PHYSICAL REVIEW B VOLUME 41, NUMBER 15 15 MAY 1990-II

Native and irradiation-induced monovacancies in *n*-type and semi-insulating GaAs

C. Corbel and F. Pierre
*Centre d'Etudes Nucléaires de Saclay, Institut National des Sciences et Techniques Nucléaires,
91191 Gif-sur-Yvette CEDEX, France*

P. Hautojärvi and K. Saarinen
Laboratory of Physics, Helsinki University of Technology, SF-02150 Espoo 15, Finland

P. Moser
*Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Institut de Recherche Fondamentale,
38041 Grenoble CEDEX, France*

(Received 20 July 1989; revised manuscript received 4 December 1989)

Defects induced by electron irradiation in semi-insulating and *n*-type GaAs crystals have been characterized by positron-lifetime measurements. We conclude that electron irradiation with energies of 1.5–3 MeV produces negative monovacancies and negative ions at low and room temperature. The results also show that the native monovacancy defects in lightly *n*-type GaAs change their properties under irradiation. We relate this change to the existence of an ionization level $-\rightarrow 0$ or $0\rightarrow +$ of the native monovacancy defects in the upper half of the band gap. We propose that irradiation produces negative Ga_{As} antisites and negative V_{Ga} vacancies. In *n*-type GaAs the behavior of the native defects under irradiation is in agreement with their earlier assignment to V_{As}.

I. INTRODUCTION

Electron irradiation in GaAs has been extensively studied by various techniques in the last two decades.[1,2] The irradiation-induced defects have mainly been identified through their electrical or optical properties. Consequently, there is still need for the direct characterization of their structures by atomic probes. Recently, a few studies have been reported, where positron annihilation has been used to characterize vacancy-type defects after electron,[3–7] neutron,[8,9] or α-particle irradiation.[10] These studies have clearly shown that electron irradiations with energies of 0.5–3 MeV produce monovacancies both at low temperatures[4–7] and at room temperature.[3–5] Irradiation-induced monovacancies have been observed in *n*-type and semi-insulating crystals. However, no systematic attempt has been made to correlate the properties of the irradiation-induced monovacancies to the conductivity type of the crystal in the as-irradiated state.

In this paper we have used the positron-lifetime technique to investigate the fluence effects on the vacancy production in *n*-type GaAs and in semi-insulating (SI) GaAs. To compare irradiation effects in SI GaAs to those in *n*-type GaAs is of special interest because before irradiation positrons detect native vacancies only in *n*-type GaAs bulk crystals.[3,5,11–17] The question is whether the irradiation-induced vacancies exhibit the same properties as the native vacancies in *n*-type GaAs.

Our earlier[17] lifetime experiments at various temperatures have shown that the native vacancies exhibit two Fermi-level-controlled transitions in the upper half of the energy-band gap. The first transition is located at 0.03 eV below the conduction-band minimum E_c. The second transition corresponding to the ionization level $-\rightarrow 0$ or $0\rightarrow +$ is located at $E_c - 0.1$ eV. The existence of these two transitions has been the main argument to relate the defects to the arsenic monovacancies. Unfortunately, positron lifetime does not discriminate whether the monovacancies are isolated or bound to other point defects like antisities or impurities.

The present positron-lifetime experiments show that in addition to vacancies, electron irradiation also produces negative ions in GaAs crystals. These negative ions act as shallow traps for positrons in SI and *n*-type GaAs. We propose that these negative ions are gallium antisites.

We observe the following properties for positron trapping at the vacancies. In *n*-type crystals, the native monovacancies become unable to trap positrons when the crystals are converted to semi-insulating during irradiation. Simultaneously, irradiation produces a new type of monovacancies which trap positrons both in *n*-type and compensated crystals. In semi-insulating and compensated GaAs, positron trapping occurs both at the irradiation-induced vacancies and at the negative ions at low temperature. From these properties, we reach the conclusion that for the midgap position of the Fermi level, the irradiation-induced monovacancies are negative while native monovacancies are neutral or positive. We have proposed earlier[4,5,17] that the arsenic vacancies are involved in the native monovacancy defects while the gallium vacancies are involved in the irradiation-induced monovacancy defects.

The paper is organized as follows. The experimental details and the positron-lifetime results are presented in Secs. II and III, respectively. The discussion of the results is divided in three parts. Section IV deals with positron annihilation in unirradiated crystals, Sec. V concerns irradiation effects in SI GaAs, and Sec. VI concentrates on irradiation-induced compensation effects in *n*-type GaAs.

II. EXPERIMENTAL DETAILS

The GaAs samples of the size $5\times5\times0.2$ mm^3 were cut either from Te- and Sn-doped crystals provided by Cambridge Instruments or from undoped SI crystals provided by Thomson. The crystals were grown by liquid-encapsulated Czochralski method. In the text hereafter, we use the following notation: The crystal labeled by GaAs (Te: 8×10^{15} cm^{-3}) is doped with Te atoms and has a net carrier concentration of 8×10^{15} cm^{-3} electrons at 300 K.

Electron irradiations were performed at fluences from 10^{15} to 4×10^{18} e^- cm^{-2} with Van der Graaf accelerators in undoped SI GaAs samples and in *n*-type GaAs(Te: 8×10^{15} cm^{-3}), GaAs(Te: 2×10^{17} cm^{-3}), and GaAs(Sn: 1.6×10^{16} cm^{-3}) samples. 1.5- and 3-MeV electron irradiations were performed at 20 K at the Laboratoire des Solides Irradiés (Ecole Polytechnique, Paris) and in Centre d'Etudes Nucléaires-Grenoble, respectively. 1.5-MeV electron irradiations at 300 K were performed in Ecole Normale, Paris. After low-temperature irradiations, the samples were mounted at 77 or 100 K in the lifetime spectrometer. The isochronal annealings [(30 min/(20–50 K)] were performed between 77 and 800 K.

After 300-K irradiation, the conductivity types of the irradiated crystals were roughly determined from electron cyclotron resonance measurements performed in Ecole Normale. The excitation frequency was 9 GHz. The detection limit of the measurements corresponds to carrier concentrations of about 10^{10} cm^{-3}.

The positron lifetimes were measured from 77 to 300 K using the conventional technique.[18,19] The experimental details were the same as earlier.[17] After source corrections, positron-lifetime spectra $n(t)$ with one or two exponential components were used to fit the data:

$$n(t)=I_1\exp(-t/\tau_1)+I_2\exp(-t/\tau_2)\ . \qquad (1)$$

The average positron lifetime τ was calculated from the decomposition of the lifetime spectra as

$$\tau=I_1\tau\tau_1+I_2\tau_2\ . \qquad (2)$$

It was also calculated as the center of mass of the experimental lifetime distribution. In the numerical fittings, the expression (2) and the center of mass coincide within ±2 ps.

The average positron lifetime is always accurately determined in spite of the uncertainties in the decomposition of the spectra. We shall see that much of the results in Sec. III concern the variation of this parameter because the decomposition of the spectra into several components is difficult in GaAs after electron irradiation. It has been shown earlier in as-grown GaAs (Refs. 17 and 20) that the difference between τ_1 and τ_2 becomes too small [ratio $(\tau_1/\tau_2)<1.2$] at low temperatures for reliable decomposition. This is due to positron trapping at negative ions. The decomposition is even more difficult in irradiated GaAs samples because the irradiation itself produces more negative ions as will be discussed below in this paper.

