

Irradiation-induced defects in *p*-type GaAs

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Electron irradiation at room temperature in *p*-type vapor-phase-epitaxy-grown GaAs produces a series of traps labeled *H0*, *H1*, *H2*, *H3*, *H4*, and *H5* situated at, respectively, 0.06, 0.25, 0.42, 0.54, 0.79, and 0.85 eV above the valence-band maximum E_v . Their introduction rates as a function of the energy of irradiation and their annealing behavior have been studied using deep-level transient spectroscopy. From a comparison of the introduction rate and the annealing kinetics of *H1* with electron traps produced by irradiation in *n*-type material, we deduced that this trap is associated with the arsenic vacancy-interstitial pair. The other traps (*H2*, *H3*, *H4*, and *H5*) are complexes of impurities with the arsenic interstitial, I_{As} , due to the fact that I_{As} is mobile under irradiation. From the annealing kinetics of these defects we deduce the activation energy associated with the I_{As} mobility (0.5 ± 0.15 eV) in *p*-type GaAs. Finally, we also demonstrate that the *E* traps situated at 0.045, 0.140, 0.30 eV below the conduction-band minimum (labeled *E1*, *E2*, *E3*, respectively) present in electron-irradiated *n*-type GaAs are also present in *p*-type material and we have verified that these defects have the thermal stability expected from studies in *n*-type GaAs, i.e., associated with the charge-state effect.

I. INTRODUCTION

The defects introduced by electron irradiations in GaAs have been the subject of a large number of works.¹⁻⁴ However, most of the studies have concentrated on the defects produced in *n*-type material. It has been demonstrated that these defects, labeled *E1*, *E2*, *E3*, *E4*, and *E5* and situated at $E_c - 0.045$ eV, $E_c - 0.140$ eV, $E_c - 0.30$ eV, $E_c - 0.76$ eV, and $E_c - 0.96$ eV, respectively, are intrinsic defects (i.e., related to vacancy and interstitial) for the following reasons. First, their introduction rate does not depend on the temperature between 4 and 300 K (Ref. 4) and is the same whatever the concentration and nature of the impurities contained in the materials,⁵ i.e., is independent on the nature of the material [Czochralski (CZ), vapor-phase-epitaxy (VPE), liquid-phase-epitaxy (LPE) grown] and on the doping concentration and nature. This strongly suggests that the defects do not interact with the various impurities contained in the material, i.e., remain unchanged after their creation. Second, the observed introduction rate is of the order of the calculated number of displacements produced by the irradiation, which can be performed after the threshold energy T_d for displacement, i.e., the minimum energy transmitted to a lattice atom (~ 10 eV) to produce a defect, has been determined.⁶⁻⁸ Third, annealing kinetics which is first order, and the amount of annealing of these defects (> 90%) which occurs around 200°C is consistent with only a situation: the recombination of vacancy-interstitial (*V-I*) pair.⁹ The sublattice As or Ga, at which these *V-I* pairs belong to has been determined. A study of the orientation

dependence of the introduction rate of all the *E* defects has shown a strong anisotropy due to the interaction of the primary defect knockon atom with its nearest neighbors of different nature. The result of this study is that the *E* defects are associated with defects in the arsenic (As) sublattice.^{10,11} This conclusion has been confirmed by a study of the variation of their introduction rate in $Ga_{1-x}Al_xAs$ alloy¹² since the introduction rate of the *E* defects is found to be independent of x . Consequently, because there are several *E* levels (*E1* and *E2* are two levels of the same defect) associated with different defects (since they have different introduction rates or different thermal behavior), the *E* defects are thought to be related to a distribution of $V_{As}-I_{As}$. As to $V_{Ga}-I_{Ga}$ pairs which are undoubtedly created by the irradiation, it is thought that they recombine directly after their creation, due to Coulomb attraction.⁴

The electronic properties of the *E* defects are reasonable known from deep-level transient spectroscopy (DLTS) studies. Their electrical energy levels have been determined and some of the associated electronic capture cross section for majority carriers has been measured [for *E3* (Refs. 13-15), *E2* (Ref. 4), and *E1* (Ref. 16)]. As to the optical capture cross sections, they have been studied for the defects *E1*, *E2*,¹⁷ and *E3*,¹⁸ allowing one to estimate the Franck-Gordon shift d_{Fc} for these three defects. Finally the annealing behavior of these defects has been extensively studied, illustrating the effect of defect charge state on the annealing of *E2* and *E3* (Ref. 19) (the defects do not anneal when they are empty) or the annealing of *E2*, *E3*, and *E5* by injection of minority carriers.²⁰⁻²²

The conclusion that the defects created are $V_{As}-I_{As}$ pairs is apparently in contradiction with the fact that complex defects such as $B-I_{As}$ (Ref. 23) and $C-I_{As}$ (Ref. 24) have also been observed, as well as the creation of the As_{Ga} antisite²⁵⁻²⁸ with an introduction rate which cannot be explained by a direct displacement of impurities of direct exchanges. The formation of these complexes involve the mobility of I_{As} . This contradiction is only apparent. Indeed, the conditions where the E defects are observed by DLTS are the following: the dose is sufficient to obtain a concentration of defects $\sim 0.1n$ (n is the concentration of free carriers) i.e., the material remains n -type and a low dose is used ($\sim 10^{15}$ and 10^{16} cm⁻²). On the contrary, the complexes are observed by ir absorption on localized vibrational modes and the antisites by EPR: Both techniques imply larger doses ($\sim 10^{17}$ and 10^{18} cm⁻²) and a material which is compensated, i.e., no more n type. The observations at low dose and high dose can be reconciled by assuming a low mobility of the I_{As} under irradiation: For low doses (DLTS) the diffusion length of I_{As} is short and the irradiation results in a distribution of $V_{As}-I_{As}$ pairs; large doses (EPR, ir) imply a larger diffusion length and consequently the possibility of I_{As} to be trapped on impurities forming complexes or making a reaction which creates As_{Ga} antisites.

Finally, some complexes, associated with I_{As} have been created by electron irradiation at high temperatures,^{29,30} i.e., temperatures greater than 200°C, a temperature at which I_{As} is thermally mobile, allowing it to escape and migrate in the material.

In p -type material, the situation is apparently more complex and few studies have been performed. The defects are labeled $H0$, $H1$, $H2$, $H3$, $H4$, and $H5$, situated at $E_v + 0.06$ eV, $E_v + 0.25$ eV, $E_v + 0.42$ eV, $E_v + 0.54$ eV, $E_v + 0.79$ eV, and $E_v + 0.85$ eV, respectively. Some of these defects have been detected in n -type GaAs under injection of minority carriers.³¹ The introduction rates have been studied versus the orientation and the energy of irradiation for only the defects $H0$ and $H1$, showing that these defects originate from the As sublattice,⁷ and only Lang³² has said that $H1$ anneals in a similar fashion than $E3$ and $E5$, i.e., around 200°C. The other defects, contrary to the n -type case (i.e., even upon low doses of irradiation), have a nature and a concentration which depend strongly on the type and doping of the material,³³ suggesting they are complex defects, formed by the association of primary defects with the impurities contained in the material. It therefore seems natural to think that I_{As} is more mobile under irradiation in p - than n -type GaAs. In order to confirm this picture, several questions have to be answered: What are the complex defects formed in p -type material? Are the E defects ($V_{As}-I_{As}$ pair) present in p materials?

