PHYSICAL REVIEW B VOLUME 51, NUMBER 20 15 MAY 1995-II

Introduction of metastable vacancy defects in electron-irradiated semi-insulating GaAs

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(Received 7 November 1994)

Positron-lifetime experiments have been performed to investigate the metastability of the point defects produced in the electron irradiation of semi-insulating GaAs. The measurements in darkness indicate the presence of Ga vacancies and Ga antisite defects in a negative charge state. Illumination at 25 K reveals another type of a defect, which has a vacancy in its metastable state. The metastable vacancies can be observed most effectively after illumination with 1.1-eV photons and they are persistent up to the annealing temperature of 80–100 K. The introduction rate of the metastable defects is about 0.3 cm^{-1}, which is close to the values reported earlier for the As antisite. The metastable properties of the defects resemble those of the well-known *EL*2 center in as-grown GaAs. We associate these defects to As antisites, which exhibit the metastability predicted by the theory: in the metastable configuration the As antisite atom relaxes away from the lattice position, leaving a Ga site vacant.

I. INTRODUCTION

The defects introduced in the electron irradiation of GaAs have been the subject of intensive research.[1–3] Electron irradiation with energies of 1–3 MeV can be used to create simple intrinsic point defects like vacancies, antisites, and interstitials in the lattice. The understanding of the properties of these elementary defects is the basic step toward a systematic analysis of more complex defect structures. For example, the properties of irradiation-induced defects can be compared to those of native defects formed during the crystal growth of GaAs. In the identification of the atomic structure of the native defects this type of comparison may thus play a very important role.

The introduction of arsenic antisite defects during the electron irradiation of GaAs has been studied especially widely. This interest largely stems from the fact that the most important native defect in semi-insulating GaAs, the *EL*2 defect, is related to the arsenic antisite. Several studies have reported the introduction of arsenic antisite defects during electron irradiation,[4–17] neutron irradiation,[18–23] and plastic deformation.[24–26] The introduction rate of this defect in 1–2-MeV electron irradiation is of the order 0.2–0.3 cm^{-1} after annealing at 300 K.[11,12]

The most interesting property of the native *EL*2 defect in as-grown GaAs is its metastability. The metastable state of the *EL*2 defect can be populated by illumination with 1.1–1.3-eV light at low temperatures of $T<100$ K, and it can be returned to the stable state by annealing at $T>120$ K. The metastable state is electrically and optically inactive. The metastability has been theoretically explained by large lattice relaxations, which take place when the defect transforms from the stable to the metastable state. According to the theoretical model, where *EL*2 is an isolated As antisite defect, the As atom in the metastable state moves from a substitutional lattice site toward the interstitial position, and leaves behind a Ga vacancy.[27,28]

Although the introduction of As antisites has been observed in electron irradiation of GaAs, the metastability of this defect has been reported only in few studies. After 300-K annealing, infrared-absorption (IR), magnetic circular dichroism (MCD), and electron-paramagnetic-resonance (EPR) experiments have shown only minor metastable effects, which have been often related to the native *EL*2 defect remaining in the sample after irradiation.[5,8,9] The detection of an irradiation-induced *EL*2-like metastable center has been reported only in some EPR and MCD experiments either after 300-K irradiation[29] or after low-temperature irradiation and annealing at 500 K.[4,6,16,17] The recovery of the irradiation-induced As antisites has been explained by complicated annealing sequences, where the As antisite may exist as isolated or in pairs with other defects depending on the annealing temperature.[6,16] The metastability of these antisites has been reported only very recently.[30]

In our previous positron experiments on as-grown GaAs, we observed a metastable vacancy when the *EL*2 defect was transformed to the metastable state.[31,32] This vacancy has a smaller open volume than the isolated monovacancies in GaAs. We concluded that the metastable vacancy belongs to the atomic structure of the metastable state of the *EL*2 defect. These discoveries can be compared to the isolated As antisite model for *EL*2.[27,28] In this model the metastable state consists of a Ga-vacancy–As-interstitial pair, the open volume of which is slightly smaller than that of the isolated Ga vacancy. The positron results are thus in perfect agreement with the vacancy-interstitial model for the structure of the *EL*2 defect.

In this work we studied whether metastable vacancies similar to those found in as-grown GaAs are produced by electron irradiation. Present results show that electron

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irradiation creates point defects, which have a vacancy in the metastable state. The introduction rate of these defects is about 0.3 cm^{-1}, which is very close to that reported earlier for the As antisite defect. The metastability of the defect resembles the properties of the native *EL*2 defect. We thus relate the defect to the electron-irradiation-induced As antisite. However, some properties of the irradiation-induced defects are different from those of the native *EL*2 defect: (i) the conversion of the defect to the metastable state requires about ten times longer illumination, and (ii) the metastable state recovers at slightly lower temperatures of 80–100 K than in the case of the native *EL*2 defect.

The details of the positron experiments of this work are given in Sec. II. In Sec. III we explain the positron trapping model and the equations needed to analyze the positron data after irradiation. The experimental results are given in Sec. IV, and they are quantitatively analyzed in Sec. V. In Sec. VI we investigate the properties of the metastable defect observed after irradiation and discuss its atomic structure. Section VII concludes the paper.

II. EXPERIMENTAL DETAILS

The positron-lifetime experiments in this work were performed on undoped semi-insulating GaAs crystals grown by the liquid-encapsulated Czochralski technique. The samples were electron irradiated with 1.5-MeV electrons at 20 K with the Van der Graaf accelerator at Laboratoire des Solides Irradiés at Ecole Polytechnique–Paris. The irradiation fluences were 1×10^{17}, 5×10^{17}, and 1.3×10^{18} $e^-\,\text{cm}^{-2}$. After irradiation we studied the recovery of vacancy defects in these samples in our previous publication.[33] Before the experiments of this work, samples irradiated to fluences of 1×10^{17} and 5×10^{17} $e^-\,\text{cm}^{-2}$ have been annealed at 300 K, and the sample irradiated with a fluence of 1.3×10^{18} $e^-\,\text{cm}^{-2}$ has been annealed at 425 K.

The positron-lifetime experiments were performed in a similar way to that explained in our earlier publications.[32,33] Two identical pieces of samples were sandwiched with a 30-μCi ^{22}Na positron source deposited on a 1.5-μm Al foil. The measurements were carried out by a fast-fast lifetime spectrometer with a time resolution of 230 ps, and typically 2×10^6 counts were collected to each spectrum. The temperature of the sample was varied from 20 to 300 K by a closed-cycle He cryocooler, which was equipped with quartz glass windows for the illumination of the sample. The illuminations of the samples were performed with 0.7–1.5-eV light obtained from a 250-W halogen lamp and a monochromator. The source-sample sandwich was illuminated simultaneously from both sides using a bifurcated optical fiber bundle. A reference fiber bundle was used for the on-line monitoring of the incident photon flux with a Si-Ge photodetector.

After subtracting the constant background and the annihilations in the source materials (215 ps, 5.4%; 450 ps, 1.9%), the lifetime spectra were analyzed with one or two exponential components,

$$n(t)=n_0[I_1\exp(-\lambda_1 t)+I_2\exp(-\lambda_2 t)]\ , \tag{1}$$

convoluted with the Gaussian resolution function of the spectrometer. In Eq. (1), n_0 is the total number of observed positron-electron annihilations, and the annihilation rate λ_i is the inverse of the positron lifetime, $\lambda_i=\tau_i^{-1}$. I_i is the relative intensity of the lifetime component τ_i in the spectrum. The average positron lifetime is calculated from the experimental lifetimes and intensities as $\tau_{\text{av}}=\Sigma I_i\tau_i$. Even a small change in the value of this parameter can be reliably connected to a change in the vacancy concentration.