III. POSITRON-LIFETIME RESULTS AFTER ELECTRON IRRADIATION

Before irradiation, the positron-lifetime spectrum is one-comptential in SI GaAs with a value of 230±1 ps at 100 and 300 K. The average positron lifetimes in GaAs (Te: 8×10^{15} cm^{-3}), GaAs(Te: 2×10^{17} cm^{-3}), and GaAs(Sn: 1.6×10^{16} cm^{-3}), are 225±1ps, 246±1 ps, 265±1 ps at 100 K and 250±1 ps, 242±1 ps, 264±1 ps at 300 K, respectively. The lifetime spectra are resolved into two components at 300 K and the results are given in Table I. The longer lifetime τ_2 has a value depending on the crystal and ranges from 265±10 to 295±4 ps.

After electron irradiation at 20 K and annealing at 77 or 100 K, the average positron lifetime τ in the GaAs crystals depends on the fluence. Figure 1 shows that the variation of τ with fluence is nonmonotonous in GaAs(Te: 8×10^{15} cm^{-3}) irradiated with 3-MeV electrons. The lifetime first decreases to 245 ps after the fluence 10^{16} e^- cm^{-2}. As fluence increases further, the average positron lifetime τ starts to increase and reaches 260 ps after irradiation at the fluence 4×10^{18} e^- cm^{-2}. Figure 2 shows that the lifetime in SI GaAs irradiated with 1.5-MeV electrons increases monotonously with fluence. The decomposition of the lifetime spectra into two components is rather difficult in GaAs(Te: 8×10^{15} cm^{-3}) as well as in SI GaAs. However, when the decomposition is possible the long lifetimes are close to 260 ps.

The recovery in irradiated GaAs(Te: 8×10^{15} cm^{-3}) and SI GaAs after 3-MeV electron irradiation at the fluence 4×10^{18} e^- cm^{-2} is shown in Fig. 3 for annealing temperatures from 77 to 500 K. The positron lifetime is measured at 77 K after each annealing temperature. The

TABLE I. Positron-lifetime spectra at 300 K in as-grown GaAs samples. The carrier concentration is given at 300 K before irradiation.

Dopant	Type	Carrier concentration (cm^{-3})	τ (ps)	τ_1 (ps)	τ_2 (ps)	I_2 (%)
	SI	$<10^{10}$	230±1			
Te	*n*	8.0×10^{15}	250±1	200±14	295±11	53±5
Te	*n*	2.0×10^{17}	242±1	184±10	265±10	71±7
Sn	*n*	1.6×10^{16}	264±1	155±7	297±2	77±2

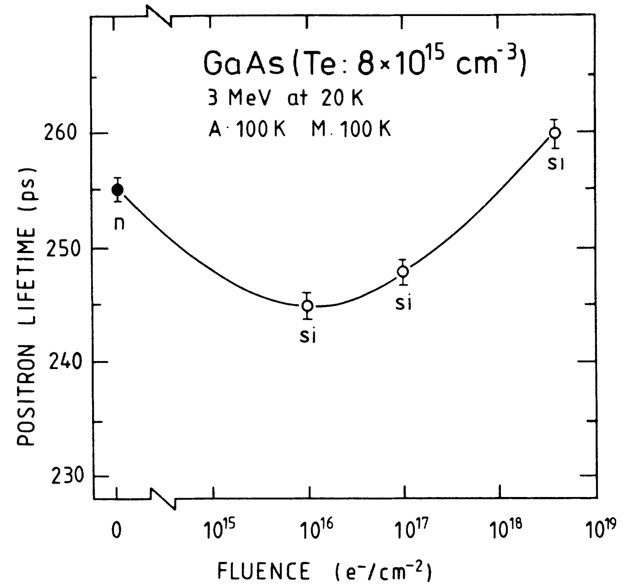

FIG. 1. Positron lifetime as a function of fluence in GaAs(Te: 8×10^{15} cm^{-3}) irradiated with 3-MeV electrons at 20 K and then annealed at 100 K. The measurement temperature is 100 K.

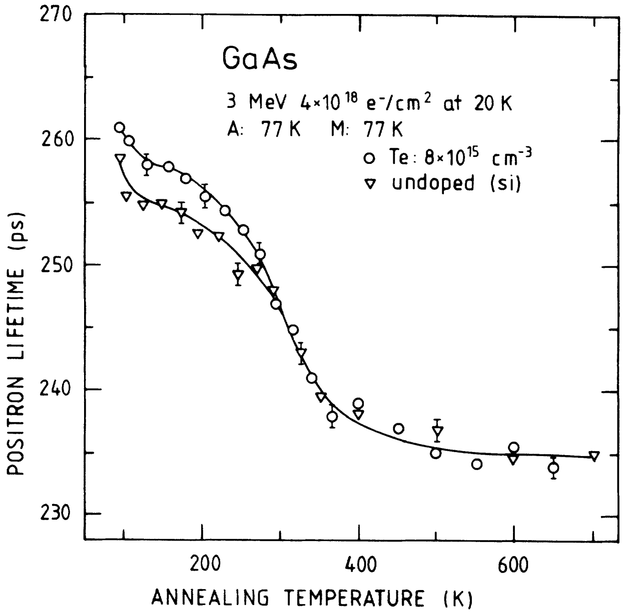

FIG. 3. Recovery of the positron lifetime in GaAs(Te: 8×10^{15} cm^{-3}) and SI GaAs after 3-MeV electron irradiation at 20 K and a fluence of 4×10^{18} e^- cm^{-2}. The measurement temperature is 77 K.

recovery is similar in both samples. The features of the recovery in GaAs(Te: 8×10^{15} cm^{-3}) have been studied in details in Ref. 4. Like GaAs(Te: 8×10^{15} cm^{-3}), the SI GaAs crystal exhibits a small stage at about 80 K. Then the main recovery takes place between 150 and 500 K. Two parts can be distinguished. In the first part between 150 and 280 K the lifetime τ decreases strongly. In the second part between 280 and 500 K the lifetime τ decreases slowly.