The aim of this paper is to describe some of the main missing information in order to answer these questions. For this, using the DLTS technique, we have studied (1) the introduction rate of the defects versus the energy of irradiation, (2) the kinetics of annealing of the H defects, and a comparative study with the annealing kinetics of the E defects, (3) the existence of the E defects in p -type GaAs (using injection of minority carriers), (4) the

thermal stability of the E defects, in p -type material, i.e., the charge-state effect on their annealing behavior. We have obtained the following results.

(1) The E defect, i.e., arsenic $V-I$ pair are present in p -type material.

(2) The traps $H0$ and $H1$ are also related with the arsenic $V-I$ pair.

(3) The $H2$, $H3$, $H4$, and $H5$ defects are complexes, involving I_{As} , and impurities contained in the material.

(4) The thermal annealing of the complex defects occurs through the mobility of the I_{As} in p -type GaAs (the associated activation energy being 0.5 eV).

(5) The charge-state dependence of the thermal stability of the E defects is in agreement with an extrapolation of their behavior found in n -type material.

II. EXPERIMENTAL TECHNIQUES

The samples used in this work are p -type VPE GaAs, doped typically with 2.5×10^{16} Zn cm⁻³. Before irradiation, only one main trap is detected by DLTS measurement. Its associated energy level is $E_v + 0.5$ eV, its capture cross section $\sigma_{P\infty}$, deduced from the extrapolation of the signature (variation of the emission rate versus the temperature) to $T^{-1} = 0$ is 1.4×10^{-16} cm², and its concentration is $\sim 10^{15}$ cm⁻³. This defect is the well-known HL3 trap,^{34,35} said to be associated with iron. An annealing at 220°C during 30 min shows this defect is stable at this temperature.

The samples were irradiated by electrons at room temperature, in the energy range 0.5–1.25 MeV and fluence range 2×10^{15} – 10^{16} cm⁻², with a flux of 2×10^{12} e⁻ cm⁻² s⁻¹. The thermal annealings were performed from 190°C to 220°C \pm 2°C under helium atmosphere. The temperature rise and decay time of the sample were minimized by introducing the sample in the oven, regulated at the desired temperature, and pulling it out of the oven under a flux of cold nitrogen.

III. EXPERIMENTAL RESULTS

A. Irradiation

The irradiation introduces five hole traps, labeled $H1$ – $H5$. Figures 1 and 2 show, respectively, a typical DLTS spectrum and the signatures of the traps. The $H0$ is not observed in these figures, because it gives rise to a DLTS peak at 50 K. The activation energy and the capture cross section of each defect are reported in Table I. A comparison is made with the previous works of Mitonneau *et al.*,³⁶ Loualiche *et al.*,³³ and Pons *et al.*⁴ We have not especially studied $H0$, which has been extensively studied by Pons.⁴ The $H2$ peak is apparently composed either after irradiation or during annealing of two peaks, labeled $H2'$ and $H2''$, as shown in Fig. 3. The activation energies and capture cross sections of the two peaks are given in Table I.

This $H2$ peak usually associated with a complex defect involving copper³⁷⁻³⁹ ($E_v + 0.40$ eV, 5.6×10^{-15} cm²) appears to be made of two components (this will be confirmed by annealing studies).

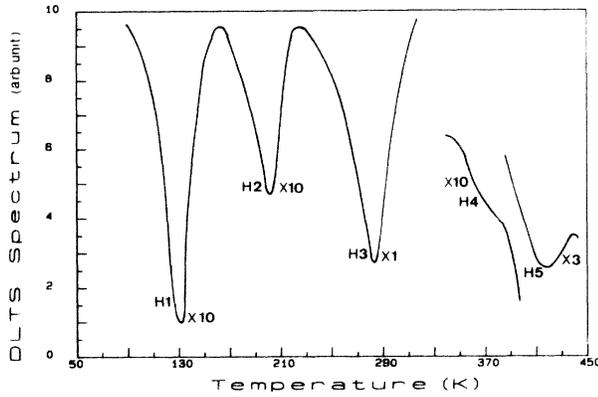


FIG. 1. Typical DLTS spectrum observed in VPE *p*-type GaAs (doped with $2.5 \times 10^{16} \text{ Zn cm}^{-3}$) after 1 MeV electron irradiation ($2.5 \times 10^{15} \text{ e}^- \text{ cm}^{-2}$ dose).

The peak *H3* is usually associated with iron (defect HL3). But, a comparison of the signatures shows (Fig. 4) that the two defects HL3 (before irradiation) and *H3* (after irradiation) are different since although they have about the same activation energy (0.50 eV), they do not have the same capture cross section (see Table I). So, it is clear that there is a defect *induced* by the irradiation which gives a DLTS peak superimposed to the HL3 one. The study of the thermal annealing of trap *H3* will confirm this conclusion.

Figure 5 shows the different introduction rates, the ratio of the concentration of the defect N_T over the fluence, versus the energy of irradiation, for the defects *H1*–*H5*. We observe that the *H1* trap exhibits a saturation around 1 MeV. It has the same behavior as that of the *E* defects in *n*-type material, i.e., follows the theoretical law of the displacement cross section versus energy. On the contrary, the defects *H2*, *H3*, *H4*, and *H5* have a quasilinear introduction rate, i.e., not the behavior expected for primary defects.

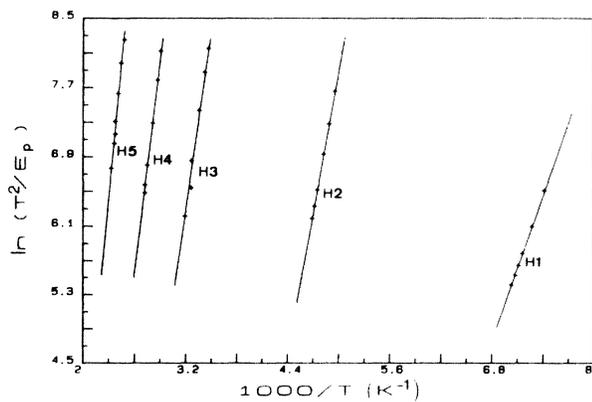


FIG. 2. Variation of emission rate versus the temperature (signature) for the defects detected after electron irradiation in VPE *p*-type GaAs.

TABLE I. Activation energies ΔE and capture cross sections σ_p of the defects created by electron irradiation in GaAs.