III. POSITRON TRAPPING AT VACANCIES AND NEGATIVE IONS

A. Positron trapping at vacancies in semiconductors

In a perfect crystal the delocalized positrons annihilate with a single lifetime τ_b. When neutral or negative vacancy defects appear in the material, positrons may get trapped at them and annihilate at the localized state with the lifetime τ_v. Because the electron density in a vacancy is lower than in the bulk, the lifetime τ_v is always longer than the bulk lifetime τ_b. The positron trapping rate κ_v from the delocalized state in the bulk into the localized state at the vacancy is proportional to the vacancy concentration c_v:

$$\kappa_v=\mu_v c_v\ . \tag{2}$$

The parameter μ_v is the positron-trapping coefficient, which depends on the charge of the vacancy defect. At positive vacancies the trapping coefficient is very small due to the Coulomb repulsion between the defect and the positron,[34] and in practice positive vacancies are not detected. At neutral vacancies the trapping coefficient is typically $\mu_v=1\times10^{15}\ \text{s}^{-1}$, and its value is independent of temperature.[34–36]

On the other hand, positron trapping at negative vacancies depends strongly on temperature. First, the positron trapping rate is proportional to $T^{-1/2}$ due to the nature of the positron initial wave function as a Coulomb wave.[34] Second, the positron may get trapped at a negative vacancy through a Rydberg precursor state. This process is strongly temperature dependent, because the positron may escape thermally back to the delocalized state during the trapping process. The temperature dependence of the positron-trapping coefficient μ_v through the Rydberg state into the ground state of the negative vacancy is then[34]

$$\mu_v(T)=\frac{\mu_R}{1+\dfrac{\mu_R/N_{\text{at}}}{\eta_R}\left[\dfrac{2\pi m^* k_B T}{h^2}\right]^{3/2}\exp\left[-\dfrac{E_{b,v}}{k_B T}\right]}\ . \tag{3}$$

In Eq. (3), $\mu_R=\mu_{R0}T^{-1/2}$ is the positron-trapping coefficient from the delocalized state to the Rydberg precursor state, and η_R is the trapping coefficient from the precursor state to the positron ground state at the vacancy. $E_{b,v}$ is the binding energy of the positron to the Rydberg precursor state, and $N_{\rm at}$ is the atomic density of the host material.

When only one type of vacancy defect in a single charge state exists in the sample, positrons can annihilate either as delocalized in the bulk (lifetime τ_b) or as trapped at the vacancy (lifetime τ_v). In this case the experimental second lifetime τ_2 is equal to the lifetime at the vacancy: $\tau_2=\tau_v$. The average lifetime is the superposition $\tau_{\rm av}=(1-\eta_v)\tau_b+\eta_v\tau_v$, where η_v is the fraction of positrons annihilating at the vacancy. The positron-trapping rate can then be calculated as

$$\kappa_v=\lambda_b\frac{\tau_{\rm av}-\tau_b}{\tau_v-\tau_{\rm av}}\ , \tag{4}$$

and the defect concentration can be estimate from Eq. (2) provided that the trapping coefficient μ_v is known. Even if the absolute value of the trapping coefficient is unknown, the positron-trapping rates give information on the relative defect concentrations [Eq. (2)]. However, when the experimental trapping rates are obtained at different measurement temperatures, they must be scaled to the same temperature according to Eq. (3) to enable the comparisons of the vacancy concentrations.

B. Positron trapping at the Rydberg states of negative ions

In semiconductors negative-ion type acceptors behave as shallow positron traps, which are able to capture positrons at Rydberg-like states with a low binding energy (<0.1 eV).[33,37] The trapped positron thus remains rather delocalized and its lifetime $\tau_{\rm st}$ is the same as in the bulk. The positron trapping rate $\kappa_{\rm st}$ at the negative ions is proportional to the ion concentration $c_{\rm st}$ as

$$\kappa_{\rm st}=\mu_{\rm st}c_{\rm st}\ , \tag{5}$$

where $\mu_{\rm st}$ is the positron trapping coefficient at the Rydberg state of the negative ion. As in the case of negatively charged vacancies it varies as a function of temperature as $\mu_{\rm st}=\mu_{\rm st0}T^{-1/2}$. When the temperature is high enough, positrons can escape from the Rydberg state to the bulk state due to the thermal detrapping, and at high temperatures the effect of negative ions is not observed.

When both vacancies and negative ions exist in samples, the average lifetime at any temperature can be expressed as a superposition $\tau_{\rm av}=(1-\eta_{\rm st}-\eta_v)\tau_b+\eta_{\rm st}\tau_{\rm st}+\eta_v\tau_v$, where $\eta_{\rm st}$ and η_v are the fractions of positrons annihilating at the negative ions and vacancies, respectively. When there is no detrapping from the ions, the positron-trapping rate at the ions can be calculated from the average lifetime as

$$\kappa_{\rm st}=\frac{\kappa_v(\tau_v-\tau_{\rm av})+\lambda_b(\tau_b-\tau_{\rm av})}{\tau_{\rm av}-\tau_{\rm st}}\ , \tag{6}$$

provided the trapping rate at the vacancies κ_v is known. In case the temperature is large enough for positrons to escape from the Rydberg states, the detrapping rate δ becomes comparable to the trapping rate $\kappa_{\rm st}$. In a thermodynamical approach these quantities are related by[38]

$$\frac{\delta}{\kappa_{\rm st}}=\frac{1}{c_{\rm st}}\left[\frac{2\pi m^*k_BT}{h^2}\right]^{3/2}\exp\left[-\frac{E_{b,\rm st}}{k_BT}\right]\ , \tag{7}$$

where m^* is the positron effective mass and $E_{b,\rm st}$ is the positron binding energy at the Rydberg state of the negative ion.

The temperature dependence of average positron lifetime in the presence of positron detrapping from the negative ions has been studied in detail in our earlier publication.[33] Depending on the positron binding energy $E_{b,\rm st}$ and concentration $c_{\rm st}$, the behavior of $\tau_{\rm av}$ can be divided into three different temperature regions. In the first region at the lowest temperatures, both vacancies and ions trap positrons and there is no detrapping from the ions ($\delta\ll\kappa_{\rm st}$). In this region the average lifetime is essentially constant as the temperature dependences of positron trapping at the ions and at vacancies cancel each other. The trapping rate at the negative ions can then be calculated from Eq. (6). In the second region the detrapping from the ions starts to play a role [$\delta\approx\kappa_{\rm st}$ in Eq. (7)], and $\tau_{\rm av}$ increases strongly because a larger fraction of positrons annihilates at the vacancies instead of at the ions. In the third region the detrapping is so strong that practically no positrons annihilate at the negative ions ($\delta\gg\kappa_{\rm st}$). Equation (4) is then valid, and the average lifetime reflects purely the temperature dependence of the positron-trapping coefficient at the vacancies [Eq. (3) in case of negative vacancies].

IV. EXPERIMENTAL RESULTS

A. Temperature dependence of positron lifetime in darkness

The positron lifetimes in the as-grown and electron-irradiated GaAs samples are shown in Fig. 1 as a function of the measurement temperature. In the as-grown sample the positron lifetime is about 233 ps at room temperature, and it decreases to 231 ps when the measurement temperature is lowered to 20 K. These positron-lifetime values are very close to those we have determined in the Zn-doped reference sample[39] for delocalized positrons in the GaAs bulk: 232.5 ps at 300 K and 231.3 ps at 25 K. Hence no vacancy defects are detected in the positron experiments on the as-grown semi-insulating GaAs sample.

The positron average lifetimes at 300 K in the electron-irradiated samples vary from 235 to 241 ps depending on the irradiation fluence. As these values are above the bulk lifetime, they indicate the presence of irradiation-induced vacancy-type defects. The decomposition of the lifetime spectrum into two components yields the second lifetime of $\tau_2=260\pm3$ ps in all irradiated samples, and at 300 K the decomposition follows the simple one-defect trapping model.[40] The lifetime spectra at 300 K thus indicate that a single-vacancy defect acts as the dominant positron trap. Since the average positron lifetime increases with the irradiation fluence in all the samples annealed at 300 K, we can conclude that the detected vacancy defect is introduced in the electron irradiation.[33] According to theoretical calculations Ga vacancies are negative and As vacancies positive in GaAs, when the Fermi level is at midgap.[41–43] The defects detected by positrons can thus be attributed to Ga vacancies since the As vacancies are repulsive to positrons.[33]

The temperature dependence of the average positron lifetime in irradiated GaAs samples is shown in Fig. 1. In all samples, the lifetime is constant at 20–100 K, after which it starts to increase as a function of temperature. At higher temperature this increase levels off and an essentially constant average lifetime is found. The onset temperature for the plateau of constant τ_{av} depends on the irradiation fluence: for the lowest fluence of $\Phi_{e^-}=1\times10^{17}$ $e^-\,\mathrm{cm}^{-2}$ the plateau starts at about 200 K, but in the sample with $\Phi_{e^-}=1.3\times10^{18}$ $e^-\,\mathrm{cm}^{-2}$ the increase of the average positron lifetime continues up to 350 K.

The temperature dependence of the average positron lifetime in the electron-irradiated samples can be understood in terms of thermal positron detrapping from negative-ion-type defects, which act as shallow positron traps.[33] These traps are shallow in the sense that the positron binding energy at them is much lower than at a vacancies, and the positron lifetime is the same as in bulk GaAs. At low temperatures of $T<100$ K, when the average lifetime in Fig. 1 is constant, all positrons are trapped either at vacancies or at shallow traps, and no detrapping occurs. The increase of the average lifetime above 100 K indicates that positrons are partially detrapped from the shallow traps, and a larger fraction of them annihilates at the vacancies. When the detrapping is complete at high temperature, only vacancy defects are detected, and the average lifetime saturates to a constant value (Fig. 1).