The behavior of the average positron lifetime τ as a function of fluence has the same characteristic in GaAs(Te: 8×10^{15} cm^{-3}) and in GaAs(Sn: 1.6×10^{16} cm^{-3}) after 1.5-MeV electron irradiation at 300 K: Figures 4 and 5 show that the lifetime τ first decreases in

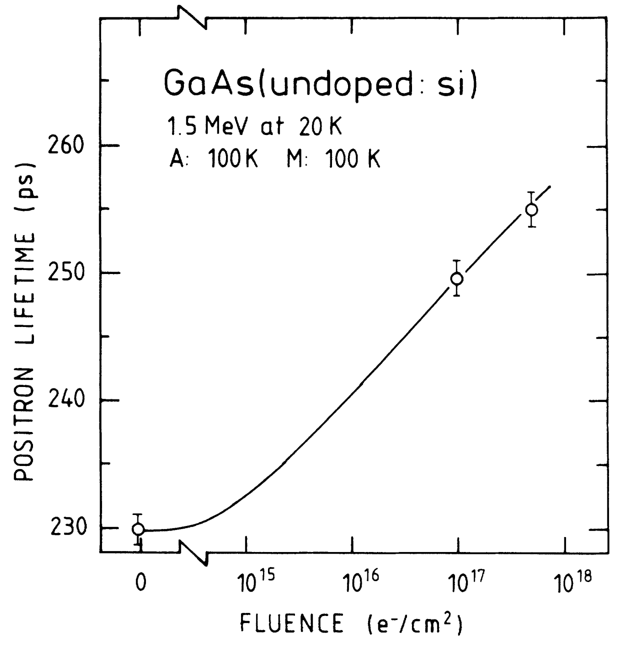

FIG. 2. Positron lifetime as a function of fluence in SI GaAs irradiated with 1.5-MeV electrons at 20 K and then annealed at 100 K. The measurement temperature is 100 K.

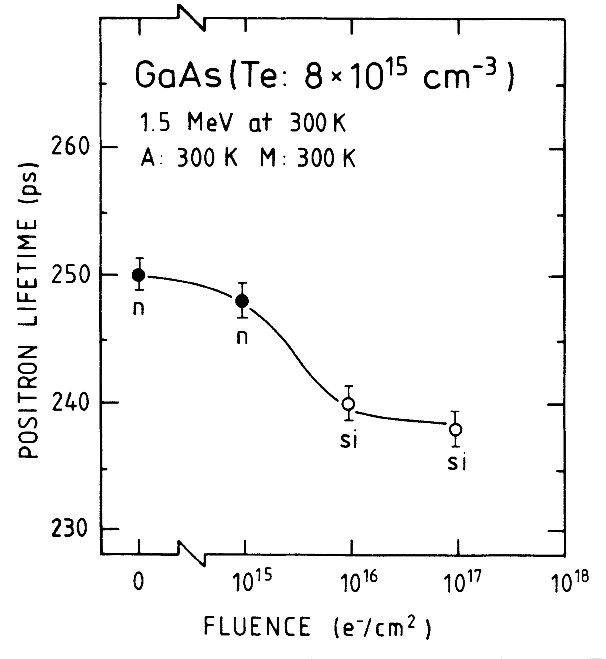

FIG. 4. Positron lifetime as a function of fluence in GaAs(Te: 8×10^{15} cm^{-3}) irradiated with 1.5-MeV electrons at 300 K and then annealed at 300 K. The measurement temperature is 300 K.

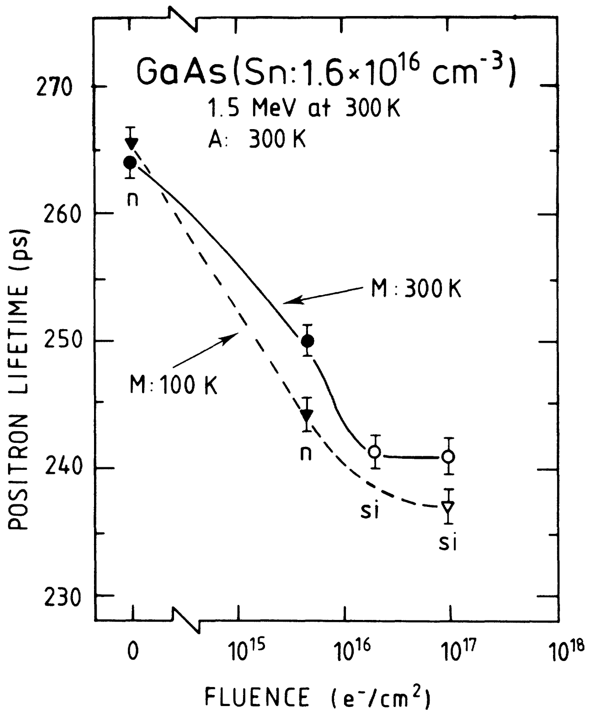

FIG. 5. Positron lifetime as a function of fluence in GaAs(Sn: 1.6×10^{16} cm^{-3}) irradiated with 1.5-MeV electrons at 300 K. The measurement temperatures are 100 and 300 K.

both samples after irradiation at the fluence of 10^{16} e^- cm^{-2}. Then as fluence increases to 10^{17} e^- cm^{-2}, the average lifetime remains nearly constant. The decomposition of the lifetime spectra in GaAs(Te: 8×10^{15} cm^{-3}) are shown in Table II. The interesting feature is the decrease of the lifetime τ_2 as the fluence increases.

In GaAs(Te: 8×10^{15} cm^{-3}), the decrease of τ after the fluence 10^{16} e^- cm^{-2} is seen after 3-MeV electron irradiation at 20 K (Fig. 1) as well as after 1.5-MeV irradiation at 300 K (Fig. 4). But at higher fluence the behavior of τ differs for these irradiations. The increase of τ observed after 20-K irradiation at higher fluences (Fig. 1) is no longer observed after 300-K irradiation (Fig. 4) because of the strong recovery between 77 and 300 K seen in Fig. 3.

Carriers in GaAs (Te or Sn) crystals are removed under irradiation. The electron cyclotron resonance measurements performed after 1.5-MeV electron irradiation at 300 K show that the GaAs(Te: 8×10^{16} cm^{-3}) crystals are already fully converted semi-insulationg ($n\leq10^{10}$ cm^{-3}) at the fluence 10^{16} e^- cm^{-2}.

TABLE II. Positron-lifetime spectra in GaAs(Te: 8×10^{15} cm^{-3}) irradiated with 1.5-MeV electrons at 300 K and then annealed at 300 K. The measurement temperature is 300 K.

Fluence (e^- cm^{-2})	τ (ps)	τ_1 (ps)	τ_2 (ps)	I_2 (%)
As-grown	250±1	200±14	295±11	53±5
10^{15}	249±1	153±6	283±5	74±2
10^{16}	239±1	154±15	253±5	86±2

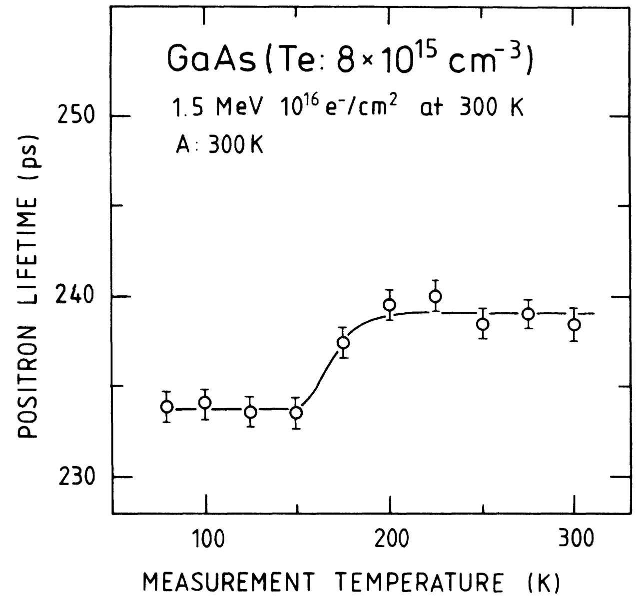

FIG. 6. Positron lifetime as a function of temperature in GaAs(Te: 8×10^{15} cm^{-3}) irradiated with 1.5-MeV electrons at a fluence of 10^{16} e^- cm^{-2} at 300 K and then annealed at 300 K.