Loulache <i>et al.</i> (Ref. 33)			Mitonneau <i>et al.</i> (Ref. 36)			Pons <i>et al.</i> (Ref. 4)			This work		
σ_p (cm ²)	ΔE (eV)	Labels	σ_p (cm ²)	ΔE (eV)	Labels	σ_p (cm ²)	ΔE (eV)	Labels	σ_p (cm ²)	ΔE (eV)	Labels
8.3×10^{-15}	0.25	<i>H1</i>	2×10^{-15}	0.29	<i>H1</i>	1.4×10^{-15}	0.25	<i>H1</i>	1.4×10^{-15}	0.25	<i>H1</i>
5.6×10^{-15}	0.40		2×10^{-16}	0.41	<i>H2(A)</i>	1×10^{-14}	0.42	<i>H2(A)</i>	1×10^{-14}	0.42	<i>H2</i>
						2.5×10^{-15}	0.36		2.5×10^{-15}	0.36	<i>H2'</i>
						6.9×10^{-15}	0.44		6.9×10^{-15}	0.44	<i>H2''</i>
1.3×10^{-15}	0.51	HL3	1.3×10^{-15}	0.53	<i>L15</i>	7.4×10^{-16}	0.54		7.4×10^{-16}	0.54	<i>H3</i>
						1×10^{-16}	0.50		1×10^{-16}	0.50	HL3
1.2×10^{-14}	0.71	HL2	1.2×10^{-14}	0.71	HL2(HB2, HS2)	6.8×10^{-14}	0.79	<i>H3(B)</i>	6.8×10^{-14}	0.79	<i>H4</i>
			1.7×10^{-13}	0.83	HL10	9×10^{-15}	0.85		9×10^{-15}	0.85	<i>H5</i>

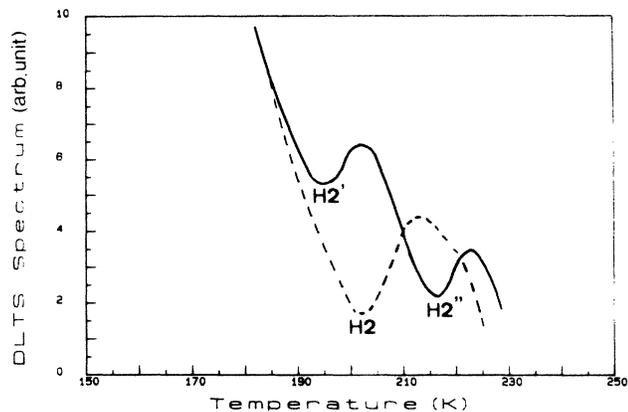


FIG. 3. Typical spectrum and signature of the $H2$ defect showing it is actually the sum of two traps $H2'$ and $H2''$.

B. Annealing

In order to obtain detailed information (activation energy and preexponential factor) on the annealing kinetics, and to determine the order of the reaction, isothermal annealings have been performed at different temperatures. The results are given in Figs. 6, 7, and 8 for $H1$, $H3$, and $H4$. As shown in Fig. 7 the defect $H3$ does not anneal completely; this is simply due to the presence of the trap $HL3$ which is superimposed to $H3$. The defect $H3$ anneals and the concentration of the remains is associated with $HL3$, which we verified, is stable at the temperatures used for these annealings ($\sim 200^\circ\text{C}$). Analysis of the peak shows clearly that $H3$ is replaced by $HL3$ at the end of annealing. The defect $H2$ has not been studied because, during the annealing, its two components $H2'$ and $H2''$, which appear as shown on Fig. 3, have relative concentrations which vary in a manner we are not able to understand.

The defect $H5$ which appears as a shoulder of another peak was not studied because its concentration is difficult to measure quantitatively. For the same reason the results concerning the trap $H4$, which appears on a shoulder on

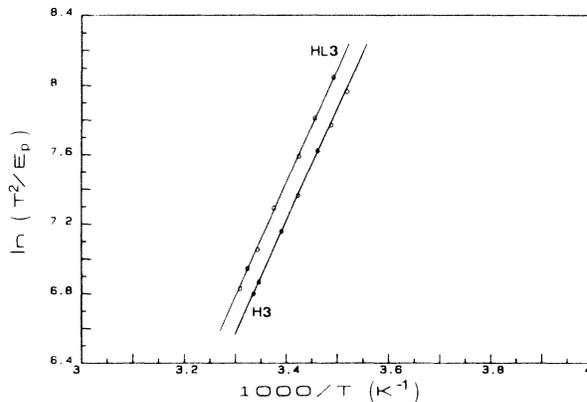


FIG. 4. Comparison of the signatures of the defects $HL3$ (present before irradiation) and $H3$ detected after irradiation.

peak $H5$, are only approximate. The linear dependence of the logarithm of the concentration N_T of these traps with the time of annealing indicates that the reaction is governed by first-order kinetics. Each of the reactions can be clearly separated into two different first-order kinetics,

$$N_T(t) = N_T e^{-\nu t} \quad (1)$$

with

$$\nu = \nu_0 \exp(-\Delta H/kT). \quad (2)$$

We have determined ν_0 and ΔH for each part of the kinetics. The values are given in Table II for each trap and compared with previously published results for the E traps.⁵ As already mentioned, the kinetics of annealing of the trap $H0$ has not been studied. We have only measured its concentration after annealing and verified that it anneals quite completely around 200°C . Table III gives the concentration of $H0$ (normalized after irradiation) versus time and temperature of annealing.

The important fact is that the annealing kinetics allow one to distinguish two groups of defects: the first one, related to $H1$, whose annealing rate corresponds to an activation energy of ~ 1.3 eV, with a preexponential factor $\nu_0 \sim 10^{10} \text{ s}^{-1}$, and the second one, related to $H3$ and $H4$, whose annealing rate has an activation energy of 0.5 eV and a preexponential factor of a few 10^2 s^{-1} .

C. Observation of minority carriers traps

Since $H0$ and $H1$ present the same annealing behavior (identical order of kinetics and ΔH and ν_0 values) as that of the E traps, which are known to be related to the arsenic $A_{As}-I_{As}$ pair, this strongly suggests they are also related to the same primary defects, i.e., that the $V_{As}-I_{As}$ pair is also present in p -type material. It is then reasonable to think that the E defects are also created in p -type GaAs. As we have recalled in Sec. I, some of the H traps are

