not directly detected, no fruitful comparison with REDR models was possible, and such a study was not attempted.

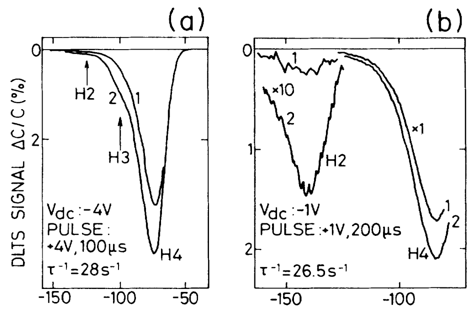

FIG. 2. Typical DLTS spectra of stage-I reactions after 1-MeV irradiations at 77 K. (a): thermal stimulation; 1, just after irradiation; 2, after heating up to 300 K. (b): electronic stimulation; 1, just after irradiation; 2, after subsequent electron injection (1A cm^{-2}, 1.6 s, 77 K).

IV. TRANSFORMATION AND FINAL ANNEALING OF THE MAIN DEEP CENTERS (STAGE II)

A. Thermally stimulated reactions

The thermal annealing of $H2$—$H4$ has previously been investigated in detail.[16,17] Briefly summarized, all three levels anneal out near 100 °C when empty of hole, with a nearly common activation energy $\simeq$1.3 eV and high preexponential factors (Table I). This latter feature shows that the annealing rates are dominated by a local reaction event (i.e., only one or a few atomic jumps).

Previous work[17] has shown that $H3$, $H4$ annealed much more slowly when occupied with a hole. In particular, it has been demonstrated that in neutral p-type InP, $H4$ in fact annealed out faster through the empty state [in spite of an unfavorable reduction factor (hole emission rate)/(hole capture rate)] than in the filled state.

The case of $H2$ is in fact very interesting: This level turns out to anneal only after a preliminary transformation $H2 \rightarrow H3$,$H4$. This phenomenon is nicely evidenced when the heating treatment is performed under O-V bias, whereas $H3$ and $H4$ are then filled with holes and thus anneal very slowly at 85 °C (time constant is 4×10^{5} s for $H4$): this is not the case of $H2$ which is mostly empty at this temperature. The Fermi level in our samples is

TABLE I. Preexponential factor and activation energy of the thermal annealing of the main deep centers empty of hole $H2$,$H3$,$H4$ (stage II). ΔS is the entropy variation assuming a single atomic jump in the reaction event. In the case of $H2$, these parameters relate to the local transformation $H2 \rightarrow H3$,$H4$.

Trap (empty of hole)	Preexponential factor (s^{-1})	$\Delta \frac{S}{k_B}$	E_{th} (eV)
$H2$	4×10^{14}	4.4	1.30
$H3$	5×10^{13}	2.3	1.24
$H4$	2×10^{15}	6	1.32

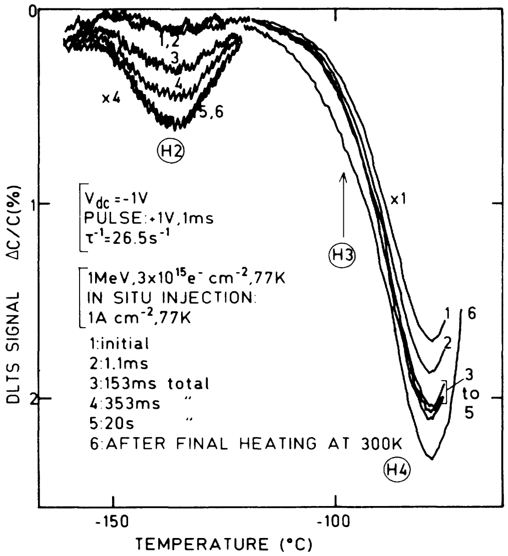

FIG. 3. Time-resolved electronic stimulation of stage-I reactions at 77 K, following a 77-K, 1-MeV *in situ* irradiation ($1 \mathrm{A\,cm^{-2}}$ pulses).