The positron lifetime in irradiated Te- or Sn-doped GaAs crystals depends on the measurement temperature. Figure 5 shows that after 300-K irradiation the positron lifetime in GaAs(Sn: 1.6×10^{16} cm^{-3}) faintly increases with increasing temperature. The positron lifetime at 300 K is 5 ps higher than at 100 K. This trend is found again

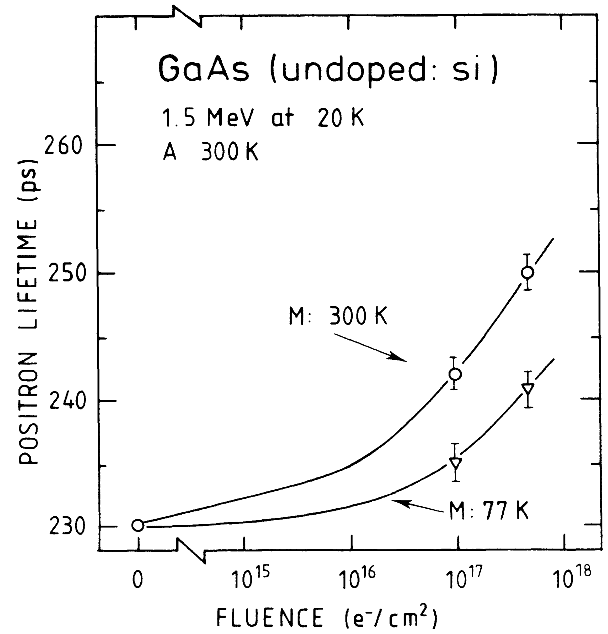

FIG. 7. Positron lifetime as a function of fluence in SI GaAs irradiated with 1.5-MeV electrons at 20 K and then annealed at 300 K. The measurement temperatures are 100 and 300 K.

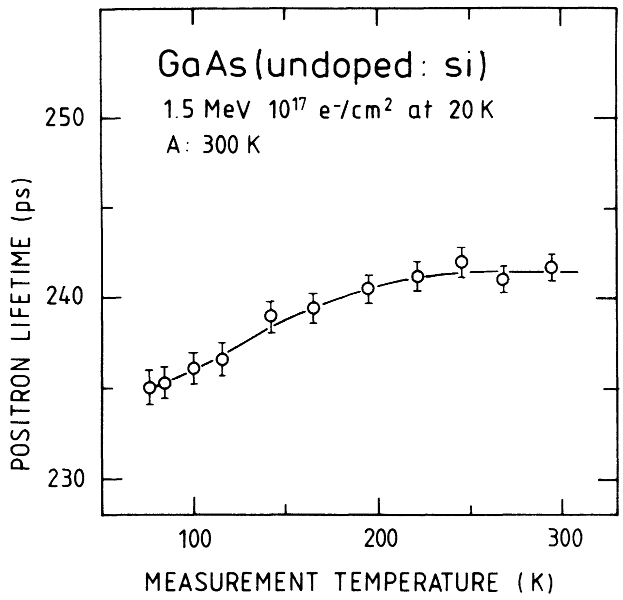

FIG. 8. Positron lifetime as a function of temperature in SI GaAs irradiated with 1.5-MeV electrons at a fluence of 10^{17} $e^- \text{cm}^{-2}$ at 20 K and then annealed at 300 K.

in GaAs(Te: 8×10^{15} cm^{-3}). This is readily seen from Fig. 6 where the positron lifetime after 300-K irradiation at the fluence 10^{16} $e^- \text{cm}^{-2}$ increases from 234 to 239 ps between 77 and 200 K. Above 200 K the lifetime remains constant.

Positron lifetime increases as a function of temperature also in SI GaAs irradiated at 20 K with 1.5-MeV electrons and then annealed at 300 K. The lifetimes at 77 K are about 8 ps less than at 300 K (Fig. 7) after the fluences 10^{17} and 5×10^{17} $e^- \text{cm}^{-2}$. Figure 8 shows that the increase occurs between 77 and 200 K after the fluence 10^{17} $e^- \text{cm}^{-2}$. No temperature dependence is observed above 200 K. Figure 9 shows that the changes of the positron lifetime in GaAs(Te: 2×10^{17} cm^{-3}) after 1.5-MeV electron irradiation at 300 K are within experimental errors.

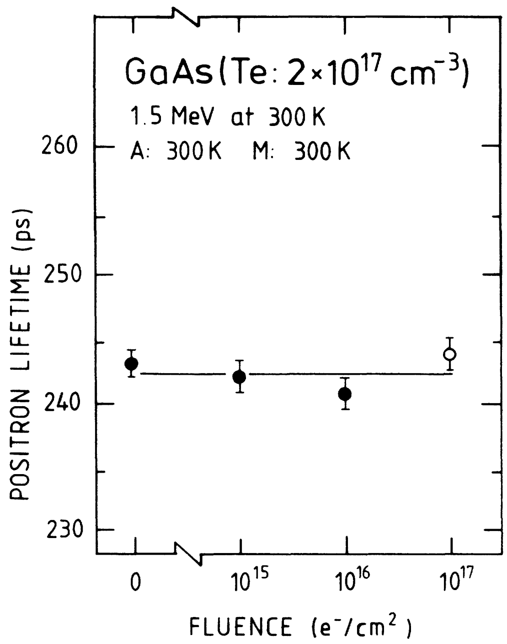

FIG. 9. Positron lifetime as a function of fluence in GaAs(Te: 2×10^{17} cm^{-3}) irradiated with 1.5-MeV electrons at 300 K and annealed at 300 K. The measurement temperature is 300 K.

IV. POSITRON ANNIHILATION IN UNIRRADIATED GaAs

In this section, we describe some basic features of the positron annihilation in a semiconductor and recall the characteristic lifetimes of the different positron annihilation states observed in as-grown GaAs (Ref. 17).

In a semiconductor such as GaAs, positrons may annihilate from the delocalized ground state in the perfect lattice or from localized states formed at defects able to trap positrons. The positron charge is positive and only neutral or negative defects in GaAs can trap positrons. It has been earlier observed and recognized[18,19] that vacancy-type defects form deep potential wells for positrons with binding energies of 1–2 eV. Positron trapping at vacancy-type defects is characterized by lifetimes longer than in bulk, because in the region of the vacancy-type defects positrons encounter less electrons than in the perfect lattice. The lifetime spectra are described in the framework of the trapping model.[18,19] The positron trapping rate k_d due to the population of defects d is the product of the defect concentration c_d and the trapping coefficient per defect μ_d

$$k_d=\mu_d c_d \; . \tag{3}$$

When the positron traps consist only of the population of defects d, the positron trapping k_d can be calculated from the average positron lifetime τ using the relation

$$k_d=\frac{1}{\tau_b}\frac{\tau-\tau_b}{\tau_d-\tau} \; , \tag{4}$$

where τ_b is the lifetime in the bulk and τ_d the lifetime in the defect.