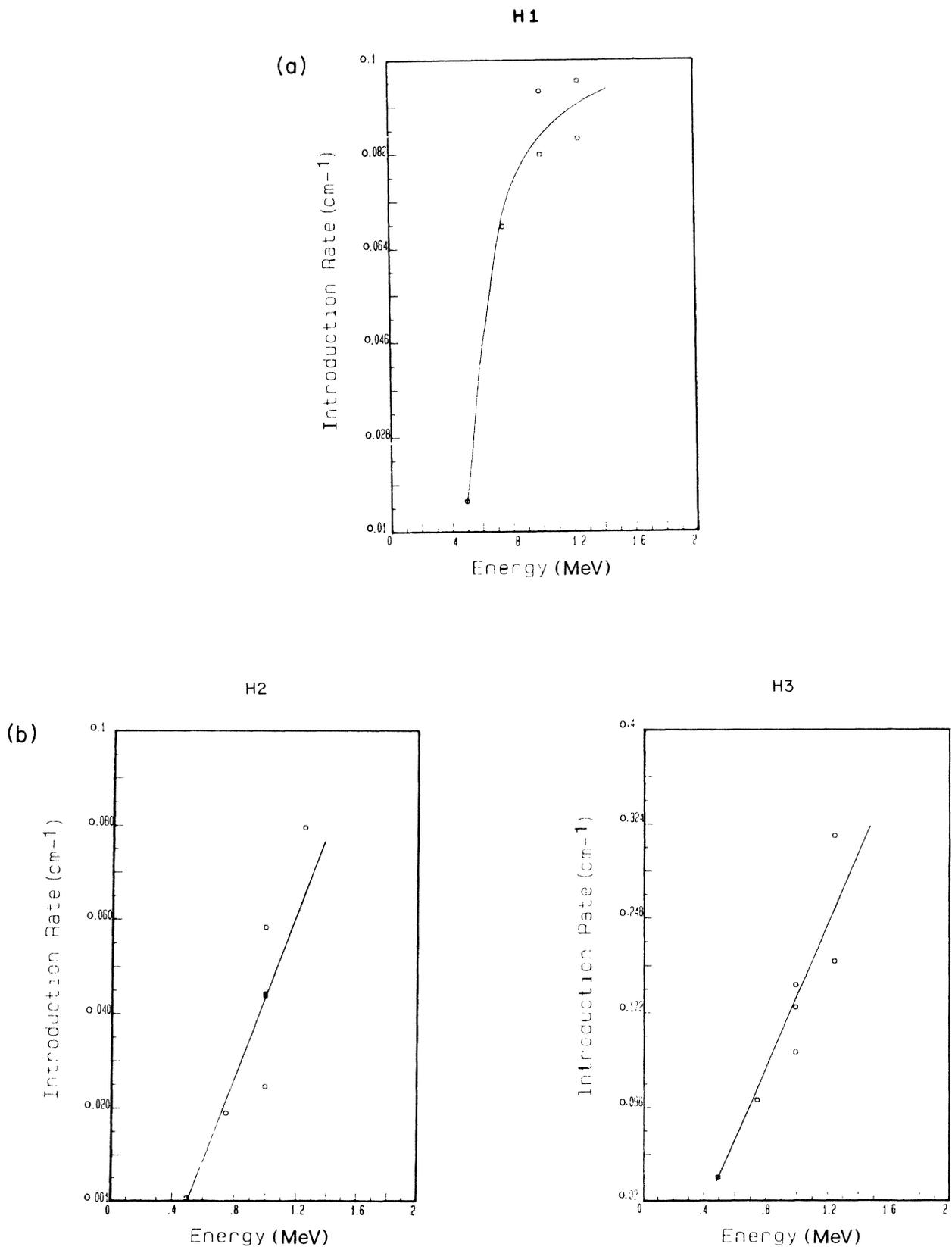


FIG. 5. Introduction rates of the various defects created by electron irradiation in *p*-type GaAs versus the energy of irradiation.

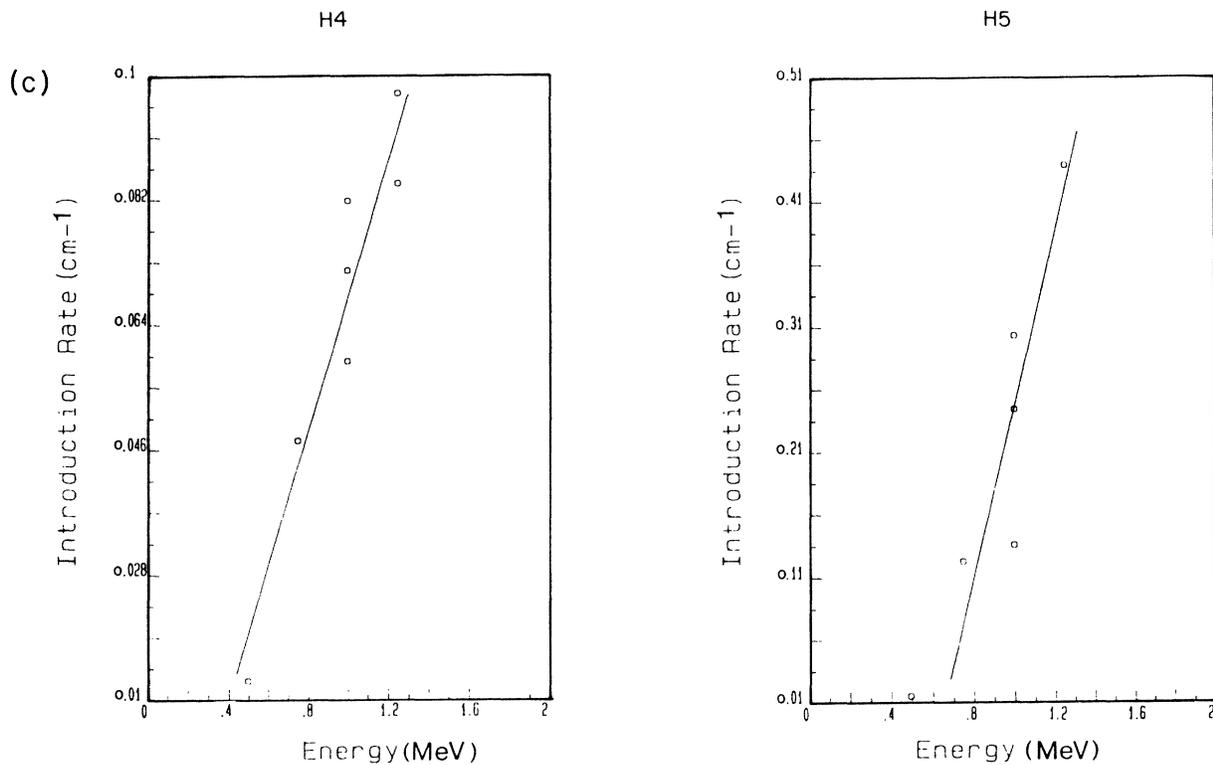


FIG. 5. (Continued).

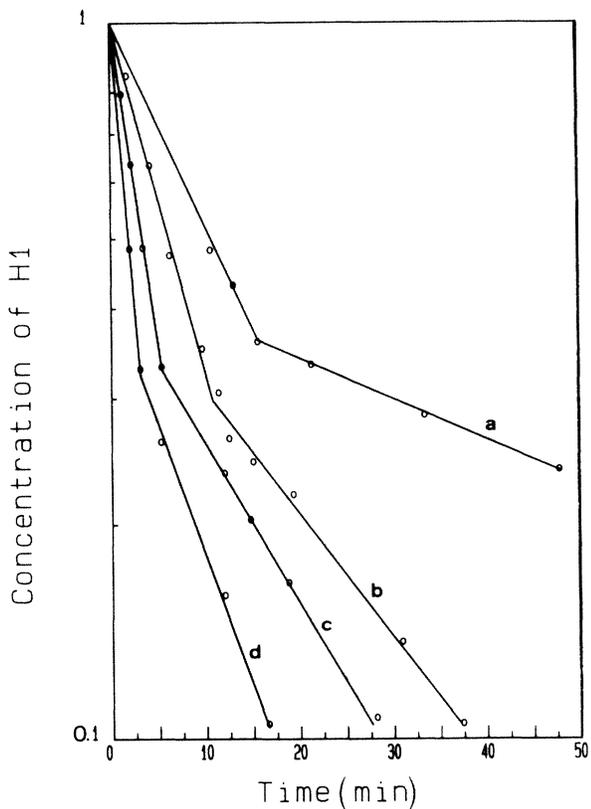


FIG. 6. Isothermal annealing of the defect *H1* at different temperatures (*a*: 190°C, *b*: 200°C, *c*: 210°C, *d*: 220°C).