The results of our earlier work indicate that the shallow positron trap is an elementary point defect introduced in the electron irradiation.[33] According to theory, As antisites as well as Ga and As interstitials are neutral or positively charged in semi-insulating GaAs, but the Ga antisites are negative.[41–43] The shallow positron traps can thus be associated with negatively charged Ga antisite defects, which trap positrons to Rydberg-like states at low temperatures.[33]

B. Metastable effects in the positron lifetime after illumination

The positron-lifetime results after illumination of the sample are shown in Fig. 2. The photon energy was

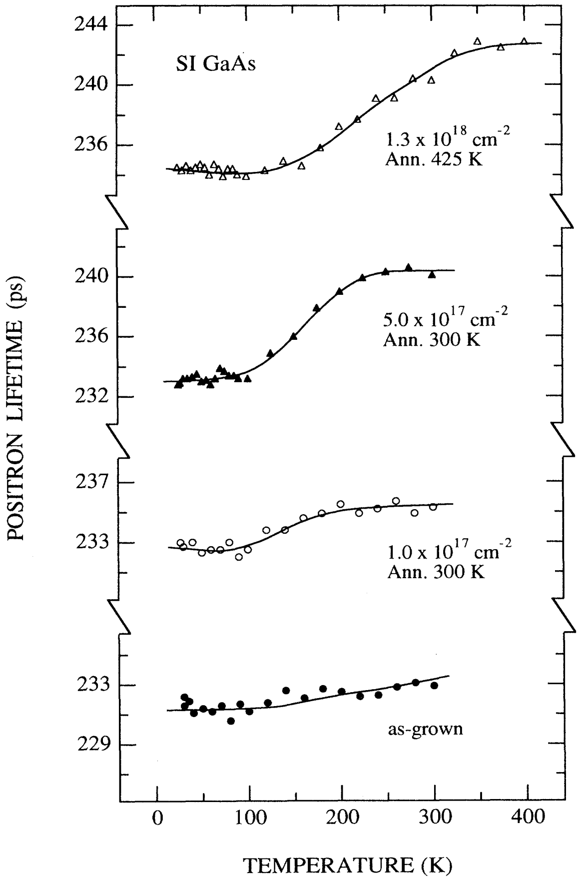

FIG. 1. Fluence effects on the temperature dependence of the positron average lifetime in semi-insulating GaAs after 1.5-MeV electron irradiation at 20 K. After irradiation the samples have been annealed either at 300 or 425 K.

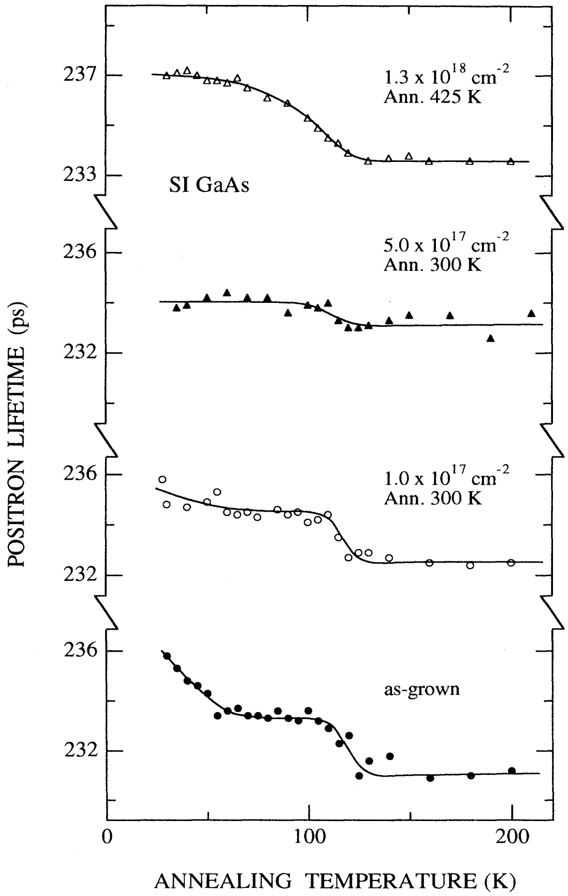

FIG. 2. The positron average lifetime as a function of the isochronal annealing temperature after 1.15-eV illumination at 25 K. All measurements have been performed in darkness at 30 K, and the annealing time was 10 min. The electron irradiation fluences are marked in the figure.

$E_{\mathrm{ph}}=1.15$ eV and the illumination with the photon flux of $\Phi_{\mathrm{ph}}=10^{16}$ s^{-1} cm^{-2} lasted for at least two hours at 25 K before the positron lifetime was measured in darkness. Between each positron experiment a 10-min isochronal annealing of the sample was performed at the temperature indicated on the horizontal axis of Fig. 2.

The results in Fig. 2 show that in all samples the positron lifetime after illumination is longer than the lifetime measured before illumination in darkness. The increase of τ_{av} both in the as-grown GaAs and in the electron-irradiated material is typically 2–3 ps. This change of the average positron lifetime is persistent at 25 K, since it remains for several days after the illumination is switched off. As explained in Sec. III and in earlier publications,[31,32] the increase of positron lifetime is a fingerprint of vacancy defects in the samples. Hence the data in Fig. 2 indicate that at 25 K more vacancy defects are observed in the samples after the illumination than before it.

The illumination effect in the as-grown GaAs disappears in isochronal annealing in two stages (Fig. 2). First, at 30–50 K the lifetime decreases about 2 ps, whereafter τ_{av} saturates to a level, which is still 1–2 ps above the values measured before illumination. An abrupt annealing stage is observed at 110–120 K, at which the illumination effect is lost completely as the average lifetime coincides with the level obtained in darkness. In the electron-irradiated samples the annealing at 30–50 K is not seen, but the recovery of the average lifetime takes place at around 100 K. When the electron-irradiation fluence is increased from $\Phi_{e^-}=1\times10^{17}$ to 1.3×10^{18} e^- cm^{-2}, the annealing stage shifts from 120 K to slightly lower temperatures of 80–90 K.

The increase of the average lifetime indicates that more vacancies are detected in all samples after the illumination. These vacancies are stable only at low temperatures, and they disappear during isochronal annealing at 80–120 K. The data closely resemble the results that we have previously obtained in as-grown GaAs, where the increase of the average lifetime after illumination was used to show that the metastable state of the *EL*2 defect contains a vacancy.[31,32] We thus conclude that metastable vacancies are also observed in electron-irradiated GaAs.

C. Generation of the metastable vacancies during illumination

To study the appearance of the metastable vacancy in more detail, we performed an illumination experiment where we kept the photon energy $E_{\mathrm{ph}}=1.15$ eV and flux $\Phi_{\mathrm{ph}}=1\times10^{16}$ s^{-1} cm^{-2} fixed, and varied the illumination time t_{ill}. The positron lifetime was measured in darkness at 25 K between each illumination. In this type of experiment the positron lifetime is thus measured as a function of the photon fluence $\Phi_{\mathrm{ph}}t_{\mathrm{ill}}$. The results obtained in as-grown GaAs and in the irradiated samples are shown in Fig. 3.

In as-grown GaAs the average positron lifetime first increases rapidly with the illumination time and then saturates. 50% of the saturation of the curve is reached at about 4×10^{17} cm^{-2}. In the sample irradiated to the fluence $\Phi_{e^-}=1\times10^{17}$ e^- cm^{-2} (not shown in Fig. 3) the increase of the average lifetime takes place more slowly, and a fluence of 10×10^{17} cm^{-2} is required to generate half of the total increase. In the sample with the largest irradiation fluence of $\Phi_{e^-}=1.3\times10^{18}$ e^- cm^{-2} a large illumination fluence such as 100×10^{17} cm^{-2} is needed to obtain half of the maximum illumination effect in τ_{av}. Since the increase of the average lifetime reflects the generation of the metastable vacancies, the data in Fig. 3 indicate that much longer illumination times are needed to create the metastability in the irradiated samples than in as-grown GaAs. Furthermore, the illumination time constant for the generation of the metastable vacancies is larger in samples which have been electron irradiated to a larger fluence.

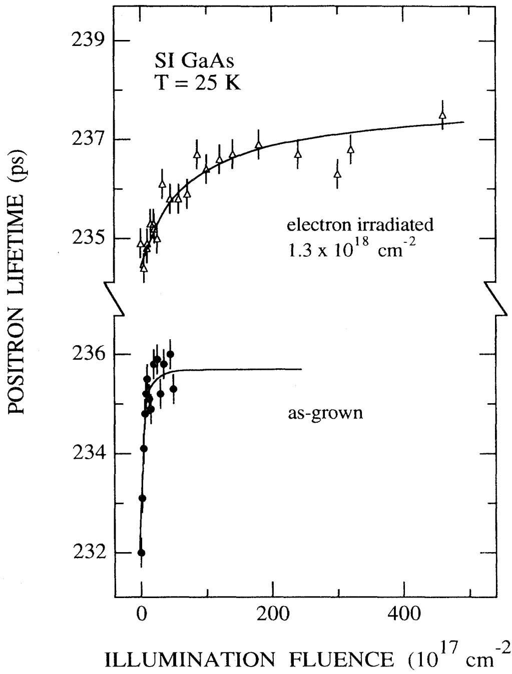

FIG. 3. Positron average lifetime as a function of the illumination fluence in as-grown and electron-irradiated (electron fluence 1.3×10^{18} e^- cm^{-2}) GaAs samples. A photon energy of 1.15 eV was used in the illumination. All experiments have been performed in darkness at 25 K between each illumination at 25 K.