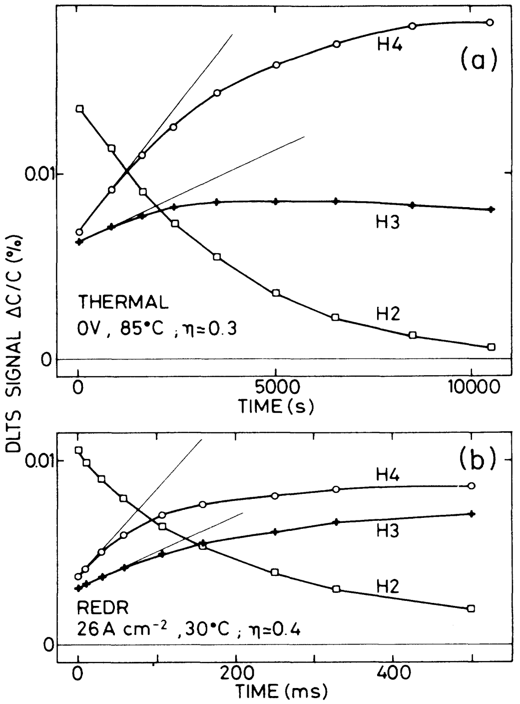

FIG. 5. Kinetics of the $H2 \rightarrow H3,H4$ transformation both for a pure thermal process (a) and for REDR one (b). The branching ratio η is determined by the initial slopes of the curves, since a slight annealing of $H3,H4$ takes places at long times.

indeed situated $\simeq 0.17$ eV above the valence band, that is to say, very near $H2$ whose thermal depth is only 0.19 eV. This fortunate situation enabled us to perform a selective annealing of $H2$ alone. We see in Fig. 4 that the disappearance of $H2$ is thus very clearly accompanied by a simultaneous increase of $H3$ and $H4$ amplitudes (see also Fig. 5). Once again, the high prefactor of this transformation indicates that the moving entity undergoes only one or a few atomic jumps in the process.

B. Recombination enhancement of the reactions: Comparison with the Weeks-Tully-Kimerling theory

Recombination enhancement of stage-II reactions has been very easily achieved in p-type InP.[16,17] The saturation could be obtained for $H4$ (Fig. 6), at a current density depending on temperature ($0.1 A \mathrm{\,cm^{-2}}$ at 173 K and $\simeq 3 \mathrm{\,A\,cm^{-2}}$ at 293 K in our samples). In the case of $H2,H3$, saturation could not be obtained up to at least $30 \mathrm{\,A\,cm^{-2}}$. A comparison of experimental data with theory is particularly easy in the saturated case, where the

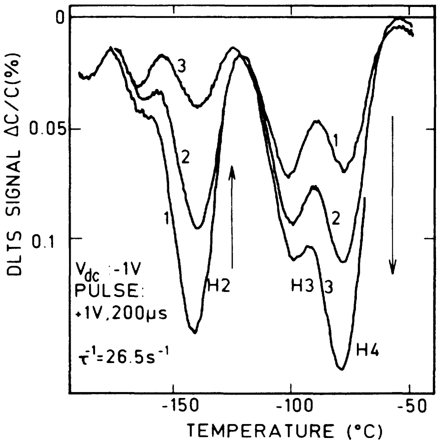

FIG. 4. Thermal transformation $H2 \rightarrow H3,H4$ at 85°C under 0 V. 1, initial (note: $H4$ was subjected to a preliminary REDR anneal leaving $H2$, $H3$ unchanged); 2, after 1600 s; 3, after 5000 s.

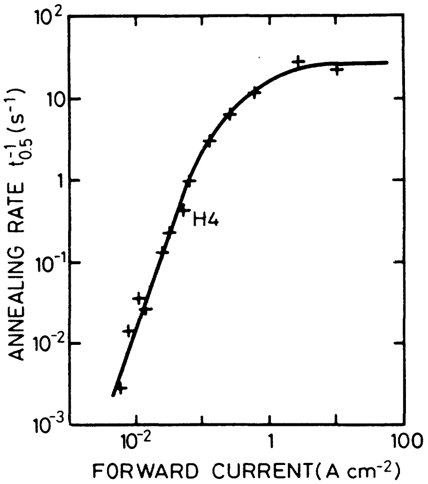

FIG. 6. Forward current density dependence of the recombination-enhanced annealing of $H4$ at 20°C. $t_{0.5}$ is the time necessary to anneal 50% of $H4$. A clear saturation occurs around $3 \mathrm{\,A\,cm^{-2}}$.

injection efficiency plays no role any more and where the only unknown parameter is the majority carrier cross section.

The activation energies and preexponential factors of the recombination-enhanced reactions are indicated in Table II. Also mentioned are the activation energies E_{WTK} predicted by the theory of Weeks, Tully and Kimerling[2] (WTK), determined from the DLTS thermal depth for each level, not taking into account possible activation energies E_σ of capture cross sections. In view of these uncertainties, it is clear that the agreement is reasonably good. In particular, it is satisfying to observe that a difference in E_{REDR} for $H3$ and $H4$ with nearly equal activation energies and that for $H2$ with a much smaller activation energy was observed.