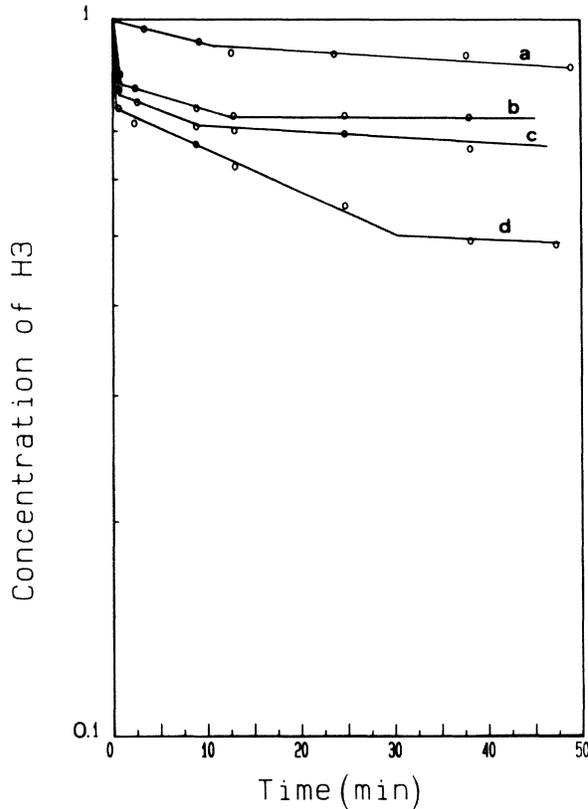


FIG. 7. Isothermal kinetics of the defect *H3* at different temperatures (*a*: 190°C, *b*: 200°C, *c*: 210°C, *d*: 220°C).

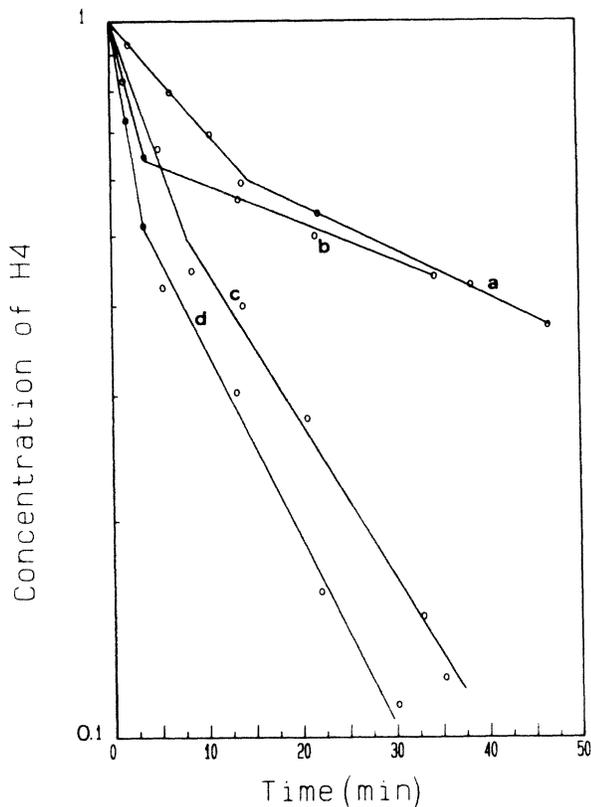


FIG. 8. Isothermal kinetics of the defect $H4$ at different temperatures (a ; 190°C, b : 200°C, c : 210°C, d : 200°C).

indeed observed ($H0$, $H1$) in n -type material, detected by DLTS using injection of minority carriers. We therefore attempted the detection of E traps in p -type materials.

Figure 9 shows a typical DLTS spectrum observed in p -type material under injection. One can see the two principal defects $E1$ and $E2$ (at 25 and 60 K). The peaks observed exhibit a large width: this is due to the effect of the electric field (phonon-assisted tunneling emission)^{16,40} on the emission rate, an effect which cannot be reduced in case of injection. We also detected a peak where $E3$ (180 K) should be. We verified this peak is associated to $E3$ by measuring the signature of this trap (Fig. 10): We found values $E_c - E_T = 0.34$ eV and $\sigma_n = 1 \times 10^{-14}$ cm²; values in good agreement with the electrical characteristics of the defect $E3$ determined in n -type material.⁴ Two other peaks appear, at a temperature where $E4$ and $E5$ should be present. Unfortunately, the DLTS measurements did not provide accurate values for the energy level and the capture cross section of these peaks because of the presence of the majority trap $HL3$, in the same temperature range which has a large concentration that is very important in comparison with the one from the $E4$ and $E5$ traps.

We have also studied the thermal stability of the E defects in p -type materials. As it is difficult to measure absolute value of concentrations under injection, we have performed only relative measurements, i.e., a comparison between the concentration of the defect $H0$ and of the E

TABLE II. Activation energies ΔH and preexponential factors ν associated with the thermal annealing rates for the defects $H1$, $H3$, and $H4$ and comparison with the defects $E4$, $E3$, $E5$, $E2$, and $P3$.

	$H1$ (part 1)	$H1$ (part 2)	$H3$ (part 1)	$H3$ (part 2)	$H4$ (part 1)	$H4$ (part 2)	$E4$	$E3, E5, E'2$	$E''2$	$P3$
ΔH (eV)	1.1 ± 0.2	1.3 ± 0.2	0.50 ± 0.15	0.51 ± 0.15	0.52 ± 0.15	~ 0.5	1.5 ± 0.2	1.55 ± 0.15	1.6 ± 0.15	1.5 ± 0.5
ν (s ⁻¹)	5×10^8	3×10^{10}	600	155	300	~ 100	$10^{13 \pm 1}$	$10^{13.5 \pm 0.5}$	$10^{12.5 \pm 0.5}$	$10^{9 \pm 1.5}$

TABLE III. Normalized concentration of *H0* after various thermal annealing treatments.

Temperature of annealing (°C)	190	200	210	220	
Time of annealing (min)	0	25	25	30	
Concentration of <i>H0</i>	1	0.075	0.1	0.1	0.9

defects during annealings. Table IV gives the concentration of *E2* following two annealing steps at 200°C and 220°C, after 25 min (the concentration is normalized to one after irradiation). We observe that the defect *E2* does not anneal. In the same way, just by observing the relative amplitudes of the DLTS peaks, we can say that *E1* and *E3* do not anneal. As to the *E4* and *E5* traps, their concentration is too difficult to measure (due to the presence of *HL3*) to be sure that the same conclusion applies. Thus, on the contrary to the case of *n*-type GaAs, the defects *E1*, *E2*, and *E3* do not anneal in *p*-type materials.