The results of Fig. 4 show the persistent increase of positron lifetime as a function of the photon energy. In this experiment the illumination fluence has been kept constant for each photon energy, and the fluence was $\Phi_{\mathrm{ph}}t_{\mathrm{ill}}=6\times10^{17}$ cm^{-2} for the as-grown sample and $\Phi_{\mathrm{ph}}t_{\mathrm{ill}}=3\times10^{19}$ cm^{-2} for the electron-irradiated sample. The positron lifetime was measured in darkness at 25 K between each illumination, and between each experiment the sample was annealed in darkness at 200 K to remove the metastability completely.

In as-grown GaAs the data in Fig. 4 show no illumination effects for photon energies below $E_{\mathrm{ph}}=1.05$ eV. Between $E_{\mathrm{ph}}=1.05$ and 1.35 eV there is a clear increase in

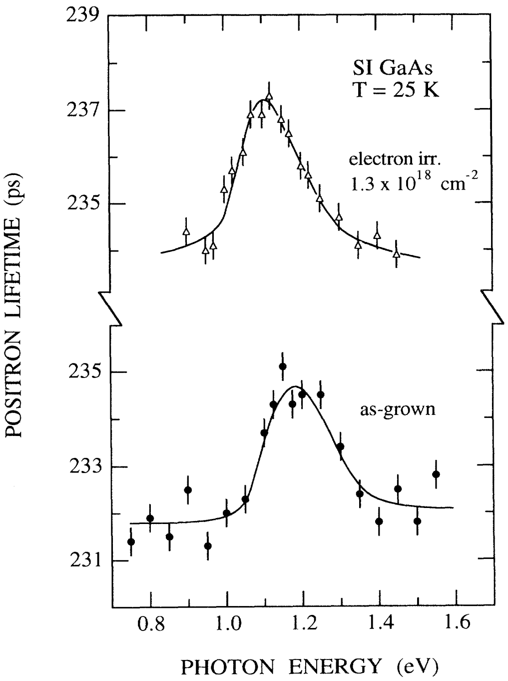

FIG. 4. Positron average lifetime as a function of the photon energy in as-grown and electron-irradiated (electron fluence 1.3×10^{18} e^- cm^{-2}) GaAs samples. All spectra were measured in darkness at 25 K after illumination of the sample with 1.15-eV light at 25 K. The photon fluence was the constant of 6×10^{17} cm^{-2} in the as-grown sample and 3×10^{19} cm^{-2} in the irradiated sample.

the average positron lifetime with a well-marked peak centered at $E_{\mathrm{ph}}=1.15$ eV. The full width at half maximum of this peak is about 0.2 eV, and a small illumination effect can be detected up to $E_{\mathrm{ph}}=1.4$ eV. The data obtained for the as-grown GaAs (Fig. 4) are similar to that presented in our earlier publication.[32] As discussed there, the spectrum of Fig. 4 reflects the photon energy dependence for the generation of metastable vacancies, when the *EL*2 defect is transformed to the metastable state.

The upper part of Fig. 4 shows the generation of the metastable vacancy in electron-irradiated GaAs. The photon fluence we have chosen is now higher than in the case of as-grown GaAs, because in the irradiated samples much longer illumination times are needed to produce the metastability, as demonstrated in Fig. 3. In the irradiated samples (Fig. 4), there is no illumination effect at photon energies below $E_{\mathrm{ph}}=1.0$ eV, but between $E_{\mathrm{ph}}=1.0$ and 1.3 eV the average positron lifetime goes through a well-marked maximum. Hence the metastable vacancy in the electron-irradiated GaAs can be generated by illumination with the photon energies of $E_{\mathrm{ph}}=1.0-1.3$ eV and the effect is strongest at 1.1 eV. Above $E_{\mathrm{ph}}=1.3$ eV no illumination effect is observed. When compared to results obtained in as-grown GaAs, the peak of τ_{av} in Fig. 4 in electron-irradiated GaAs is somewhat narrower and also shifted to slightly lower photon energies.

D. Temperature dependence of positron lifetime in the metastable state

After illuminating the sample at 25 K the positron lifetime can be studied as a function of measurement temperature below the annealing stage at 80–120 K. As explained in Sec. III, the temperature dependence of the positron trapping can be used to obtain information about the charge state of the vacancy defect. The results of such experiments are presented in Fig. 5. Before the positron measurements the samples were illuminated at 25 K with 1.15-eV photons for at least 2 h with a photon flux of $\Phi_{\mathrm{ph}}=10^{16}$ s^{-1} cm^{-2}, whereafter positron-lifetime experiments were performed in darkness. Since there is recovery in the as-grown sample already below 50 K, the data in Fig. 5 show the positron lifetimes after annealing at temperatures, which are higher than the measurement temperatures indicated by the horizontal axis of Fig. 5. The annealing temperatures were 80 K for the as-grown

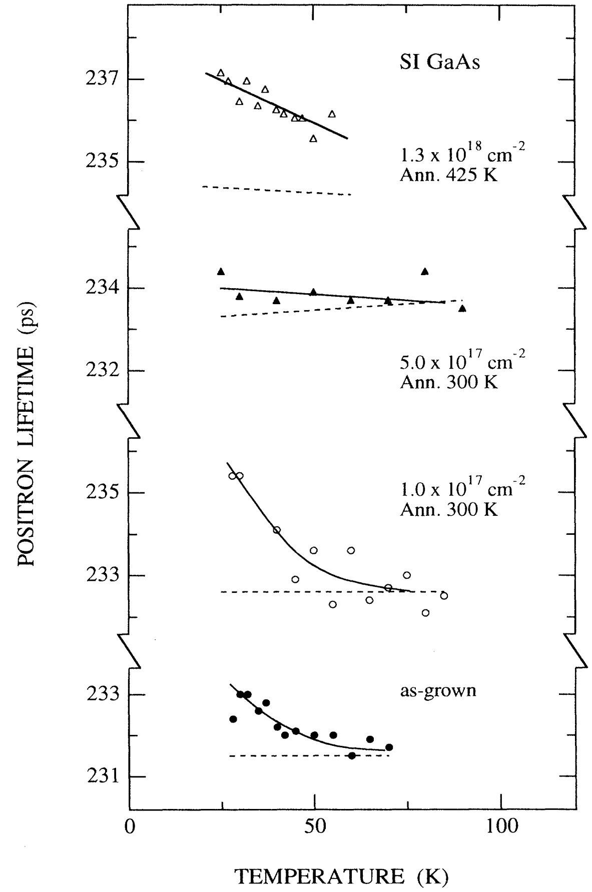

FIG. 5. Average positron lifetime as a function of measurement temperature. The measurements were performed in darkness after 1.15-eV illumination of the samples at 25 K. After illumination and before the experiments the samples were annealed at 80 K (as-grown sample), at 90 K (1×10^{17}- and 5×10^{17}-e^- cm^{-2}-irradiated samples), or at 70 K (1.3×10^{18}-e^- cm^{-2}-irradiated sample). The reference levels corresponding to the positron lifetimes measured in darkness before any illumination are marked by the dashed lines.

sample, 90 K for the samples irradiated to the fluences of 1×10^{17} e^- cm^{-2}, and 5×10^{17} e^- cm^{-2} and 70 K for the samples irradiated to the fluence 1.3×10^{18} e^- cm^{-2}. This preparation procedure guarantees that we measure only the temperature dependence of positron trapping at the metastable vacancy recovering at 80–120 K in all samples, and that the temperature dependence is not mixed with the annealing stages taking place already below 50 K. The reference levels corresponding to the positron lifetimes measured in darkness before any illumination are marked by the dashed lines in Fig. 5.

In as-grown GaAs the average lifetime decreases clearly with increasing temperature (Fig. 5). This indicates that positron trapping to the metastable vacancy is enhanced at low temperatures. In our earlier publication we associated this effect with the negative charge of the metastable vacancy.[31,32] In the samples irradiated to the fluences 1×10^{17} and 5×10^{17} e^- cm^{-2} the average lifetime decreases with increasing temperature like in as-grown GaAs, and at about 50 K the curves coincide with their reference levels (Fig. 5). The behavior of the average lifetime is somewhat different in the sample with the highest irradiation fluence of 1.3×10^{18} e^- cm^{-2}, and in the range of 25–60 K it does not reach the reference level. We conclude that both in the as-grown and irradiated samples the average lifetime shows a negative temperature dependence after illumination at 25 K. However, the dependence becomes less prominent when the irradiation fluence increases.