We consequently conclude that nonradiative recombination on the defect is indeed the driving force of these reactions, and moreover that they occur as the result of electron capture on the corresponding trap level $H2$, $H3$, or $H4$ monitored by DLTS. This conclusion is consistent with our discussion of Ref. 17 showing that in the case of $H4$, REDR on $H4$ itself was by far the most probable mechanism, as opposed to another one recently proposed.[3] Furthermore, it is also clear from Table II that *the totality or near totality of the energy* of the trapped-hole—free-electron pair is indeed used to promote the reaction. The main argument proposed in Ref. 18 to criticize WTK theory therefore does not seem to apply here; nevertheless, we will see below that more subtle characteristics of the recombination enhancement are not rendered by WTK theory.

C. "Coherent" recombination of $H2$ and limitations of the Weeks-Tully-Kimerling theory in the H2→H3,H4 transformation

Since we have experimentally found that $H2$ disappeared exponentially, the kinetic equations pertaining to its transformation $H2 \rightarrow H3,H4$ are the following:

$$\frac{d[H2]}{dt}=-(K_3+K_4)[H2],\quad \frac{d[H3]}{dt}=K_3[H2]\ ,$$

$$\frac{d[H4]}{dt}=K_4[H2]\ .$$

Consequently,

$$[H3](t)=[H2(0)]\frac{K_3}{K_3+K_4}\exp[-(K_3+K_4)t]\ ,$$

$$[H4](t)=[H2(0)]\frac{K_4}{K_3+K_4}\exp[-(K_3+K_4)t]$$

and finally

$$\frac{[H3]}{[H4]}(t)=\frac{K_3}{K_4}=\eta\ ,$$

where $[H3]$ and $[H4]$ are the concentrations of levels $H3$ and $H4$ specifically formed by the transformation of $H2$.

Although, in principle, very easy to obtain from DLTS spectra, the determination of η is complicated by two factors

(a) The relation between peak amplitude and deep-center concentration depends on various parameters like level depth and DLTS conditions; however, the uncertainty is not very large, especially for relative measurements ($H3$ versus $H4$).

(b) The above equations implicitly assume a negligible annealing of $H3$ and $H4$. This is a more serious difficulty especially at high temperatures and low current densities (see Fig. 5, for instance, where $H3$, $H4$ are found to anneal slightly at long times).

For that reason, a careful "filtering" procedure was applied to reject the doubtful experiments and ensure with good confidence the reliability of the determined η's. The result of this procedure is shown in Table III, giving approximate values of η at various temperatures and current densities, and for the two stimulations, thermal and electronic. From these data, we can make a few remarks.

(i) Under recombination enhancement, the reaction produces only $H4$ below $\simeq 50\,^\circ\mathrm{C}$, and both $H3$ and $H4$ above: η_{REDR} increases with T (Fig. 7).

(ii) η_{REDR} is smaller at large current densities than at low ones. Before discussing these two points, let us first recall how such recombination enhanced reactions are understood in the framework of WTK theory:[2] The extra vibrational energy ΔE acquired by the center after carrier capture (electron in the present case) is supposed to be in-

TABLE II. Experimental (E_{REDR}) versus Weeks-Tully-Kimerling predicted E_{WTK} (not taking account E_σ activation energies of capture cross sections) activation energies of stage-II reactions under electronic stimulation. E_T-E_V are the trap level depths obtained from the DLTS signature plots and E_{th} the reaction activation energies under pure thermal stimulation (all values in electron volts).

	Trap	E_{th}	E_T-E_V	$E_{\mathrm{WTK}}(E_\sigma)$	E_{REDR}
Nonsaturated REDR	$H2$	1.30	0.19	0.09	0.12
	$H3$	1.24	0.32	0.16	0.24
Saturated REDR	$H4$	1.32	0.37	0.29	0.24

TABLE III. Branching ratio η of the transformation $H2 \rightarrow H3,H4$ at various temperatures T and current densities J, and for both a thermal and an electronic (REDR) stimulation.