The lifetime of 230 ps measured before irradiation in SI GaAs has been previously attributed to positron annihilation from the delocalized state in the bulk. The higher average lifetimes in GaAs(Te: 8×10^{15} cm^{-3}), 255 ps at 100 K, and 250 ps at 300 K, are due to positron trapping in native defects. The properties of these native defects have been discussed earlier.[17] It has been shown that the native defects involve monovacancies and exist in different configurations depending on the Fermi-level position. The lifetime transitions associated with the configuration changes occur when the Fermi level is below the conduction band at $E_c-0.03$ and $E_c-0.1$ eV. In GaAs(Te: 8×10^{15} cm^{-3}), the native defects have different configurations at low and high temperatures. The increase of the positron lifetime from 258 to 295 ps reflects the configuration change as the Fermi level moves below $E_c-0.03$ eV in the band gap when temperature increases. We have proposed[17] that these native defects involve arsenic vacancies and that the lifetime transition 258→295 ps is related to the charge-state transition $V_{\mathrm{As}}^{2-} \rightarrow V_{\mathrm{As}}^{1-}$.

V. VACANCIES AND NEGATIVE IONS IN SI GaAs AFTER IRRADIATION

In this section, we discuss the irradiation effects in SI GaAs and reach the conclusion that irradiation produces negative monovancies and negative ions in SI GaAs.

Electron irradiation at 1.5 and 3-MeV energies induces positron trapping at vacancy-type defects in SI GaAs. This is directly evidenced by the increase of the average positron lifetime in Figs. 2 and 3 after electron irradiation. The decomposition of the lifetime spectra in 1.5-MeV irradiated SI GaAs shows that the lifetime due to the vacancy defects is 260±5 ps at low temperatures as well as after annealing at 300 K. After 3-MeV electron irradiation at 4×10^{18} e^- cm^{-2} only one component is resolved and the lifetime is saturated at a level of 260 ps. Similar results have been obtained earlier after 3-MeV electron irradiation[4] or 1.5-MeV electron irradiation.[6,7,21] According to theoretical calculations, the lifetime of 260 ps in GaAs is a typical value for positrons trapped at monovacancies.[22,23] Divacancies V_{As}-V_{Ga} would produce a significantly higher lifetime of 310–320 ps.[23] Thus we conclude that positrons are trapped at monovacancies.

In irradiated SI GaAs the positron trapping is temperature dependent. This property has been found earlier,[6,7] but here it is examined in more details. The increase of the positron lifetime from 77 to 300 K in Figs. 7 and 8 implies that the positron trapping at the vacancies increases as temperature increases. It will be shown elsewhere[21] that the onset temperature, above which the positron trapping at the vacancies becomes temperature independent, increases with the irradiation dose. This indicates that the temperature dependence of the positron trapping at vacancies is not an intrinsic property of the trapping coefficient μ_d at the vacancies.

We explain the temperature dependence of τ by the competition between positron trapping at vacancies and at other defects. The other defects become dominant traps at low temperatures. These defects give rise to a lifetime well below 260 ps, since the positron lifetime decreases when the temperature decreases. At low temperature the positron lifetimes in Figs. 7 and 8 tend towards the limit of 230 ps. This lifetime value is the same as that measured in the bulk. Positron trapping characterized by bulk lifetime points out to positron trapping at Rydberg states around negative ions, as it had been discussed earlier.[23] These negative ions are shallow traps for positrons in the sense that the positron binding energy is small (50 meV). Positrons can easily escape from the shallow traps once they gain energy enough from the crystal temperature. This thermal detrapping[23] well explains the positive temperature dependence of the positron trapping after electron irradiation. The analysis of the curve $\tau = f(T)$ in terms of positron trapping at shallow traps and at monovacancies yields to an estimation of the positron binding energy at the negative ions.[23] We have done such analysis for the curve in Fig. 8. The positron binding energy for irradiation-induced negative ions in SI GaAs is then found to be 37±6 meV.[21] This value is close to those found for negative ions in as-grown n-type crystals.[23]

It has been observed in n-type GaAs that the positron trapping in the native monovacancies disappears when the Fermi level decreases below $E_c - 0.1$ eV.[17] In irradiated SI GaAs we observe positron trapping at irradiation-induced vacancies, when the Fermi-level position is about midgap. We can therefore conclude that the irradiation-induced monovacancies are different from the native monovacancy defects. The native monovacancy defects are neutral or positive in SI GaAs. The irradiation-induced vacancies are neutral or negative in SI GaAs since they trap positive positrons. As positron traps, they are able to compete at low temperatures with negative ions. This property provides good evidence that they are negative rather than neutral. As we have discussed earlier,[3,4,17] a simple explanation is that the arsenic vacancy is involved in the native defects, whereas the gallium vacancy is involved in the irradiation-induced defects.

To discuss the nature of the irradiation-induced ions, we use the property that they are negative at the midgap position of the Fermi level. We assume that they are intrinsic defects, because we have observed them after irradiation in various crystals (n type, SI, or even p type).[21] Ion-type intrinsic defects created at irradiation are interstitials As_i or Ga_i, or antisites $\mathrm{As}_{\mathrm{Ga}}$ or $\mathrm{Ga}_{\mathrm{As}}$. The tetrahedral interstitials As_i ($\mathrm{As}_i\mathrm{As}_4$ and $\mathrm{As}_i\mathrm{Ga}_4$) and Ga_i ($\mathrm{Ga}_i\mathrm{Ga}_4$ and $\mathrm{Ga}_i\mathrm{As}_4$) are generally believed to be positive for any Fermi-level position in the gap.[24,25] $\mathrm{As}_{\mathrm{Ga}}$ antisites are positive at midgap according to EPR and electron-nuclear double resonance (ENDOR) experiments.[26,27] Only $\mathrm{Ga}_{\mathrm{As}}$ antisites are negative at and below the midgap. They have been recently assigned to the ionization levels below the midgap located at $E_v + 78$ and $E_v + 203$ meV (Ref. 28) above the maximum E_v of the valence band.

As we have seen above, positrons give evidence that irradiation induces negative vacancies and negative ions in SI GaAs. Therefore we reach the conclusion that acceptorlike defects exist after irradiation at Fermi level around midgap. Evidence that 1-MeV electron irradiation at 80 K creates electron-trapping levels below midgap has been obtained by Rezazadeh and Palmer[29] in a vapor-phase epitaxial n-type GaAs (Sn) layer where the carrier concentration had been decreased from 2×10^{15} to 1.85×10^{15} cm^{-3} by irradiation. From deep-level transient spectroscopy (DLTS) and capacitance-voltage measurements, the authors estimate that about 80% of the electron-trapping defects produced at 80 K give rise to levels located below midgap. After annealing at 300 K, they found that about 60% of these defects have disappeared. More recently, Look and Sizelove[30] have measured from Hall experiments that 1-MeV electron irradiation at room temperature produces acceptors below the ionization level $E_c - 0.295$ eV ($E3$ in DLTS). They found a very high production rate of 5±1 cm^{-1} for these acceptors[30,31] and proposed that they represent damage in the

Ga sublattice.[31] The results obtained by electrical characterization[29–31] and our present results obtained by positron annihilation support each other. They show that a part of the irradiation-induced defects are similarly electron traps both in *n* type and SI GaAs. This suggests that a part of the defects produced by irradiation have the same nature (ions or/and vacancies from our measurements) in *n* type and SI GaAs. We may expect that the acceptor defects seen by positrons in SI GaAs have the same charge or, possibly, are more negative in *n* type than in SI GaAs. Therefore, our positron results support the conclusion obtained from Hall measurements by Looks and Sizelove[30,31] that acceptors below $E_c - 0.295$ eV are created by irradiation. Further they show that the acceptors have their $- \rightarrow 0$ ionization levels below midgap.