V. POSITRON TRAPPING AT THE METASTABLE VACANCIES IN ELECTRON-IRRADIATED GaAs

A. Introduction of Ga vacancies and Ga antisites

In experiments performed in darkness the defect trapping positrons in electron-irradiated GaAs are the Ga vacancies and Ga antisites. Ga antisites behave as shallow positron traps, and they have no effect on the positron average lifetime at the high-temperature region, where the detrapping is complete (see Sec. III). The positron-trapping rate at V_{Ga} can thus be estimated at 300 K simply using Eq. (4) with $\tau_v=260$ ps. The values are presented in Fig. 6. It should be mentioned that in case of the largest irradiation fluence $\Phi_{e^-}=1.3\times10^{18}$ e^- cm^{-2} we have used the data after 300-K annealing taken from our previous publication.[33]

The positron-trapping rates at the Ga vacancy in Fig. 6 increase linearly with the irradiation fluence. This behavior manifests the introduction of the Ga vacancies in the electron irradiation. By using the positron-trapping coefficient of $\mu_v=1.4\times10^{15}$ s^{-1},[33] the introduction rate $\Sigma_v=c_v/\Phi_{e^-}$ of Ga vacancies after annealing at 300 K becomes $\Sigma_v=0.1$ cm^{-1}. This value is quite low because the main recovery stage of Ga vacancies is below room temperature at about 200–300 K,[33,44] but the positron result is in reasonable agreement with that obtained from EPR experiments (0.03 cm^{-1} after 1.0-MeV irradiation at 300 K).[45]

The positron-trapping rate at the Ga antisites can be calculated at the low-temperature region ($T<100$ K), at which the detrapping of positrons from the Rydberg states of $\mathrm{Ga_{As}}$ plays no role. For this calculation we need to know the positron trapping rate κ_v at Ga vacancies at low temperature. By studying the temperature dependence of positron trapping at native Ga vacancies in as-grown GaAs, we determined the following values for the parameters in Eq. (3): $E_{b,v}=15$ meV, $\mu_{R0}=6\times10^{16}$ s^{-1}K$^{1/2}$, and $\eta_R=3\times10^{11}$ s^{-1}.[46] After scaling the values of κ_v from 300 to 30 K, the positron-trapping rate κ_{st} at the Ga antisites can be calculated from Eq. (6) by substituting $\tau_{\mathrm{st}}=\tau_b$. The results are given as a function of the irradiation fluence in Fig. 6.

The data in Fig. 6 show that the positron-trapping rate κ_{st} at Ga antisites increases linearly as a function of the irradiation fluence. In accordance with our previous results,[33] this behavior indicates that Ga antisite defects are produced in the electron irradiation. The concentration of the Ga antisites can be obtained by fitting Eq. (7) to the temperature dependence of the average lifetime (Fig. 1) with E_b and c_{st} as free parameters.[33] From this analysis we obtain the value of $E_{b,\mathrm{st}}=52\pm5$ meV for the positron-binding energy in all the curves of Fig. 1. By combining the positron-trapping rate κ_{st} and the fitted concentration c_{st} [Eq. (5)], we get the value of $\mu_{\mathrm{st}0}=(5.0\pm1.5)\times10^{16}$ s^{-1}K$^{1/2}$ for the prefactor of the positron-trapping coefficient $\mu_{\mathrm{st}}=\mu_{\mathrm{st}0}T^{-1/2}$ at the Rydberg state of $\mathrm{Ga_{As}}$.

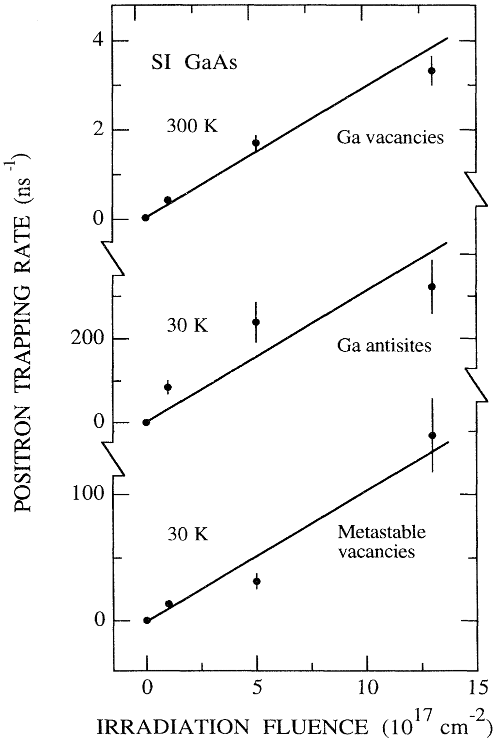

FIG. 6. Positron-trapping rate at Ga vacancies, Ga antisite defects, and metastable vacancy defects as a function of the electron-irradiation fluence. The trapping rates at Ga antisites and at the metastable vacancies have been determined at the measurement temperature of 30 K, and the trapping rate at the Ga vacancies at 300 K. After irradiation with 1.5-MeV electrons at 20 K the samples have been annealed at 300 K.

Finally, we use this value to convert all the trapping rates κ_{st} to the concentrations c_{st}.

The concentrations of the Ga antisites in the samples are much larger than the concentration of Ga vacancies, and the introduction rate $\Sigma_{\text{st}}=c_{\text{st}}/\Phi_{e^-}$ of Ga_{As} after 300-K annealing is as high as $\Sigma_{\text{st}}=1.4\ \text{cm}^{-1}$. This value is in good agreement with our previous estimates,[33] although now we have also introduced the temperature dependences of μ_v and μ_{st} into the analysis. The much higher introduction rate of Ga_{As} compared to that of V_{Ga} reflects the fact that Ga vacancies anneal mainly below room temperature, whereas Ga antisites are stable at least up to 450 K.[33]

B. Introduction of the metastable vacancies

After illumination at low temperatures metastable vacancies are observed both in the as-grown and electron-irradiated GaAs samples. In as-grown GaAs the metastable vacancy belongs to the atomic configuration of the metastable state of the *EL*2 defect, and recently we determined the positron lifetime of $\tau_{v^*}=245$ ps at this center.[32] In the electron-irradiated samples the metastable vacancies resemble in many ways those observed in as-grown GaAs: both the photon energies for the vacancy generation and the annealing temperatures of the metastable vacancies are close to each other.

In this section we shall analyze quantitatively the concentration of the metastable vacancies in electron-irradiated GaAs. After illumination at 30 K the positrons may annihilate either in the bulk or as trapped at Ga vacancies, at Ga antisites or at the metastable vacancies. The average positron lifetime can then be written

$$\tau_{\text{av}}=(1-\eta_v-\eta_{\text{st}}-\eta_{v^*})\tau_b+\eta_v\tau_v+\eta_{\text{st}}\tau_{\text{st}}+\eta_{v^*}\tau_{v^*}\ , \qquad (8)$$

where the fraction η_i of positrons annihilate at the site i, the index i corresponding to Ga vacancy (v), Ga antisite (st), and metastable vacancy (v^*), respectively. In the positron-trapping model the annihilation fractions η_i are proportional to the trapping rates κ_i as $\eta_i=\kappa_i/(\lambda_b+\Sigma\kappa_i)$, when no detrapping takes place. The positron trapping rate at the metastable vacancy can thus be solved from Eq. (8), yielding

$$\kappa_{v^*}=\frac{(\lambda_b+\kappa_{\text{st}})(\tau_{\text{av}}-\tau_b)+\kappa_v(\tau_{\text{av}}-\tau_v)}{\tau_{v^*}-\tau_{\text{av}}}\ . \qquad (9)$$

In Eq. (9) we assume that positron lifetime at the Ga antisite is the same in bulk GaAs, and that the lifetime at the metastable vacancy is in all samples the same as in the as-grown sample, i.e., the lifetime $\tau_{v^*}=245$ ps at the metastable state of *EL*2.[32] We assume further that the positron-trapping rates at the Ga vacancies κ_v and at the Ga antisites κ_{st} remain after illumination the same as determined in darkness and shown in Fig. 6 (see below). The trapping rates κ_{v^*} at the metastable vacancy calculated from the data of Fig. 2 are shown in Fig. 6 as a function of the irradiation fluence.