IV. DISCUSSION

A. Introduction rate

From the study of the introduction rate, we learn that:

(1) *H1* follows exactly the same behavior as that of *E5* (see Pons⁷), i.e., the same introduction rate versus the energy of irradiation. This suggests that *H1* is related to a primary defect like *E5*. Since as shown by Pons,⁷ *H1* has also the same orientation dependence of the introduction rate versus crystallographic orientation, we can conclude that *H1* is associated with the $V_{As}-I_{As}$ pair. Because their concentrations are identical they could be both asso-

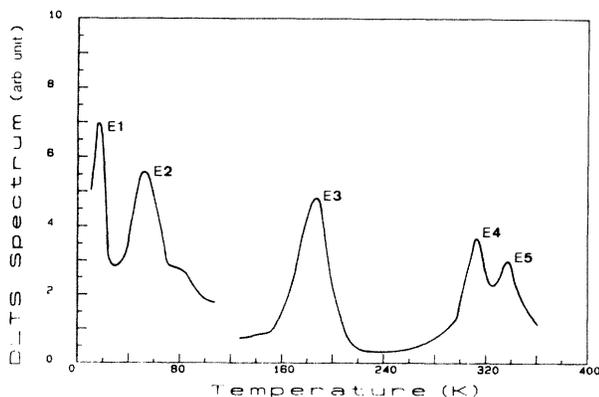


FIG. 9. Typical spectrum of the *E* defects detected in *p*-type GaAs under injection of minority carriers. (Typical polarization: bias of 0 V, and pulse of 3 V height and 100 μ s width.)

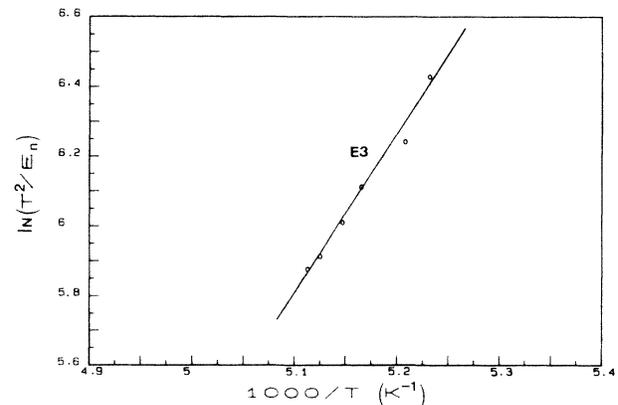


FIG. 10. Signature of the defect *E3* detected in *p*-type GaAs under injection of minority carriers.

ciated with the same defect, i.e., be two different levels of the same defect.

(2) *H2*, *H3*, *H4*, and *H5* do not exhibit at all the same behavior, i.e., do not follow the theoretical variation of the cross section for displacement versus the energy of irradiation as would be the case for primary defects or for complex defects in case their time of formation is short compared to the time of irradiation.

This behavior suggests that (i) *H2*, *H3*, *H4*, and *H5* are complex defects and (ii) their formation depends on the conditions of irradiation.

By analogy with the case of *n*-type material, we can assume that these complexes are formed by the association of I_{As} with some impurity and that the mobility of I_{As} depends on the conditions of irradiation. This mobility is rather low since the existence of *H0* and *H1* shows that after irradiation there still exist primary $V_{As}-I_{As}$ pairs. However they are more mobile than in *n*-type material (i.e., the mobility depends on Fermi level position) since, in this case, after a low dose of irradiation, there are only primary defects present.

Such a situation is not particular to GaAs, but rather a general case. In germanium, the recovery of the $V-I$ pair, associated with the mobility of the interstitial,^{41,42} is greater in *p* type than in *n* type. But, ionizing radiation (due to electron irradiation or light illumination) can in-

TABLE IV. Normalized concentration of *E2* in *p*-type material after various thermal annealing treatments.

Temperature of annealing (°C)	200	220
Time of annealing (min)	25	25
Concentration of <i>E2</i>	0.096	1.0

duce the recovery of the $V-I$ pair, stable up to 65 K in n -type, at low temperature (4 K).⁴⁴ In silicon the interstitial is mobile at 4 K, so that the $V-I$ pair cannot be observed even after irradiation at low temperatures.

Such low-temperature mobility is interpreted⁴⁵ by an athermal migration via an ionization enhanced migration.^{45,46} The existence of such a mechanism for migration cannot be verified for the self-interstitial since it has never been observed. However it is directly verified in the case of boron interstitial in silicon which is observed by EPR and whose lattice configuration changes from a bond-centered interstitial configuration to a split $\langle 100 \rangle$ interstitial configuration when its charge state changes from Bi^+ to Bi^- .⁴⁷

Such athermal mobility is a function of the rates for trapping electrons and holes and therefore, depends on their relative concentrations, i.e., on the level of injection of the minority carriers by the irradiation. Since the concentration of injected carriers $\Delta p = (\Delta n)$ is⁴

$$\Delta p = E\tau\phi | RW, \quad (3)$$

where E and ϕ are the irradiation energy and flux, R the range (~ 1 mm for 1 MeV in GaAs), W the average energy required to form an electron-hole pair [$W=4.5$ eV in GaAs (Ref. 48)], and τ the lifetime ($\sim 10^{-7}$ s), the mobility of I_{As} is proportional to the energy of irradiation E .

When the mobility is low enough, then the number of complexes formed is also proportional to E . Indeed, let us consider the number $N(t)$ of I_{As} which diffuse to sinks, X impurities (i.e., acting as spherical traps of radius r_0) to create complexes $X-I_{\text{As}}$. Both the interstitials and the sinks are randomly distributed and the sink concentration is large compared to the interstitial concentration. The number of defects which disappear in the sinks per unit time is proportional to the number of interstitials $N(t)$ present at time t :

$$\frac{dN}{dt} = -KN, \quad (4)$$

that is,

$$N(t) = N_0 e^{-Kt}, \quad (5)$$

where the rate constant K is proportional to the diffusion coefficient D of the interstitials,

$$K = \beta D, \quad (6)$$

the coefficient β depending on the geometrical shape of the sinks.

As shown in Ref. 49 the number of complexes formed (6) at a time t is proportional to Dt . Since D is proportional to Δp , then $N(t)$ is proportional to E according to (3).

In conclusion, the experimental behavior of the introduction rate of the defects $H2$, $H3$, $H4$, and $H5$ (linear with the energy of irradiation) can be understood as a consequence of the formation of complexes $I_{\text{As}}-X$, through the diffusion of the I_{As} driven by the ionization produced by the electron beam.

The validity of this picture will now be verified by the analysis of the kinetics of thermal annealing.

B. Thermal behavior

The results described in this section concerning the thermal behavior of the traps $H1$, $H2$, $H3$, $H4$ and $H5$ show also that these defects have to be classified in two groups, with regard to the activation enthalpy energy ΔH and to the preexponential factor ν_0/N_j associated with these thermal annealing rates⁵⁰

$$\nu = (\nu_0/N_j) \exp\left[\frac{\Delta S}{k}\right] \exp\left[-\frac{\Delta H}{kt}\right], \quad (7)$$

where ΔS is the entropy changes associated with the migration process, ν_0 is a lattice frequency ($\nu_0 = 6 \times 10^{12}$ s⁻¹ for GaAs), and N_j is the average number of jumps before annealing.