VI. IRRADIATION EFFECTS ON THE NATIVE VACANCIES IN *n*-TYPES GaAs

We discuss here the results in *n*-type GaAs with emphasis on the irradiation effects in lightly doped *n*-type GaAs, where the donor compensation is achieved after low fluences. We shall see that in addition to the production of vacancies and negative ions, the shift of the Fermi level during irradiation, in light *n*-type GaAs changes the positron trapping at the native monovacancies.

A. Irradiation-induced defects in *n*-type GaAs

We have seen in Sec. III that lightly *n*-type GaAs(Te: 8×10^{15} cm^{-3}) is converted to semi-insulating after 1.5-MeV room-temperature irradiation at the fluence 10^{16} cm^{-2}. This is in good agreement with previous results obtained in similar irradiation conditions.[26] The carrier removal by electron irradiation in *n*-type GaAs has been observed with a large variety of donors (for a review see Ref. 1) and recently studied after irradiation at 80 K,[29] 300 K,[31,32] and 570 K.[33] When compensation is achieved, the Fermi level is found to be pinned at $E_c - 0.76$ eV (Ref. 26) or at $E_v + 0.295$ eV (Ref. 31) depending on fluence and initial doping.

It is reasonable to assume that the GaAs(Te: 8×10^{15} cm^{-3}) crystals irradiated at 20 K with 3-MeV electrons and subsequently annealed at 100 K are semi-insulating at 100 K after the fluence 10^{16} e^- cm^{-2}. First the carrier removal rate at low temperature is expected to be at least as high as at room temperature because recovery effects are smaller at low temperature than at room temperature (see, e.g., Fig. 3). Second, Rezazadeh and Palmer[29] found already a carrier removal rate of 1 cm^{-1} after 1-MeV electron irradiation at 80 K with a low flux of 2 nA cm^{-2}. We have irradiated at higher flux and higher energy and consequently, we expect a higher carrier removal rate. For example, for 1-MeV electrons, the carrier removal rate ranges from 0.5 to 5 cm^{-1} and higher values seem to correspond to higher fluxes.[1]

While compensation occurs, it is clear that simultaneously irradiation in lightly *n*-type GaAs induces monovacancies giving rise to a lifetime of about 260 ps as seen in Table II. First, Fig. 1 shows that vacancy-type defects are created: The positron lifetime increases as fluence increases above 10^{16} e^- cm^{-2}. Second, when the two-component analysis is possible, the spectra in compensated GaAs(Te: 8×10^{15} cm^{-3}) exhibit long components of about 260 ps as seen in Table II. Third, the similarity of the recovery curves in Fig. 3 after 20-K electron irradiation at the fluence 4×10^{18} e^- cm^{-2} gives strong evidence that the nature of the vacancy-type defects is the same in compensated GaAs(Te: 8×10^{15} cm^{-3}) as in SI GaAs.

There is also creation of negative ions in compensated GaAs(Te: 8×10^{15} cm^{-3}) and in *n*-type GaAs(Sn: 1.6×10^{16} cm^{-3}). The slight positive temperature dependence observed in Figs. 5 and 6 is similar to that observed in SI GaAs and may be discussed in terms of detrapping from Rydberg states around negative ions as we already did in Sec. V above for irradiated SI GaAs.

In compensated GaAs(Te: 8×10^{15} cm^{-3}), positrons show the creation of the same kind of acceptor defects as in SI GaAs: monovacancies and ions which are negative at midgap. We may assume that irradiation creates these acceptors continuously during and after the conversion of the *n*-type crystal to semi-insulating since, as discussed above, electrical measurements indicate creation of electron-trapping levels below midgap[29] or below $E_c - 0.295$ eV (Ref. 31) in *n*-type GaAs. According to Ref. 31, the electron-trapping levels below $E_c - 0.295$ eV are acceptor levels and produced at the rate of 5 cm^{-1} by 1-MeV irradiation at room temperature. It is tempting to correlate the results in Refs. 29–31 to our results and to conclude that the acceptors we observe after annealing at room temperature represent about 40% of the acceptors produced at low temperature. The annealing of these acceptors leads to the decrease of the average positron lifetime we observe in Fig. 3. Knowing from our study that the acceptors after annealing at room temperature are vacancies and ions, we can then attribute the decrease of τ between 77–300 K to the disappearance of the negative vacancies rather than to the appearance of negative ions.

After irradiation at 10^{17} e$^-$ cm^{-2} at room temperature, we observe positron trapping only at the vacancies. We can apply the trapping model with one type of defects to calculate the total positron trapping rate at the vacancies from Eq. (4). The average e^+ lifetime at 300 K is 240±2 ps and we measured the same value both after low-temperature 1.5-MeV irradiation and annealing at 300 K in SI GaAs (Fig. 7) and in compensated *n*-type GaAs (Fig. 4) after room temperature 1.5-MeV irradiation. The trapping rate corresponding to this average lifetime is about 2 ns^{-1} [Eq. (4)]. We may also use the data in Ref. 31 to obtain an order-of-magnitude estimation of the concentration of the irradiation-induced vacancy (V_{Ga} in our model).

To estimate the introduction rate $\mathcal{R}$ of gallium vacancies at 300 K, we assume the following relations. (i) The total acceptor introduction rate is 5 cm^{-1}. (ii) There are no acceptors other than V_{Ga}^{3-} trapping three electrons and $\mathrm{Ga}_{\mathrm{As}}^{2-}$ trapping two electrons, so that their respective introduction rate $\mathcal{R}[V_{\mathrm{Ga}}^{3-}]$ and $\mathcal{R}[\mathrm{Ga}_{\mathrm{As}}^{2-}]$ verify: $3\mathcal{R}[V_{\mathrm{Ga}}^{3-}]+2\mathcal{R}[\mathrm{Ga}_{\mathrm{As}}^{2-}]=5.0$. (iii) We put arbitrarily $\mathcal{R}[V_{\mathrm{Ga}}]=\mathcal{R}[\mathrm{Ga}_{\mathrm{As}}]$. With these assumptions, we get 1.2 cm^{-1} for the upper limit of the introduction rate of V_{Ga}^{3-}.