The positron-trapping rate at the metastable vacancy increases linearly in Fig. 6 as a function of the irradiation fluence. This behavior shows that the concentration of the metastable vacancies increases with the irradiation fluence. For example, in the sample irradiated to $\Phi_{e^-}=1.3\times10^{18}\ e^-\ \text{cm}^{-2}$ the trapping rate is $\kappa_{v^*}=147\ \text{ns}^{-1}$, which indicates that the concentration of metastable vacancies is almost 150 times larger than that observed in as-grown GaAs, where $\kappa_{v^*}=1\ \text{ns}^{-1}$. We thus conclude that metastable vacancies are produced by the electron irradiation.

We have studied the influence of the assumption made in the estimation of κ_{v^*} above. The conclusion is that systematical errors in τ_{v^*} and in κ_v and κ_{st} have an effect on the absolute values of the trapping rate κ_{v^*}, but do not affect the linear increase of κ_{v^*} as a function of the irradiation fluence Φ_{e^-}.

The positron trapping rate κ_{v^*} can be converted to the concentration of metastable vacancies with the positron-trapping coefficient μ_{v^*}. For the vacancy in the metastable state of the *EL*2 defect values in the range of $\mu_{v^*}=(1-2)\times10^{16}\ \text{s}^{-1}$ at 30 K have been estimated.[32,47] As the irradiation-induced metastable vacancy closely resembles that detected in as-grown GaAs, we use the value $\mu_{v^*}=1.5\times10^{16}\ \text{s}^{-1}$ in the analysis of the electron-irradiated samples. The introduction rate $\Sigma_{v^*}=c_{v^*}/\Phi_{e^-}$ of the metastable vacancies becomes $\Sigma_{v^*}=0.3\ \text{cm}^{-1}$.

We can summarize the analysis of this section as follows. The positron-lifetime results show that the electron irradiation of GaAs introduces a metastable defect, which has a vacancy in the metastable state. The metastable vacancy can be generated most efficiently with 1.1-eV photons, and after illumination the vacancy recovers thermally at 80–120 K. The introduction rate of the defect containing the metastable vacancy is $0.3\ \text{cm}^{-1}$.

VI. THE NATURE OF THE METASTABLE VACANCY

In this section we shall investigate the properties of the metastable vacancy detected in the positron experiments. We will also correlate these findings to the results of previous experiments and theoretical calculations. We shall further discuss the atomic structure of the defect, which contains the vacancy in its metastable state.

A. Optical cross section for the generation of the metastable vacancy

The persistent increase of the average positron lifetime as a function of the illumination fluence was shown in Fig. 3. These results indicate that the effect observed in τ_{av} becomes slower when the electron-irradiation fluence is larger. To analyze quantitatively the increase of the positron-lifetime data with the illumination fluence, we have calculated the positron-trapping rate at the metastable vacancy similarly as in Sec. V B using Eq. (9). The transient of the trapping rate as a function of the illumination fluence can be analyzed quantitatively by defining the optical cross section for the generation of the metastable vacancy as

$$\kappa_{v*}(t_{\mathrm{ill}})=\kappa_{v*}^{\mathrm{tot}}(1-e^{-(\sigma_{v*}\Phi_{\mathrm{ph}})t_{\mathrm{ill}}}) , \tag{10}$$

where the parameter $\kappa_{v*}^{\mathrm{tot}}$ is the total positron trapping rate at the metastable vacancies. Notice that in Eq. (10) the optical cross section σ_{v*} is not necessarily connected to any individual optical process, but it is rather an effective value that we use to describe the time constant of the transient in the positron-trapping rate.

The data in Fig. 7 show the logarithmic plot of the quantity $(1-\kappa_{v*}/\kappa_{v*}^{\mathrm{tot}})$, which gives the fraction of defects in the stable state as a function of the illumination fluence $\Phi_{\mathrm{ph}}t_{\mathrm{ill}}$. It is seen that the data follow the exponential behavior of Eq. (10) for about two decades. The optical cross section σ_{v*} can thus be obtained from the slopes of the data in Fig. 7.

The analysis of Fig. 7 indicates that the generation of the metastable vacancy is a much slower process in electron-irradiated GaAs when compared to the similar transition in the as-grown GaAs. This behavior reflects large differences in the optical cross section σ_{v*}. In as-grown GaAs we previously determined the value of $\sigma_{v*}=2\times10^{-18}$ cm^2 at $E_{\mathrm{ph}}=1.15$ eV for the optical generation of the metastable vacancy related to the atomic structure of the metastable state of the *EL*2 defect.[32] By fitting Eq. (10) to the data of Fig. 7, we get the cross sections of $\sigma_{v*}=2\times10^{-18}$ cm^2 in the as-grown sample and $\sigma_{v*}=1\times10^{-19}$ cm^2 in the sample with the electron-irradiation fluence of $\Phi_{e^-}=1.3\times10^{18}$ e^- cm^{-2}, respectively. Order-of-magnitude-longer illumination times are therefore needed to generate the metastable vacancy in the irradiated GaAs than in the as-grown material.

The optical cross section σ_{v*} in electron-irradiated GaAs needs to be corrected against the strong light absorption in the samples. In our experimental setup the positrons are implanted within 50 μm from the sample surface, whereas the illumination enters the sample from the *other* side. Since the typical sample thickness is 500 μm, the photon flux at the region encountered by positrons is smaller than the incident flux Φ_{ph}. We have determined by infrared-absorption measurements that this attenuation is a factor of 3 at the photon energy of 1.15 eV in the sample irradiated to the electron fluence $\Phi_{e^-}=1.3\times10^{18}$ e^- cm^{-2}. Taking this absorption into account, the optical cross section for the generation of the metastable vacancy becomes $\sigma_{v*}=3\times10^{-19}$ cm^2, which is still an order of magnitude smaller than the value found in the as-grown reference sample.

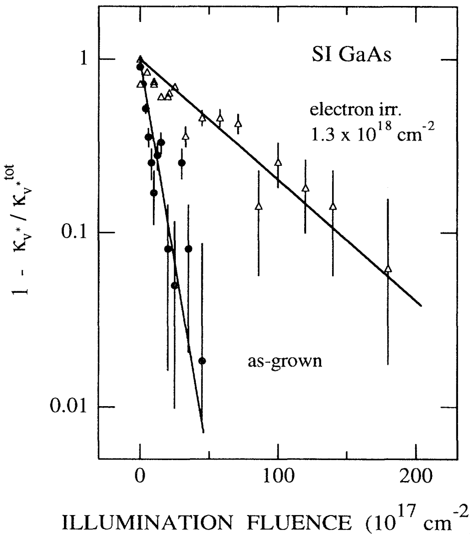

FIG. 7. The logarithmic plot corresponding to Eq. (10). The data show the fraction of metastable defects in the stable state as a function of 1.15-eV illumination fluence, as calculated from the positron-trapping rate at the metastable vacancy κ_{v*}. The slopes of the data give the optical cross section σ_{v*} for the generation of the metastable vacancy.

The photon energy dependence of the metastable vacancy generation is shown in Fig. 4. The figure indicates that at photon energies below 1.0 eV and above 1.3 eV no metastable vacancies are observed. However, metastable vacancies could be generated with 1.0–1.3-eV photons, and the most effective illumination photon energy was 1.1 eV. When compared to the as-grown reference sample, we observe that the peak in Fig. 4 has shifted to slightly lower photon energies in the irradiated samples. In addition to the much lower optical cross section discussed above, the generation of the metastable vacancy in electron-irradiated GaAs thus has its maximum efficiency at slightly lower photon energies than in the as-grown material.

However, the two peaks in Fig. 4 can be compared to each other only qualitatively, because the absorption spectrum of the irradiated samples varies considerably as a function of the photon energy. Especially above 1.2 eV the background absorption increases rapidly, and the sample becomes almost opaque at photon energies above 1.3 eV. This absorption reduces the photon flux from its incident value at the sample region probed by the positrons, as discussed above. The absorption may thus have some influence on the shape of the curves in Fig. 4.

B. Annealing of the metastable vacancy

In as-grown GaAs the metastable vacancy is part of the metastable state of the *EL*2 defect.[31,32] After illumination at low temperatures the metastable state of the *EL*2 defect recovers thermally at 120 K with a thermal activation energy of about 0.3 eV. The metastable vacancy detected in the positron experiments disappears accordingly at 120 K.[31,32] To investigate the thermal stability of the metastable vacancy observed in electron-irradiated GaAs, the positron-trapping rate κ_{v*} has been plotted in Fig. 8 as a function of the isochronal annealing temperature. The trapping rates have been calculated from Eq. (9) using the positron lifetime data of Fig. 2.