	T (°C)	J (A cm^2)	η
Electronic	-97	24	0
Stimulation	-30	26	$\simeq 0.05$
	$+20$	5.2	$\simeq 1.2$
		11.7	$\simeq 0.5$
		26	$\simeq 0.2$
		65	$\simeq 0.2$
	$+30$	26	$\simeq 0.4$
	$+60$	26	$\simeq 0.5$
Thermal	$+85$	0	$\simeq 0.3$
stimulation	$+99$	0	$\simeq 0.4$
	110	0	$\simeq 0.4$

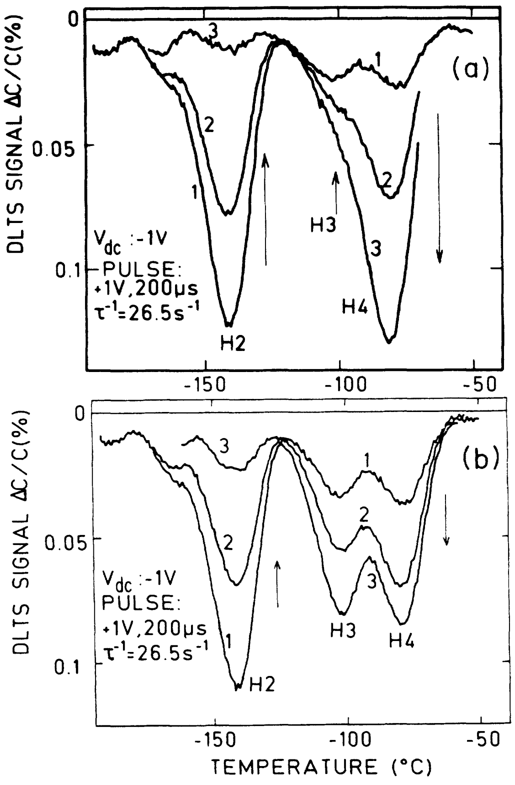

FIG. 7. Electronic stimulation of the transformation $H2 \rightarrow H3, H4$ under 26 $\mathrm{A\,cm^{-2}}$ in two similar n^+p junctions ($p = 5\times10^{16} h^+\,\mathrm{cm^{-3}}$). (a): Transformation at $-80\,°\mathrm{C}$; 1, initial; 2, after 0.5 s; 3, after 2.8 s. (b): Transformation at 30°C; 1, initial; 2, after 0.11 s; 3, after 0.5 s. $H4$ alone is formed at $-80\,°\mathrm{C}$, but both $H3$ and $H4$ are formed at 30 °C.

stantaneously shared by S local modes, thus at once resulting in a statistical equilibrium of the defect. It is the major approximation of the theory, since such an equilibrium cannot be attained in less than a phonon period, i.e., $\simeq 10^{-12}$ s in reality. The next step is then either energy relaxation through random phonon emission, or occurrence of the reaction with the (weak) probability that the energy went into the corresponding mode before vanishing. The result of the calculation is the enhanced rate:

$$K = R\frac{k^{\neq}}{k_{-1}(\bar{E})}\left[\frac{E^* - \Delta E}{E^*}\right]^{S-1} \exp[-(E^* - \Delta E)/k_B T]$$

in the limit $E^* - \Delta E \gg (S-1)k_B T$, for the sake of simplicity. Here R is the recombination rate (i.e., presently electron capture rate on $H2$), $k^{\neq}$ and $k_{-1}(\bar{E})$ are, respectively, rates of energy flow within the defect molecule and towards the lattice, and E^* is the activation energy of the reaction under pure thermal stimulation.

There is no difficulty in including several reaction paths in the theory, each being characterized by its own E^*, the other parameters being identical. Now if one considers ratios of reaction rates such as $\eta_{\mathrm{REDR}} = K_3/K_{4,\mathrm{REDR}}$, one obtains

$$\eta_{\mathrm{REDR}} = [(E_3^* - \Delta E)E_4^*]^{S-1}[(E_4^* - \Delta E)E_3^*]^{-(S-1)} \times \exp[-(E_3^* - E_4^*)/k_B T] \, .$$

Therefore, η_{REDR} may be thermally activated as is indeed apparent from our data [remark (i)]. However, it is also clear from the above expression, that in the framework of WTK theory, η_{REDR} does not depend on R. It is nevertheless, experimentally observed that this result does not hold in the $H2 \rightarrow H3$, $H4$ transformation, as is readily apparent from the dependence of η_{REDR} on the current density J (Table III). It is, in fact, completely unexpected from any theory[2,3,18] or REDR. In simple terms, it seems indeed at first sight logical that once carrier capture is achieved, the preference for the defect to transform into $H3$ or into $H4$ should by no means be influenced by the presence of the other carriers and therefore should not vary with J. (For clarity in the reader's mind let us recall that REDR occurs in a fixed charge state of the defect that corresponds to level $H2$ filled with a hole for a maximum value of the energy release, from Sec. IV B; consequently, a charge state dependence of the transformation rates which would induce a current density dependence of η is irrelevant here.)