Thus after irradiation at the fluence 10^{17} $e^{-1}\,\mathrm{cm}^{-2}$, the positron trapping rate of 2 ns^{-1} corresponds to the gallium vacancy concentration $[V_{\mathrm{Ga}}] \leq 1.2\times10^{17}$ cm^{-3}. From Eq. (3) we get for the positron trapping coefficient $\mu_d \geq 1.6\times10^{-8}$ $\mathrm{cm}^3\,\mathrm{s}^{-1}$ or $5.7\times10^{14}\,\mathrm{cm}^{-3}\mathrm{s}^{-1}$. This lower limit agrees with those estimated earlier.[17,34]

B. Native monovacancy defects under irradiation

As mentioned in the introduction and in Sec. V, there are already native monovacancy defects in *n*-type GaAs before irradiation. 1.5-MeV irradiation at room temperature induces a significant decrease of the average positron lifetime in GaAs(Te: $8\times10^{15}\mathrm{cm}^{-3}$) after the fluence of 10^{16} cm^{-2} (Fig. 4). At room temperature, the decrease of τ means that the positron trapping in the native 295-ps monovacancies disappears. This is readily seen in Table II where τ_2 decreases from 295±11 to 253±5 ps as fluence increases up to 10^{16} $e^{-1}\,\mathrm{cm}^{-2}$. The lack of positron trapping by the 295-ps configurations may reflect two situations: Either (1) other defects created by irradiation induce a lifetime shorter than 295 ps and there is a competition for positron trapping at these defects and at the 295-ps configurations or (2) the 295-ps configurations disappear under irradiation. We successively examine these two possibilities.

Trapping at the negative ions gives rise to a lifetime of 230 ps, which is shorter than 295 ps. However, trapping at the negative ions cannot compete at 300 K with positron trapping at the 295-ps native vacancies because after 1.5-MeV electron irradiation at the fluence of 10^{16} $e^{-}\,\mathrm{cm}^{-2}$ the average positron lifetime remains constant above 200 K in compensated GaAs(Te: 8×10^{15} cm^{-3}) (Fig. 6). This means that the thermal detrapping from the negative ions is already complete at temperatures above 200 K. We therefore conclude that trapping at negative ions cannot explain the decrease of the average lifetime in GaAs(Te: 8×10^{15} cm^{-3}) after 300-K irradiation.

Trapping at the irradiation-induced vacancies give rise to a lifetime of 260 ps, which is shorter than 295 ps. We can qualitatively predict how the average positron lifetime varies after irradiation when competition between positron trapping at the 260-ps irradiation-induced vacancies and at the 295-ps native vacancies occurs. Before irradiation only the 295-ps native vacancies trap positrons, and the average lifetime has a value of 250 ps (see Table I). This value is shorter than 260 ps. Consequently, after irradiation, additional trapping at the 260-ps vacancies increases τ. In Fig. 4, τ does not increase but decreases. Thus the only explanation to the decrease of the average positron lifetime after electron irradiation is the disappearance of the 295-ps configuration of the native monovacancies.

We have already reported earlier[17] that the positron trapping in the 295-ps configuration disappears when the Fermi level moves down in the gap below $E_c - 0.1$ eV due to temperature. Here we observe the same phenomena due to irradiation. We have seen in Sec. III that at room temperature lightly *n*-type GaAs(Te: 8×10^{15} cm^{-3}) crystals are converted to semi-insulating after 1.5-MeV irradiation at the fluence 10^{16} $e^{-}\,\mathrm{cm}^{-2}$. By shifting down the Fermi level to midgap, irradiation removes positron trapping in the 295-ps configuration. This confirms our earlier conclusion[17] that the native monovacancies in GaAs(Te: 8×10^{15} cm^{-3}) have a ionization level at about $E_c - 0.1$ eV where their charge state changes from negative to neutral $- \rightarrow 0$, or from neutral to positive $0 \rightarrow +$. This property has been used in Ref. 17 to argue that the native monovacancies are arsenic vacancies.

After irradiation at the fluence 10^{16} e^{-} cm^{-2}, the average positron lifetime measured at 100 K decreases after 1.5-MeV irradiation at room temperature (Fig. 6) as well as after 3-MeV irradiation at 20 K and subsequent annealing at 100 K (Fig. 1). The decreases resemble those observed in Figs. 4 and 5 at room temperature and they mean also that positron trapping at the native monovacancies decreases. However, here the decrease in the positron trapping concerns the 260-ps configuration of the native defects, since measurements are performed at 100 K.[17] Again, the disappearance of positron trapping at the 260-ps configurations indicates that either (1) other defects created by irradiation give rise to lifetime shorter than 260 ps with positron trapping competing at these defects and the 260-ps configurations or (2) the 260-ps configurations disappear under irradiation. At 100 K, trapping at negative ions is effective and yields to lifetime of 230 ps. It is therefore less straightforward than for measurements at 300 K to decide between the two explanations we proposed. The following argument leads us to decide in favor of the explanation (2) for the decrease of τ. We note that the values at which τ decreases in irradiated and compensated GaAs(Te: 8×10^{15} cm^{-3}) are in qualitative agreement with those expected in SI GaAs for similar irradiation. In GaAs(Te: 8×10^{15} cm^{-3}), τ measured at 100 K decreases to 245 ps after 3-MeV irradiation at low temperature and at 10^{16} $e^{-}\,\mathrm{cm}^{-2}$ (Fig. 1). In SI GaAs, extrapolation of the data in Fig. 2 gives the range 235–240 ps for the value of τ after 1.5-MeV electron irradiation at low temperature and at 10^{16} $e^{-}\mathrm{cm}^{-2}$. This suggests that when the GaAs(Te: 8×10^{15} cm^{-3}) crystals are compensated there is no contribution of the 260-ps native defects in the lifetime characteristics at low temperature. The conversion of the GaAs(Te: 8×10^{15}) crystals into compensated material removes the 260-ps configuration of the native monovacancies. We expect the following sequence: The 260-ps configuration is first replaced by the 295-ps configuration and then by the configuration which is unable to trap positrons.

The positron lifetime in the GaAs(Te: 2×10^{17} cm^{-3}) crystal remains unchanged under electron irradiation up to the fluence 10^{17} $e^{-}\,\mathrm{cm}^{-2}$. This behavior possibly reflects the balance between disappearance of the native defects and creation of the irradiation defects.

In summary, we observe that at low temperature when positron trapping in the native monovacancy defects in *n*-type GaAs has disappeared under irradiation, further irradiation introduces new monovacancy defects able to trap positrons. We conclude that the charge of the irradiation-induced monovacancy defects is negative in SI GaAs, whereas the charge of the native monovacancy defects is neutral or positive. These results mean that the irradiation-induced monovacancy defects have an atomic structure different from the native monovacancy defects. The atomic structure may differ in two ways. (1) The atomic structures contain the same vacant site (V_{Ga} or V_{As}) associated with one or several distinct first neighbors. As a result of this (these) first neighbor(s), the charge is different when the Fermi level is at midgap. (2) The atomic structures involve two distinct vacant sites, i.e., either V_{Ga} or V_{As}. We propose that the vacant sites are different. We associate V_{As} to the native defects, because it has ionization levels in the upper half of the band gap.[24,25] V_{Ga} is associated to the irradiation-induced defects, because it has negative states below midgap.[24,25]

VII. CONCLUSION

By investigating the positron lifetime in electron irradiated GaAs, we have shown that negative monovacancy defects and negative ions are produced in SI GaAs and in compensated Te- or Sn-type GaAs. We observe both defects after 1.5- or 3-MeV electron irradiation and after low- or room-temperature irradiation.