The kinetics of $H1$ is the sum of two first-order kinetics which have the same activation energy, ~ 1.3 eV. This value is equal, within experimental accuracy, to the activation energy found for the E defects. The preexponential factor, $\sim 10^{10}$ s⁻¹, is also in the same range as that of the E defect. As demonstrated by Pons *et al.*,⁵ these values are characteristics of the recombination of close $V-I$ pairs. The trap $H1$ having identical kinetics is therefore also related to such a pair. The fact that the kinetics is the sum of two first-order kinetics, with the same activation energy is explained by an effect of the charge state of the defect. As described by Pons, this is also the case for the $E2$ defect.¹⁸ It is therefore possible that $H1$ and $H2$ are two levels of the same defects. The difference between their introduction rate (1.5 cm⁻¹ for $E2$, 0.1–0.2 cm⁻¹ for $H1$) can be explained by the fact that they are measured in different types of materials (n and p , respectively), where the behavior of the interstitial is different. I_{As} being more mobile in p type, the concentration of pairs which remain after irradiation is smaller in p type than in n type.

As to the other defects, $H3$ and $H4$, they anneal also with first-order kinetics, but with an activation energy of 0.5 eV and a preexponential factor of a few 10^2 s⁻¹, i.e., $N_j \sim 10^{10}$ assuming $\Delta S/k \sim 1$. Such a value is characteristic of long-range diffusion. In addition, the annealing of these complexes have the same characteristics for all the traps, so that their annealing is associated with the migration of the same entity, i.e., I_{As} . In this picture, we can conclude that the activation energy associated with the As interstitial mobility is 0.5 eV. For these defects, we observe again two first-order kinetics, with the same activation energy (0.5 eV); this may be attributed to a variation of the Fermi level position during annealing, i.e., of the state of the I_{As} during annealing.

We note also that these observations are in agreement with a recent work on EL2,⁵¹ identified as a complex $\text{As}_{\text{Ga}}-I_{\text{As}}$ and whose activation energy of formation, related to the mobility of I_{As} , is ~ 0.6 eV.

C. Existence of the E defects

We have also detected the E defects in p -type material, in agreement with the previous conclusions that $V-I$ pairs in the As sublattice are present, like in n type. We have noted that, on the contrary that what happens in n -type

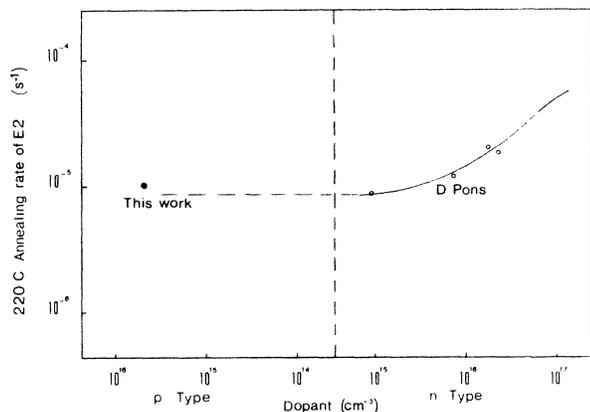


FIG. 11. Rates of annealing of the *E2* trap as a function of the doping concentration in *n*-type GaAs according to Ref. 19. Comparison with our result on *p*-type GaAs.

material, the defects *E1*, *E2*, and *E3* do not anneal around 200°C (no definitive conclusion could be obtained for *E4* and *E5*). This is actually in full agreement with the model of thermal annealing in *n* type. Pons¹⁹ has demonstrated that the defects *E2* and *E3* do not anneal when they are empty (for this, he used a reverse polarization during annealing and compared the concentration of the defects which were either in the space-charge region, i.e., empty, or, in the bulk, i.e., filled). In addition, using variable doping concentration, he demonstrated that the variation of the annealing rate can be quantitatively accounted for using the so-called "normal ionization enhanced" mechanism.⁴⁶ In our case, in *p*-type material, doped $\sim 2.5 \times 10^{16} \text{ cm}^{-3}$, it is clear that the defects associated with *E1*, *E2*, and *E3* are always empty and should not anneal, as shown in Fig. 11, where we have plotted the annealing rate data for *p* type as an extrapolation of the *n*-type case. The annealing rate of *E2* in the empty case, at 220°C, is $\sim 10^{-5} \text{ s}^{-1}$, in agreement with the previous work of Pons.²⁹

V. CONCLUSION

Our study has demonstrated that the defects produced by electron irradiation in *p*-type GaAs are of both types:

primary, i.e., $V_{\text{As}}-I_{\text{As}}$ pairs, and complexes involving impurities and I_{As} . The reason is that I_{As} is slightly mobile during irradiation, inducing a broad distribution of $V_{\text{As}}-I_{\text{As}}$ pairs. After irradiation some of the pairs and isolated V_{As} are still present with complexes formed by the interaction of I_{As} with impurities contained in material. We have shown also that this picture is fully consistent with the one deduced for defects in *n*-type GaAs. Indeed we have detected the *E* defects known to be associated with a distribution of $V_{\text{As}}-I_{\text{As}}$ pairs; in *n* type, I_{As} is less mobile and interaction of I_{As} with impurities is only observed for high doses which render the material semi-insulating.

Several properties of the *H* and *E* traps have been established during the study: (i) The trap *H0* anneals around 200°C. (ii) The trap *H1* is a primary defect associated with the arsenic-vacancy-interstitial pair. It anneals also at 200°C with an activation energy of 1.3 eV. (iii) The other traps (*H3*, *H4*, *H5*) are related to I_{As} impurity complexes. They anneal at 200°C with an activation energy of 0.5 eV. (iv) The defects *E1*, *E2*, *E3*, *E4*, and *E5* are also created in *p*-type GaAs. (v) *E1*, *E2*, and *E3* do not anneal in *p*-type GaAs, at 200°C as in *n* type because of a charge-state effect. (vi) The trap *HL3* is not created by the irradiation but is a native defect. Another defect, a complex involving I_{As} , having similar characteristics, is created during irradiation. (vii) The so-called *H2* trap is actually due to the superposition of two different traps, *H2* and *H2'*, whose characteristics are respectively, $E_v + 0.36 \text{ eV}$, $\sigma_p = 2.5 \times 10^{-15} \text{ cm}^2$ and $E_v + 0.44 \text{ eV}$, $\sigma_p = 6.9 \times 10^{-15} \text{ cm}^2$. These two traps may involve copper, i.e., be $I_{\text{As}}-\text{Cu}$ complexes. (viii) The activation energy associated with the interstitial mobility in *p* type is $0.5 \pm 0.15 \text{ eV}$.

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¹D. V. Lang and L. C. Kimerling, *International Conference on Lattice Defects in Semiconductors, Freiberg, Germany, 1974*, IOP Conf. Proc. No. 23 (IOP, London, 1975), Vol. 23, p. 581.

²D. V. Lang, *International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976*, IOP Conf. Proc. No. 31, edited by N. B. Urli and J. W. Corbett (IOP, Bristol, 1977), p. 70.