In the author's opinion, the answer to this mystery probably lies in a recent theory by Sumi predicting "coherent" recombinations (CR) at high enough carrier densities.[19] The main idea is that once capture of one type of carrier is achieved by a deep center, quasi-instantaneous ($\simeq 10^{-12}$ s) capture of a carrier of the other type (i.e., recombination) can happen, provided there are enough of them present. This last capture would be driven by the extra defect vibrational energy resulting from the first capture, and would take place before the system had relaxed fully through random emission of phonons.

From the calculations of Sumi, the probability of such a coherent recombination is $P_{\mathrm{coh}} \simeq 10(n_2/n_{2T})$ at low injection, where n_2 and n_{2T} are, respectively, the electron concentration (injected in our case) and the effective density of states in the conduction band (5×10^{17} $\mathrm{cm^{-3}}$ at 300 K). Taking low injection textbook formulas,[20] an order of magnitude estimate of the injected electron concentration in our samples is $\simeq 10^{15} e^-\,\mathrm{cm^{-3}}$ under 10 $\mathrm{A\,cm^{-2}}$. From this we deduce $P_{\mathrm{coh}} \simeq 0.02$, which means that only one recombination out of 50 is coherent. Now, and in view of our above remark on the lack of vibrational equilibrium when the reaction starts, it is clear that the probability of reaction must not be the same, whether the electron capture occurs coherently or normally. For instance, in a simple one-dimensional configuration coordinate picture, the defect vibrational energy immediately after a coherent recombination must be larger than after a Schockley-Read one, and therefore the reaction probability higher (Fig. 8).

We can thus write for the probability P_{REDR} of a reaction, after a recombination:

$$P_{\mathrm{REDR}} = (1 - P_{\mathrm{coh}})P_{\mathrm{SR}} + P_{\mathrm{coh}}P_{\mathrm{Sumi}} \, ,$$

where P_{SR} and P_{Sumi} are, respectively, the probability of a reaction in the classical Shockley-Read picture of a

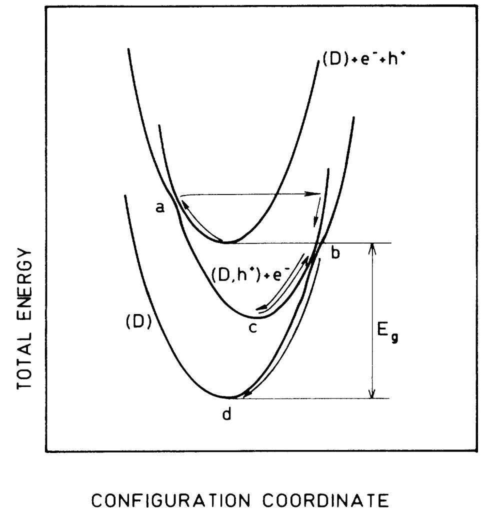

FIG. 8. One-dimensional configuration coordinate diagram for a recombination at a deep level. $(D)+e^{-}+h^{+}$ is the defect with a free-electron–hole pair, (D,h^{+}) is the defect after hole capture, and (D) after recombination. A classical Shockley-Read recombination is described by the $a\rightarrow b\rightarrow c\rightarrow b\rightarrow d$ path, while a coherent recombination follows the $a\rightarrow b\rightarrow d$ path.

recombination and that in the case of a coherent recombination.

In fact, two such expressions can be written for the two possible reaction paths of $H2$; therefore, η_{REDR} is given by the formula

$$\eta_{\mathrm{REDR}}=\frac{(1-P_{\mathrm{coh}})P_{\mathrm{SR}}(H2\rightarrow H3)+P_{\mathrm{coh}}P_{\mathrm{Sumi}}(H2\rightarrow H3)}{(1-P_{\mathrm{coh}})P_{\mathrm{SR}}(H2\rightarrow H4)+P_{\mathrm{coh}}P_{\mathrm{Sumi}}(H2\rightarrow H4)} .$$