From our study, we conclude that acceptor levels are introduced below midgap by irradiation. We associate these acceptors to damage in the Ga sublattice and attribute them to the gallium vacancy (or to a complex involving the gallium vacancy) and the $\mathrm{Ga}_{\mathrm{As}}$ antisite (or a complex involving the $\mathrm{Ga}_{\mathrm{As}}$ antisite), respectively.

The irradiation effects observed here by positron annihilation in SI GaAs and compensated Te- or Sn-doped GaAs are similar to those observed earlier in *n*-type GaAs by electrical techniques. From electrical measurements in irradiated *n*-type GaAs, it has been concluded that electron traps below midgap[29] or, more precisely, acceptor levels below $E_c - 0.295$ eV (Refs. 30 , 31, and 35) are produced. A natural conclusion is that the same defects generating acceptor levels below midgap are created in *n*-type GaAs, compensated Te-or Sn-doped GaAs and SI GaAs. According to our study, at least two distinct intrinsic defects give rise to these acceptor levels: an ion and a monovacancy.

Another important observation is that the native vacancy defects in *n*-type GaAs change their properties under irradiation. They are no longer detected by positrons and this is shown to be due to the compensation occurring under irradiation. This result is consistent with our earlier conclusion[17] that the native defects associated with V_{As} have an ionization level $- \to 0$ or $0 \to +$ at $E_c - 0.1$ eV.[17]

ACKNOWLEDGMENTS

We are grateful to J. von Bardeleben for his support and many valuable discussions. We also thank him for his assistance in irradiation experiments at Ecole Normale and for the cyclotron resonance experiments he kindly performed for us.

---

[1] D. V. Lang, *Radiation Effects in Semiconductors,* IOP Conf. Proc. Ser. No. 31 (IOP, Bristol, 1977), p. 70, and references cited therein.

[2] D. Pons and J. C. Bourgoin, J. Phys. C **18**, 3839 (1985).

[3] C. Corbel, P. Moser, and M. Stucky, Ann. Chim. (Paris) **8**, 733 (1985).

[4] P. Hautojarvi, P. Moser, M. Stucky, C. Corbel, and F. Plazaola, Appl. Phys. Lett. **48**, 809 (1986).

[5] M. Stucky, C. Corbel, B. Geoffroy, P. Moser, and P. Hautojarvi, in *Defects in Semiconductors, Materials Science Forum* (Trans Tech, Aedermannsdorf, Switzerland, 1986), Vol. 10–12, p. 265.

[6] R. Wurschum and H. E. Schaefer, Phys. Status Solidi A **103**, 101 (1987).

[7] R. Wurschum and H. E. Schaefer, J. Phys. Condens. Matter (to be published).

[8] G. Dlubek, R. Krause, O. Brummer, and J. Tittes, Appl. Phys. A **42**, 125 (1987).

[9] G. Dlubek, A. Dlubek, R. Krause, and O. Brummer, Phys. Status Solidi A **107**, 111 (1988).

[10] A. Sen Gupta, S. V. Naidu, and P. Sen, App. Phys. A **40**, 95 (1985).

[11] J. L. Cheung, J. P. Karins, J. V. Corbett, and L. C. Kimmerling, J. Appl. Phys. **50**, 2962 (1979).

[12] D. P. Kerr, S. Kupca, and B. G. Hogg, Phys. Lett. **88A**, 429 (1982).

[13] S. Dannefaer, J. Phys. C **15**, 599 (1982).

[14] S. Dannefaer, D. P. Kerr, and B. G. Hogg, Phys. Rev. B **30**, 3355 (1984).

[15] S. Dannefaer and D. P. Kerr, J. Appl. Phys. **60**, 91 (1986).

[16] G. Dlubek, O. Brummer, F. Plazaola, and P. Hautojarvi, J. Phys. C **19**, 3318 (1986); G. Dlubek and R. Krause, Phys. Status Solidi A **102**, 443 (1987); G. Dlubek, A. Dlubek, R. Krause, O. Brummer, K. Friedland, and R. Rentzsch, *ibid.* **106**, 419 (1988).

[17] C. Corbel, M. Stucky, P. Hautojarvi, K. Saarinen, and P. Moser, Phys. Rev. B **38**, 8192 (1988).

[18] *Positrons in Solids,* Vol. 12 of *Topics in Current Physics,* edited by P. Hautojarvi (Springer, Heidelberg, 1979).

[19] *Positron Solid State Physics,* edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[20] K. Saarinen, P. Hautojarvi, A. Vehanen, R. Krause, and G. Dlubek, Phys. Rev. B **39**, 5287 (1989).

[21] C. Corbel, F. Pierre, P. Hautojarvi, K. Saarinen, and P. Moser (unpublished).

[22] M. J. Puska, O. Jepsen, O. Gunnarsson, and R. M. Nieminen, Phys. Rev. B **34**, 2965 (1986); M. J. Puska, Ref. 5, p. 277; M. J. Puska, Phys. Status Solidi A **102**, 11 (1987).

[23] M. J. Puska and C. Corbel, Phys. Rev. B **38**, 9874 (1988).

[24] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1377 (1985).

[25] R. W. Jansen and O. F. Sanchez, Phys. Rev. B **39**, 3192 (1989).

[26] H. J. von Bardeleben, J. C. Bourgoin, and A. Miret, Phys. Rev. B **34**, 1360 (1986).

[27] H. J. von Bardeleben and D. Stievenard, in *Defects in Electronic Materials,* edited by M. Stavola, S. J. Pearton, and G. Davies (MRS, Pittsburgh, PA, 1987), p. 351.

[28] G. Roos, A. Schoner, G. Pensi, K. Krambrock, B. K. Meyer, J. M. Spaeth, and J. Wagner, in *Defects in Semiconductors, Materials Science Forum,* edited by G. Ferenczi (Trans Tech,

Aedermannsdorf, Switzerland, 1989), Vol. 38–41, p. 951.

[29] A. A. Rezazadeh and D. W. Palmer, J. Phys. C **18**, 43 (1985).

[30] D. C. Look and J. R. Sizelove, J. Appl. Phys. **62**, 3660 (1987).

[31] D. C. Look, Solid State Commun. **64**, 805 (1987).

[32] W. Farner and D. C. Look, J. Appl. Phys. **50**, 2970 (1979).

[33] D. Stievenard, J. C. Bourgoin and O. Pons, Physica B+C (Amsterdam) **116B**, 394 (1983).

[34] J. Mäkinen, C. Corbel, and P. Hautojärvi, P. Moser, and F. Pierre, Phys. Rev. B **39**, 10 102 (1989).

[35] W. O. Siyanbola and D. W. Palmer, J. Semicond. Sci. Tech., Inst. Phys., U. K., **5**, 7 (1990).