In the as-grown sample the positron-trapping rate and thus the concentration of the metastable vacancies decreases rapidly down to zero, when the metastable state of the *EL*2 recovers at 120 K. In the electron irradiated sample ($\Phi_{e^-}=1.3\times10^{18}$ e^- cm^{-2}) the recovery stage of the positron-trapping rate has a much larger magnitude,

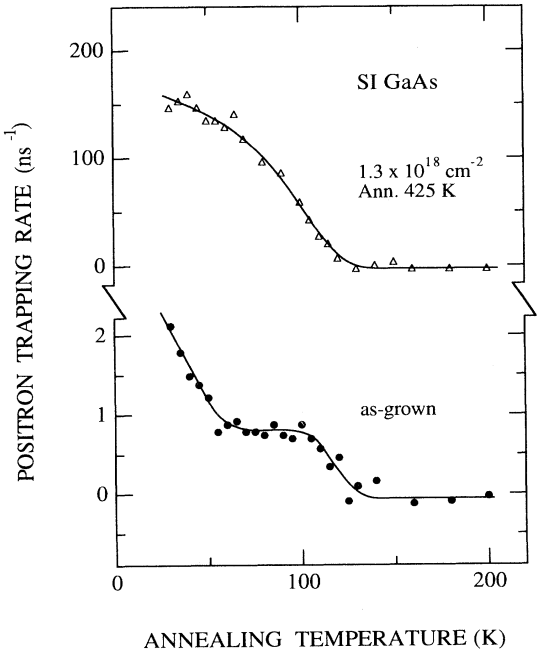

FIG. 8. The positron-trapping rate at the metastable vacancy as a function of the isochronal annealing temperature after 1.15-eV illumination at 25 K. All measurements have been performed in darkness at 30 K, and the annealing time was 10 min. The figure shows the data obtained in the as-grown and electron-irradiated GaAs.

since the irradiation has increased the concentration of the metastable vacancies as shown already in Fig. 6. In the electron-irradiated sample ($\Phi_{e^-} = 1.3 \times 10^{18}$ e^- cm^{-2}) the annealing of the metastable vacancy starts at clearly lower temperatures than in as-grown GaAs, at about 80 K, and the recovery is already complete at 110 K. When the irradiation fluence of the samples becomes larger, the annealing stage thus shifts to lower temperatures.

This shift of the recovery temperature in the electron-irradiated samples can be understood as follows. In the as-grown sample the vacancy in the metastable *EL*2 defect is the only positron trap present after light illumination at 20 K. The electron irradiation introduces another defect, which has a vacancy in its metastable state. This vacancy recovers at slightly lower temperatures of $T_{\mathrm{ann}} = 80-100$ K than the metastable vacancy in as-grown GaAs ($T_{\mathrm{ann}} = 120$ K). Hence at low irradiation fluences ($\Phi_{e^-} = 10^{17}-10^{18}$ e^- cm^{-2}) both native and irradiation-induced metastable vacancies may trap positrons. The annealing of the vacancy observed in the experiments then shifts gradually to lower temperatures when the concentration of the irradiation-induced metastable vacancies increases compared to that of the native ones. Finally after a large irradiation fluence of $\Phi_{e^-} = 1.3 \times 10^{18}$ e^- cm^{-2} the effect of the native metastable vacancies is completely lost in preference to the metastable defects introduced in the electron irradiation, and the annealing stage of the metastable vacancy has moved completely to 80–100 K. Notice that in this case no annealing stage is observed at 120 K in Fig. 8, because the saturated positron trapping at the large number of irradiation-induced defects V_{Ga} and $\mathrm{Ga}_{\mathrm{As}}$ completely masks the effect of the native metastable vacancies.

Our preliminary experiments indicate that in the electron-irradiated sample there is also an optical recovery of the metastable vacancy under 1.3-eV illumination. This optical recovery is not detected in as-grown GaAs at 25 K, and may thus explain the differences in the generation of the metastable vacancy in as-grown and irradiated samples. If an optical recovery process is competing with the generation processes, it may have a large influence on both the measured value of the optical cross section σ_{v^*} [Eq. (10)] and on its photon energy dependence.

We can conclude that the metastable vacancy introduced in the electron irradiation recovers at lower temperatures (80–100 K) than the vacancy in the metastable state of the native *EL*2 defect (120 K). This indicates a slightly lower thermal barrier for the annealing of the metastable state. In comparison to the values of 0.3–0.35 eV reported for the metastable *EL*2,[2,32,48] the recovery at 80–100 K of the irradiation-induced metastable vacancy corresponds roughly to an activation energy of 0.2–0.3 eV.

C. The charge state of the metastable vacancy

Positron trapping at neutral vacancies is independent of temperature, whereas at negative vacancies it is strongly enhanced at low temperatures (Sec. III A). In as-grown GaAs, positron trapping at the vacancy in the metastable state of the *EL*2 defect has been found to be strongly temperature dependent. This indicates that the vacancy is negatively charged although the total charge of the *EL*2* state may be neutral.[32]

The temperature dependence of the positron average lifetime in electron-irradiated GaAs after illumination has been studied in the experiments shown in Fig. 5. It is observed that the positron average lifetime increases with decreasing temperature in the electron-irradiated samples. Furthermore, the difference between the average lifetime after illumination and the reference level (the dashed line in Fig. 5) becomes larger when the temperature is decreased. The positron trapping at the metastable vacancy is thus enhanced at low temperatures. As explained in Sec. III, this type of behavior shows that the vacancy is negatively charged.

In the sample with the largest irradiation fluence of $\Phi_{e^-} = 1.3 \times 10^{18}$ e^- cm^{-2}, the *native* metastable vacancies make no contribution to the temperature dependence of the average lifetime (Fig. 5), since their concentration is much lower than that of the irradiation-induced defects. The data in Fig. 5 still show enhanced positron trapping at the metastable vacancy at low temperatures. We can thus conclude that both native and irradiation-induced metastable vacancies are negatively charged. However, in both cases the *total* charge of the defect may also be neutral although the vacancy detected by positron experiments is negatively charged.[32]

D. Microscopic structure of the defect containing the metastable vacancy

The analysis presented in the previous sections indicates the following properties of the metastable vacancies in electron irradiated GaAs. (i) The defects with the vacancy in the metastable state are introduced in the 1.5-MeV electron irradiation at 20 K, and after annealing the samples at 300 K the introduction rate is $\Sigma_{v^*}=0.3\ \text{cm}^{-1}$. (ii) The defect can be converted to the metastable state by 1.0–1.3-eV light illumination at 20 K. The conversion can be described by an effective optical cross section of $\sigma_{v^*}=3\times10^{-19}\ \text{cm}^2$. (iii) The metastable state is persistent at 20 K and recovers thermally at 80–100 K. (iv) The vacancy in the metastable state is negatively charged.

These properties closely resemble those that we have previously determined for the metastable state of the *EL*2 defect in as-grown GaAs.[31,32] We have shown that the metastable state *EL*2* contains a vacancy, which has a smaller open volume than isolated Ga or As vacancies. The native metastable vacancy can be generated by illumination with 1.05–1.4-eV photons, and the optical cross section is $\sigma_{v^*}=2\times10^{-18}\ \text{cm}^2$ for 1.15-eV photons. This value is larger than that found for the irradiation-induced metastable vacancy, but the photon energy range of 1.05–1.4 eV for their excitation is almost the same. The thermal recovery of the native metastable vacancy takes place at 120 K. This temperature is slightly higher than that of 80–100 K determined for the irradiation-induced metastable vacancy. However, the properties of the metastable vacancies observed after electron irradiation are so similar to those of the native metastable vacancy that we relate them to the same defect.

The atomic structure of the *EL*2 defect is generally believed to contain the arsenic antisite.[2] A theoretical model has been developed to explain the metastability of the isolated As antisite in terms of two different forms of the *sp* hybridization.[27,28,49] In the stable state the As atom is in the Ga lattice site bonded with four sp^3 orbitals, but in the metastable state the As atom relaxes along [111] direction toward the interstitial position, forming three sp^2 bonds with neighboring As atoms. This relaxation leaves behind a Ga vacancy, which has a smaller open volume than the isolated V_{Ga}. Positron experiments in as-grown GaAs reveal a small Ga vacancy in the metastable state of *EL*2, and are thus in good agreement with the vacancy-interstitial relaxation model of the isolated As_{Ga}.

The introduction of the arsenic antisite defects in electron irradiation has been reported by several authors. For 1–3-MeV electrons introduction rates of typically 0.2–0.3 cm^{-1} have been determined.[11,12] After low-temperature irradiations the annealing of the As antisites has been explained by complicated recovery sequences, where As_{Ga} may exist either as isolated or associated to Ga antisites or As interstitials depending on the annealing temperature.[6,16] Evidence for the metastability of the irradiation-induced As_{Ga}-related defect has been found after 500-K annealing,[4,6,16,17] and recently also after 300-K annealing.[29,30]

The present positron results indicate that defects with metastability similar to *EL*2 are introduced in electron irradiation at 20 K followed by annealing at 300 K. The metastability of *EL*2 is generally attributed to the As antisites. The introduction rate of the detected defects $\Sigma_{v^*}=0.3\ \text{cm}^{-1}$ is close to that reported for As antisites. It is thus natural to identify the metastable defects observed in this work to arsenic antisites.