At very low current densities, it becomes

$$\eta_{\mathrm{REDR}}\simeq\frac{P_{\mathrm{SR}}(H2\rightarrow H3)}{P_{\mathrm{SR}}(H2\rightarrow H4)}=\eta_{\mathrm{SR}} ,$$

while at very large J, we obtain

$$\eta_{\mathrm{REDR}}\simeq\frac{P_{\mathrm{Sumi}}(H2\rightarrow H3)}{P_{\mathrm{Sumi}}(H2\rightarrow H4)}=\eta_{\mathrm{Sumi}} .$$

The experimental transition between these two regimes is observed near 10 $\mathrm{A\,cm^{-2}}$, and it results in a decrease of η_{REDR} as J increases. Consequently, we obtain the relation $P_{\mathrm{Sumi}}(H2\rightarrow H4)\simeq 50P_{\mathrm{SR}}(H2\rightarrow H4)$ since we assume $P_{\mathrm{Sumi}}>P_{\mathrm{SR}}$ (see Appendix), which nicely stresses the dramatic effect of a coherent recombination on defect reactions.

Finally, a partial confirmation of the present interpretation stems from the current density dependence of the decay rate of $H2$ (Fig. 9), which is superlinear. Such a behavior is indeed expected since when CR processes start to be effective, a rapid increase of the REDR probability should occur (P_{SR} to P_{Sumi} transition).

As a last comment, it is likely that a minor modification of Sumi's theory of recombination enhancement[18] could lead to a good account of the phenomena we discovered. It is indeed a dynamic theory, for which a natural connection with the theory of coherent recombination by the author[19] should be easily established (see Appendix).[21]

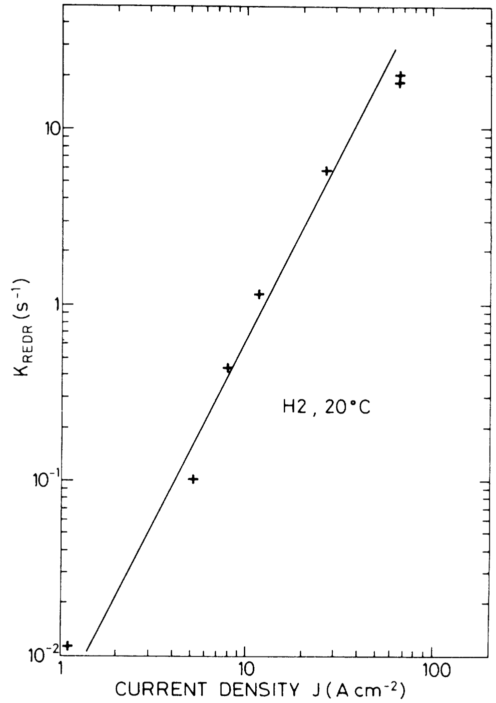

FIG. 9. Injected current density dependence of $H2$ decay rate at 293 K.

V. REMARKS ON THE MICROSCOPIC NATURE OF THE REACTIONS (STAGE I and II)

As it has been shown earlier,[15,16] all the main deep centers $H2$–$H4$ produced by an electron irradiation are due to primary electron-phosphorus nucleus collisions. Moreover, at very low energies, where the only primary defects are the Frenkel pairs V_P-P_i of the phosphorus sublattice, all the reactions presented in this paper are fully obtained. For that reason, we conclude that they all result from the mobility of one of the phosphorus entity P_i or V_p. A model description of all these reactions and others in n-type and p-type InP is discussed elsewhere.[22]

VI. SUMMARY AND CONCLUSIONS

We have presented a detailed study of several secondary defect reactions involving the local mobility of V_{P} or P_i in InP. Two thermal stages have been observed following 77-K irradiations. The first one results in additional deep-center formation, while the second leads to the final annealing of the dominant deep-hole traps. All these reactions could be recombination enhanced, which sometimes qualitatively modified the nature of the reactions. A fairly good agreement was found with the Weeks-Tully-Kimerling theory as far as the reduced activation energies of stage-II reactions under recombination enhancement were concerned. However, a detailed investigation of the REDR deep-center transformation $H2\rightarrow H3,H4$ as a function of temperature and current density has shown qualitative differences with a pure thermal process. We have concluded the following.

(i) Local vibrational equilibrium was not attained within the defect center before the reaction proceeded.

(ii) Coherent recombination at $H2$ modifies the enhanced rates of transformation into $H3$ or $H4$. It is the first time to our knowledge that this mechanism, recently proposed by Sumi,[19] is invoked to explain experimental results.