³A. Mircea and D. Bois, *International Conference on Radiation Effects in Semiconductors, Nice, 1978*, IOP Conf. Proc. No. 46, edited by J. H. Albany (IOP, London, 1979), p. 82.

⁴For a recent review, see D. Pons and J. C. Bourgoin, *J. Phys. C*

18, 3839 (1985).

⁵D. Pons, A. Mircea, and J. C. Bourgoin, *J. Appl. Phys.* 51, 4150 (1980).

⁶J. C. Bourgoin and M. Lannoo, *Point Defects in Semiconductors: Experimental Aspects* (Springer, Berlin, 1983), Chap. 8.

⁷D. Pons, *Physica (Utrecht)* 116B, 388 (1983).

⁸D. Pons, P. M. Mooney, and J. C. Bourgoin, *J. Appl. Phys.* 51, 2038 (1980).

⁹S. Loualiche, G. Guillot, and A. Nouailhat, *Solid State Commun.* 44, 41 (1982).

¹⁰D. Pons, *J. Appl. Phys.* 55, 2839 (1984).

- ¹¹D. Pons and J. C. Bourgoin, *Phys. Rev. Lett.* **17**, 1293 (1981).
- ¹²S. Loualiche, G. Guillot, A. Nouailhat, and J. C. Bourgoin, *Phys. Rev. B* **26**, 7090 (1982).
- ¹³C. H. Henry and D. V. Lang, *Phys. Rev. B* **15**, 989 (1977).
- ¹⁴D. Pons, *J. Appl. Phys.* **55**, 3644 (1984).
- ¹⁵D. Stievenard, M. Lannoo, and J. C. Bourgoin, *J. Appl. Phys.* **55**, 1477 (1984).
- ¹⁶D. Pons and J. C. Bourgoin, in *Defects in Semiconductors*, edited by L. C. Kimerling and J. M. Parrey (The Metallurgical Society of AIME, Coronado, California, 1985), p. 989.
- ¹⁷S. Loualiche, A. Nouailhat, G. Guillot, and M. Lannoo, *Phys. Rev. B* **30**, 5822 (1984).
- ¹⁸A. Chantre, G. Vincent, and D. Bois, *Phys. Rev. B* **23**, 5335 (1981).
- ¹⁹D. Pons, *Defects and Radiation Effects in Semiconductors, 1980*, IOP Conf. Proc. No. 59, edited by R. R. Hasiguti (IOP, London, 1981), p. 269.
- ²⁰L. C. Kimerling and D. V. Lang, *International Conference on Lattice Defects in Semiconductors, Freiburg, Germany, 1974*, IOP Conf. Proc. No. 23 (IOP London, 1975), p. 589.
- ²¹D. V. Lang and C. H. Henry, *Phys. Rev. Lett.* **35**, 1525 (1975).
- ²²D. Stievenard and J. C. Bourgoin, *Phys. Rev. B* **33**, 8410 (1986).
- ²³M. R. Brozel and R. C. Neuwman, *J. Phys. C* **8**, 243 (1978).
- ²⁴F. Thompson, S. R. Morrison, and R. C. Neuwman, *International Conference on Radiation Damage and Defects in Semiconductors, Reading, England, 1972*, IOP Conf. Proc. No. 16 (IOP, London, 1973), p. 371.
- ²⁵R. B. Beall, R. Murray, R. C. Neuwman, and J. E. Whitehouse, *J. Phys. C* (to be published).
- ²⁶H. J. Von Bardeleben and J. C. Bourgoin, *J. Appl. Phys.* **58**, 1041 (1985).
- ²⁷R. B. Beall, R. C. Neuwman, J. E. Whitehouse, and J. Woodhead, *J. Phys. C* **18**, 3273 (1985).
- ²⁸N. K. Goswami, R. C. Neuwman, and J. E. Whitehouse, *Solid State Commun.* **40**, 473 (1981).
- ²⁹D. Stievenard, J. C. Bourgoin, and D. Pons, *Physica (Utrecht)* **116B**, 394 (1983).
- ³⁰D. Stievenard and J. C. Bourgoin, *J. Appl. Phys.* (to be published).
- ³¹D. V. Lang and L. C. Kimerling, *Phys. Rev. Lett.* **33**, 489 (1974).
- ³²D. V. Lang, *International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976*, IOP Conf. Proc. No. 31, edited by N. B. Urli and J. W. Corbett (IOP, Bristol, 1977), p. 70.
- ³³S. Loualiche, A. Nouailhat, G. Guillot, M. Gavand, A. Laugier, and J. C. Bourgoin, *J. Appl. Phys.* **53**, 8691 (1983).
- ³⁴K. Sakai and T. Ikoma, *J. Appl. Phys.* **5**, 165 (1974).
- ³⁵P. Leyral, F. Litty, G. Bremond, A. Nouailhat, and G. Guillot, in *Semi-Insulating III-V Materials*, edited by S. Makram-Ebeid and B. Tuck (Sheva, Evian, France, 1982), p. 192.
- ³⁶A. Mitonneau, G. M. Martin, and A. Mircea, *Electron Lett.* **13**, 666 (1977).
- ³⁷D. V. Lang and R. A. Logan, *J. Electron. Mater.* **4**, 1053 (1975).
- ³⁸H. P. Gislason, P. G. Wang, and B. Monemar, *J. Appl. Phys.* **58**, 240 (1985).
- ³⁹N. Kullendorff, L. Lanson, and L. A. Ledebro, *J. Appl. Phys.* **54**, 3703 (1983).
- ⁴⁰S. Makram-Ebeid and M. Lannoo, *Phys. Rev. Lett.* **48**, 1281 (1982).
- ⁴¹R. A. Callcott and J. W. MacKay, *Phys. Rev.* **161**, 698 (1967).
- ⁴²R. E. Whan and F. L. Vook, *Phys. Rev.* **153**, 814 (1967).
- ⁴³J. C. Bourgoin and M. Lannoo, in *Point Defect in Semiconductors: Experimental Aspects* (Springer, Berlin, 1983), Chap. 9, p. 264.
- ⁴⁴I. Arimura, *IEEE Trans. Nucl. Sci.* **21**, 21 (1974).
- ⁴⁵J. C. Bourgoin and J. W. Corbett, *IEEE Trans. Nucl. Sci.* **18**, 11 (1971).
- ⁴⁶J. C. Bourgoin and J. W. Corbett, *Rad. Effect.* **36**, 157 (1978).
- ⁴⁷J. R. Trowell and G. D. Watkins, *Phys. Rev. B* **22**, 921 (1980).
- ⁴⁸C. A. Klein, *J. Appl. Phys.* **39**, 2029 (1968).
- ⁴⁹J. C. Bourgoin and M. Lannoo, in *Point Defects in Semiconductors: Experimental Aspects* (Springer, Berlin, 1983), Chap. 9, p. 251.
- ⁵⁰See, for example, B. Tuck, *Introduction to Diffusion in Semiconductors* (Peregrinus, Stevenage, 1974), p. 125.
- ⁵¹H. J. von Bardeleben, D. Stievenard, A. Huber, and J. C. Bourgoin, *Appl. Phys. Lett.* **47**, 970 (1985).