The irradiation-induced As antisites have some properties which are slightly different from those detected for *EL*2 in earlier positron experiments or by using other techniques. The generation of the metastable state associated to the irradiation-induced As_{Ga} requires a ten times larger illumination fluence than that associated with the native As_{Ga} (*EL*2 defect). Further, the recovery of the metastable state takes place at about 20-K lower temperature in irradiated GaAs than in as-grown GaAs. A possible explanation for these differences may be that the atomic surrounding of the As antisites changes in the electron irradiation at 20 K and in the consequent annealing at 300 K due to the creation of other intrinsic defects and to the thermal recovery processes of them.

VII. CONCLUSIONS

We have studied the introduction of metastable defects in the 1.5-MeV electron irradiation of semi-insulating GaAs by positron-lifetime measurements. After irradiation at 20 K and subsequent annealing at 300 K, the positron experiments indicate the presence of two negatively charged defects, which are identified as Ga vacancies and Ga antisites. Their introduction rates are $\Sigma(V_{\text{Ga}})=0.1\ \text{cm}^{-1}$ and $\Sigma(\text{Ga}_{\text{As}})=1.4\ \text{cm}^{-1}$, respectively.

After illuminating the irradiated GaAs samples at 25 K, we find that positron lifetime increases persistently to larger values than obtained before illumination. This effect shows that a metastable vacancy is generated during the illumination of the samples. The metastable vacancy can be observed most effectively after illumination with 1.1-eV photons and it recovers during annealing at 80–100 K in darkness. The quantitative analysis of positron-lifetime data indicates that the concentration of the metastable vacancies increases linearly with the electron-irradiation fluence. We thus conclude that electron irradiation creates defects, which can be converted into a metastable state involving a vacancy. The introduction rate of these defects is about 0.3 cm^{-1} in the 1.5-MeV electron irradiation at 20 K, followed by the annealing of the sample at 300 K. This value is close to that estimated previously for the As antisites.

The metastable vacancies introduced in the electron irradiation are similar to those we have previously found as native defects in as-grown GaAs. These native metastable vacancies have been associated with the *EL*2 defect, which is generally related to the As antisite defect. We thus infer that irradiation-induced and native metastable vacancies have the same origin and that they belong to the atomic structure of the metastable state of the As antisite defect. This conclusion is in good agreement with the theory, which predicts that in the metastable state the As antisite atom moves from the Ga lattice site toward the interstitial position, leaving the Ga site vacant.

The present positron-lifetime experiments show further that some properties of the electron-irradiation-induced As antisites are different from those of the native ones. First, in irradiated GaAs the conversion of the defect to the metastable state requires about ten times larger photon fluence. Second, the metastable state recovers in irradiated GaAs at about 20-K lower temperatures than in as-grown GaAs. These differences may be related to the presence of other defects in the irradiated material, which change the atomic surrounding of the As antisite defects from that existing in the as-grown GaAs.

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[1] *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986).

[2] J. C. Bourgoin, H. J. von Bardeleben, and D. Stiėvenard, J. Appl. Phys. **64**, R65 (1988).

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

[4] A. Pillukat and P. Ehrhart, Appl. Phys. Lett. **60**, 2794 (1992).

[5] A. Pillukat and P. Ehrhart, Phys. Rev. B **45**, 8815 (1992).

[6] K. Krambrock, J.-M. Spaeth, C. Delerue, G. Allan, and M. Lannoo, Phys. Rev. B **45**, 1481 (1992).

[7] E. Christoffel, A. Goltzene, and C. Schwab, J. Appl. Phys. **66**, 5648 (1989).

[8] M. O. Manasreh and D. W. Fischer, Phys. Rev. B **39**, 3871 (1989).

[9] M. O. Manasreh and D. W. Fischer, Appl. Phys. Lett. **53**, 2429 (1988).

[10] N. K. Goswami, R. C. Newman, and J. E. Whitehouse, Solid State Commun. **40**, 473 (1981).

[11] R. B. Beall, R. C. Newman, J. E. Whitehouse, and J. Woodhead, J. Phys. C **17**, 2653 (1984).

[12] H. J. von Bardeleben and J. C. Bourgoin, J. Appl. Phys. **58**, 1041 (1985).

[13] H. J. von Bardeleben, D. Stiėvenard, D. Deresmes, A. Huber, and J. C. Bourgoin, Phys. Rev. B **34**, 7192 (1986).

[14] D. Stiėvenard and J. C. Bourgoin, J. Appl. Phys. **59**, 743 (1986).

[15] D. Stiėvenard, X. Boddaert, J. C. Bourgoin, and H. J. von Bardeleben, Phys. Rev. B **41**, 5271 (1990).

[16] J.-M. Spaeth, K. Krambrock, and M. Hesse, Mater. Sci. Forum **143-147**, 217 (1994).

[17] A. Pillukat and P. Ehrhart, Mater. Sci. Forum **83-87**, 947 (1992).

[18] A. Goltzene, B. Meyer, and C. Schwab, Appl. Phys. Lett. **54**, 907 (1989).

[19] M. O. Manasreh, D. W. Fischer, and B. C. Covington, Phys. Rev. B **37**, 6567 (1988).

[20] M. O. Manasreh and D. W. Fischer, Phys. Rev. B **39**, 3239 (1989).

[21] M. O. Manasreh, P. F. McDonald, S. A. Kivlighn, J. T. Minton, and B. C. Covington, Solid State Commun. **65**, 1267 (1988).

[22] R. Wörner, U. Kaufman, and J. Schneider, Appl. Phys. Lett. **40**, 141 (1982).

[23] J. Schneider and U. Kaufmann, Solid State Commun. **44**, 285 (1982).

[24] E. R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinski, J. Appl. Phys. **53**, 6140 (1982).

[25] P. Omling, E. R. Weber, and L. Samuelson, Phys. Rev. B **33**, 5880 (1986).

[26] J. Krüger and H. Alexander, Mater. Sci. Forum **83-87**, 899 (1992).

[27] J. Dabrowski and M. Scheffler, Phys. Rev. Lett. **60**, 2183 (1988); Phys. Rev. B **40**, 10 391 (1989).

[28] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **60**, 2187 (1988).

[29] F. C. Rong, W. R. Buchwald, H. Harmatz, E. H. Poindexter, and W. L. Warren, Appl. Phys. Lett. **59**, 2281 (1991).

[30] M. Hesse, F. K. Koschnick, K. Krambrock, and J.-M. Spaeth, Solid State Commun. **92**, 207 (1994).

[31] R. Krause, K. Saarinen, P. Hautojärvi, A. Polity, G. Gärtner, and C. Corbel, Phys. Rev. Lett. **65**, 3329 (1990).

[32] K. Saarinen, S. Kuisma, P. Hautojärvi, C. Corbel, and C. LeBerre, Phys. Rev. B **49**, 8005 (1994).

[33] C. Corbel, F. Pierre, K. Saarinen, P. Hautojärvi, and P. Moser, Phys. Rev. B **45**, 3386 (1992).

[34] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).

[35] J. Mäkinen, C. Corbel, P. Hautojärvi, P. Moser, and F. Pierre, Phys. Rev. B **39**, 10 162 (1989).

[36] J. Mäkinen, P. Hautojärvi, and C. Corbel, J. Phys. Condens. Matter **3**, 7217 (1991).

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

[38] M. Manninen and R. Nieminen, Appl. Phys. A **26**, 93 (1981).

[39] K. Saarinen, P. Hautojärvi, P. Lanki, and C. Corbel, Phys. Rev. B **44**, 10 585 (1991).

[40] R. N. West, in *Positrons in Solids,* edited by P. Hautojärvi, Topics in Current Physics Vol. 12 (Springer, Heidelberg, 1979).

[41] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985).

[42] M. J. Puska, J. Phys. Condens. Matter **1**, 7347 (1989).

[43] H. Xu and W. Lindefelt, Phys. Rev. B **41**, 5975 (1990).

[44] C. Corbel, F. Pierre, P. Hautojärvi, K. Saarinen, and P. Moser, Phys. Rev. **41**, 10 632 (1990).

[45] Y. Q. Jia, H. J. von Bardeleben, D. Stiėvenard, and C. Delerue, Phys. Rev. B **45**, 1645 (1992).

[46] Details of the temperature dependence of positron trapping in GaAs will be published separately.

[47] C. LeBerre, C. Corbel, M. R. Brozel, S. Tüzemen, S. Kuisma, K. Saarinen, and P. Hautojärvi, J. Phys. Condens. Matter **6**, L759 (1994).

[48] D. W. Fischer, Phys. Rev. B **37**, 2968 (1988).

[49] J. Dabrowski and M. Scheffler, Mater. Sci. Forum **83-87**, 735 (1992).