ACKNOWLEDGMENT

The author is very grateful to M. Gilleron for growing the specially designed epitaxial structures used in this work, and to S. Vuye for diode processing.

APPENDIX: COHERENT-RECOMBINATION-ENHANCED DEFECT REACTIONS IN THE FRAMEWORK OF DYNAMIC THEORIES

The effects described in Sec. IV C can be given a theoretical approach in the framework of the dynamic formalism developed by Sumi.[18,19] The system can exist in three situations: in one (D) the defect is alone with a total energy function V_0; in another, $(\mathrm{D})+h^+ + e^-$ of energy V_1 there is an additional free-electron—hole pair; finally, $(D,h^+)+e^-$ corresponds to the state after hole capture, of energy function V_2. If hole capture occurs at $t=0$, any thermally averaged configuration coordinate $\overline{Q}$, linear combination $\overline{Q}=\sum_\lambda V_\lambda \overline{Q}_\lambda$ of normal lattice modes can be written[19]

$$\overline{Q}(t)=2\sum_\lambda (V_\lambda^2/h\omega_\lambda)[1-\cos(\omega_\lambda t)]$$
$$-[\overline{Q}(0)/D^2]\sum_\lambda (2\eta_\lambda+1)V_\lambda^2\cos(\omega_\lambda t)\ , \qquad \text{(A1)}$$

with the same notations as in Ref. 19; η_λ is the average number of phonons in mode Q_λ and $D=\sum_\lambda(2\eta_\lambda+1)V_\lambda^2$. In a one-dimensional description, the coordinate Q (hereafter labeled Q_p) is chosen to minimize the energy of the second (i.e., electron here) capture along its path. It is, in fact, possible that a coherent recombination was rendered easier along another path than the most favorable one of the Schockley-Read recombination. For the sake of simplicity this possibility, which would necessitate a two-dimensional representation for V_2, will not be discussed further here. The large number of phonons involved in (A1), related to the strong interaction with the whole surrounding lattice will cause a rapid damping relaxation of $\overline{Q}$, achieved in $\simeq 10^{-12}$ s. Now the defect can undergo a transition $(D,h^+)+e^- \to (D)$ in the course of (or after) this relaxation. At each time t a distribution function $R(Q,t)$ can be explicitly defined for the probability density of finding the defect in configuration coordinate Q, as well as probability $P(E)$ of electron capture without reemission. Finally, Sumi's expression for the electron capture rate is

$$W(t)=\frac{2\pi}{h}\frac{n_2}{n_{2T}}\int_0^\infty dE\,T(E)R(E+E_{\mathrm{FC}},t)P(E)$$
$$\times\exp\left[-\frac{E}{k_{BT}}\right]\ , \qquad \text{(A2)}$$

where the integration is on electron energy and the crossing point between V_2 and V_0 is for $Q_p=E_{\mathrm{FC}}$. n_2 and n_{2T} are the electron concentration and the effective density of states in the conduction band, $T(E)$ an explicit function related to the coupling strength between a free-electron state of energy E and the deep electron trap (D,h^+), and E_{FC} the Franck-Condon energy. The transient part of this function (i.e., $t \lesssim 10t_0$, where t_0 is an average phonon period) gives direct access to the probability of coherent recombination:

$$P_{\mathrm{coh}}=1-\exp\left[\int_0^{10t_0} W(t)dt\right]\ ,$$

while the steady part $W(\infty)$ is the Shockley-Read recombination rate. Under low injection, $n_2 \ll n_{2T}$; thus, $W(t) \ll 1/t_0$ and $P_{\mathrm{coh}} \simeq 0$; the reverse is true under high injection.

Now, once capture has occurred at t_c, either pure relaxation can occur, or defect reaction. Therefore, another configuration coordinate Q_R is needed for the easiest reaction path. As above, the system describes a trajectory defined by $(Q_p(t),Q_R(t))$ in a two-dimensional plane. In Sumi's treatment of REDR,[18] $Q_p(t_c)$ has a fixed value, $Q_R(t_c)$ exhibiting a thermal distribution. In the present case, $Q_p(0)$ is also distributed near E_{FC} because of the distribution of electron energies. Moreover, the defect has a finite velocity $dQP/dt(t_c)$ because it has not lost all its initial kinetic energy resulting from the hole capture, in the case of the coherent recombination; the same is true for the coordinate $Q_R(t_c)$ and $dQ_R/dt(t_c)$, whose distribution should also be calculated from their initial values at the moment of hole capture, the average $\overline{Q}_R(t)$ obeying a law similar to (A1) between 0 and t_c. P_{Sumi} is therefore the calculated thermal yield of the REDR, once of these new boundary conditions are taken into account. It is clear that because of this extra kinetic energy, of average value $\overline{E}_{\mathrm{coh}}$ the residual activation energy of the REDR should be roughly reduced by $\overline{E}_{\mathrm{coh}}$, compared to the conventional REDR activation energy of a Shockley-Read recombination. The experimental relation $P_{\mathrm{Sumi}}(H2\to H4)\simeq 50P_{\mathrm{SR}}(H2\to H4)$ thus results in $\overline{E}_{\mathrm{coh}}\simeq 100$ meV, i.e., a factor of 2 smaller than the initial vibrational energy of the defect just after hole capture, close to the trap depth 190 meV of $H2$.

Finally, a short comment applies to the situation described in Sec. IV C, where there are two possible paths $H2\to H3$ and $H2\to H4$ from the same initial defect state $(H2,h^+)$. Likewise, from the discussion on the branching reactions in the WTK theory (Sec. IV C), it is equally possible to define a reaction rate per reaction path and therefore ratios like η. In light of the above discussion, it is clear that P_{Sumi} should always be greater than P_{SR} for a given path. In that specific example, it appears, moreover, that $P_{\mathrm{Sumi}}/(P_{\mathrm{SR}}\ (H2\to H3)$ is not so large as $P_{\mathrm{Sumi}}/P_{\mathrm{SR}}\ (H2\to H4)$, since $\eta=K_3/K_4$ decreases with the current density, i.e., with P_{coh}.

[1] J. Bourgoin and M. Lannoo, *Point Defects in Semiconductor II* (Springer-Verlag, Berlin, 1983).

[2] J. D. Weeks, J. C. Tully, and L. C. Kimerling, Phys. Rev. B **12**, 3286 (1973).

[3] M. K. Sheinkmann, JETP Lett. **38**, 330 (1983).

[4] D. V. Lang and L. C. Kimerling, Phys. Rev. Lett. **33**, 489 (1974).

[5] D. V. Lang and L. C. Kimerling, Appl. Phys. Lett. **28**, 248 (1976).

[6] J. R. Troxell, A. P. Chatterjee, and G. D. Watkins, Phys. Rev. B **19**, 5336 (1979).

[7] R. M. Feenstra and T. C. McGill, Phys. Rev. Lett. **47**, 925 (1981).

[8] M. Levinson, J. L. Benton, H. Temkin, and L. C. Kimerling, Appl. Phys. Lett. **40**, 990 (1982).

[9] P. R. Tapster, P. J. Dean, and M. S. Skolnick, J. Phys. C **15**, L1007 (1982).

[10] J. Suski, J. Bourgoin, and H. Lim, J. Appl. Phys. **54**, 2852 (1983).

[11] S. W. Sun, A. P. Constant, C. D. Adams, and B. W. Wessels, J. Cryst. Growth **64**, 149 (1983).

[12] A. Sibille, Appl. Phys. Lett. **48**, 593 (1986).

[13] A. Sibille and J. Bourgoin, Appl. Phys. Lett. **41**, 956 (1982).

[14] We will not consider here the level labeled $H5$ (A. Sibille and J. Bourgoin, Ref. 13) because it is of a nature quite different from that of levels $H2$—$H4$, as pointed out by a qualitatively different creation mechanism [A. Sibille, J. Suski, and G. LeRoux, Phys. Rev. B **30**, 1119 (1984)].

[15] A. Sibille, J. Suski, and G. Leroux, Phys. Rev. B **30**, 1119 (1984).

[16] A. Sibille and J. Suski, Phys. Rev. B **31**, 551 (1985).

[17] A. Sibille, in Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, 1984 [J. Electron. Mater. **14A**, 1155 (1984)].

[18] H. Sumi, Phys. Rev. B **29**, 4616 (1984).

[19] H. Sumi, Phys. Rev. Lett. **47**, 1333 (1981).

[20] S. M. Sze, *Physics of Semiconductors Devices* (Wiley, New York, 1981).

[21] In the present context, molecular dynamics studies could turn out very fruitful if the nature of the defect and its reactions are known; see P. M. Masri and A. M. Stoneham, J. Electron. Mater. **14A**, 205 (1984).

[22] A. Sibille, J. Suski, and M. Gilleron, J. Appl. Phys. **60**, 595 (1986).