Optical processes related to arsenic vacancies in semi-insulating GaAs studied by positron spectroscopy

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(Received 10 July 1995)

We have performed positron lifetime and Doppler broadening experiments under monochromatic illumination in undoped semi-insulating GaAs. A negative vacancy, identified as the Ga vacancy, is observed in darkness. Under illumination with 1.42 eV photons below 150 K another type of vacancy is observed. The illumination-induced vacancy is identified as the As vacancy and it has a negative charge state above the ionization level at 60 meV below the conduction band. Under illumination the negative charge state of the As vacancy can be populated either by the trapping of photoelectrons excited from the *EL*2 defect or by the direct optical excitation of electrons from the valence band. The latter process offers a microscopic explanation for the optical near-band-edge absorption observed in GaAs. In the samples studied in this work the concentrations of both Ga and As vacancies are between 10^{15} and 10^{16} cm^{-3}, indicating that they probably play a role in the electrical compensation of the material.

I. INTRODUCTION

The influence of intrinsic point defects on the electrical and optical properties of high-purity undoped gallium arsenide is known to be particularly important. The As-antisite-related *EL*2 defect has been studied extensively due to its role in the compensation of the residual acceptors in undoped semi-insulating (SI) GaAs and due to its interesting internal optical transition to the so-called metastable state.[1] However, there is an increasing amount of evidence that other intrinsic point defects in addition to the *EL*2 defect take part to the compensation mechanism.[2] On the other hand, experimental information on elementary defects like Ga or As vacancies in undoped GaAs is very limited. The reason for this is perhaps that the identification of vacancy defects has proved to be difficult with the conventional electrical and optical measurements as well as with electron paramagnetic resonance (EPR) experiments.

Positron spectroscopy is a powerful tool to study vacancy defects.[3] Positrons are strongly repelled by the positive ion cores in solids, and thus open volume defects act as attractive centers at which positrons can be localized. The lifetime of a positron is longer in an open volume defect than in a perfect crystal as the electron density in an open volume defect is lower than in bulk material. Also, the positron-electron momentum distribution narrows at vacancy defects reducing the Doppler broadening of the 511 keV annihilation line. Positron lifetime and Doppler broadening measurements can thus be used to obtain information on the vacancy type defects on the atomic scale.

Positrons get trapped at neutral and negative vacancies. Information on the size of the open volume and on the charge state of the defect can be obtained from the experimental data. However, positive vacancies have so far escaped observation due to the Coulombic repulsion preventing positrons to annihilate at positive centers. We have developed a new technique to study vacancies in excited charge states. In analogy with the optical deep-level transient spectroscopy (ODLTS) and the electron paramagnetic resonance measurements under illumination (photo-EPR) we have combined positron annihilation measurements in this work with *in situ* monochromatic illumination. We have applied this technique to study native vacancies in undoped SI GaAs. Preliminary results of our study have been published previously.[4] In this work our goal is to give a detailed report of our experimental method and to investigate comprehensively the positron signals as a function of the sample temperature, photon flux and photon energy. We shall further correlate our findings to the metastable behavior of the *EL*2 defect.[1] The experimental results will be modeled by describing the electron transitions under illumination by rate equations. The results on the native point defects in SI GaAs can be summarized as follows.

A negative monovacancy is observed in darkness and it is identified as the gallium vacancy. Under illumination more negative vacancy defects are detected and they are identified as arsenic vacancies. When the ionization levels of the As vacancy are populated by photoinduced electrons the As vacancy is in a negative charge state. The $-/0$ ionization level of the As vacancy is determined to be at 60 ± 10 meV below the conduction band. Our data further show that the As vacancy can be populated by photoelectrons via two different optical processes. The first process is possible when *EL*2 is in the stable state, and it is attributed to the capture of photoelectrons excited from the *EL*2 defect. The second process is efficient also when *EL*2 is in its metastable state. We associate it with the direct transition of electrons from the valence band to the ionization level of the As vacancy. The latter transition gives a microscopic explanation for the near-band-edge absorption observed in GaAs.[5] The detected vacancy concentrations of 10^{15}–10^{16} cm^{-3} are close to those of residual impurities and *EL*2 defects, indicating that the native

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TABLE I. Concentrations of *EL2* defects and gallium and arsenic vacancies in the samples studied in this work. All concentrations have been estimated using the positron lifetime results. Also the average positron lifetime values at 25 K in darkness and under 1.42 eV illumination are shown.

	$[EL2]$ (10^{15} cm^{-3})	τ_{av} (ps) in darkness	$[V_{Ga}]$ (10^{15} cm^{-3})	τ_{av} (ps) under illum.	$[V_{As}]$ (10^{15} cm^{-3})
1	16±5	238	6.7±0.5	245	16±2
2	15±5	238	6.5±0.5	245	14±2
3	47±20	241	12±1	246	15±4
4	46±19	241	11±1	246	23±5
5	4±1	232	1.4±0.4	233	0.9±0.2
6	11±4	237	6.2±0.5	244	14±2
7	110±60	240	10±1	246	26±9

vacancies have a role in the compensation of SI GaAs.

The paper is organized as follows. The experimental details are described in Sec. II and the results of the positron experiments are presented in Sec. III. Data analysis with positron trapping model is explained in Sec. IV. In Sec. V we identify the vacancies and estimate their concentrations. Properties of the photoinduced arsenic vacancies are discussed in Sec. VI together with models for their excitation under illumination. Section VII concludes the paper.

II. EXPERIMENTAL DETAILS

The positron lifetime and the Doppler broadening experiments of this work were performed on seven undoped semi-insulating GaAs samples grown by liquid-encapsulated Czochralski method. Their resistivities were 10^7–10^8 Ω cm and the *EL2* concentrations were typically between 1×10^{16} and 5×10^{16} cm^{-3}. The *EL2* concentrations estimated from the positron lifetime measurements[6–8] are listed in Table I for each sample.

The positron lifetime and the Doppler broadening experiments were performed in a conventional way.[3] Two identical sample pieces were sandwiched with a 30 μCi positron source. The source material was carrier-free ^{22}NaCl deposited on a 1.5-μm-thick Al foil. The sample sandwich was mounted in an optical cryostat equipped with quartz windows to enable illumination of the sample during measurements. The cryostat is cooled with a closed-cycle He cryocooler and it is possible to make measurements between 15 and 300 K. The illuminations were performed with monochromatic light obtained from a 250 W halogen lamp via monochromator. The sample was illuminated on both sides using a trifurcated optical fiber bundle. The third branch of the fiber bundle was used for the on-line monitoring of the incident photon flux with a Si/Ge photodetector. In the illumination set-up the photon energy range is $h\nu=0.6$–3.0 eV and the photon flux range is $\phi=10^{12}$–10^{16} cm^{-2} s^{-1}.

The positron lifetime measurements were carried out by a fast-fast lifetime spectrometer with a time resolution of 230 ps. Roughly 2×10^6 counts were collected in each spectrum within a typical counting time of 3 h. After subtracting the constant background and the annihilations in the source materials (210 ps, 5.4%; 450 ps, 1.9%), the lifetime spectra were analyzed with one or two exponential components convoluted with the Gaussian resolution function of the spectrometer. The values of the lifetimes τ_i and their intensities I_i are used to calculate the positron average lifetime $\tau_{av}=I_1\tau_1+I_2\tau_2$ which is insensitive to the uncertainties in the decomposition procedure and coincides with the center of the mass of the lifetime spectrum. The experimental error in determining the average positron lifetime is about 0.3 ps for a particular measurement setup. The measurements presented in this paper have been made on two positron lifetime apparati and within a period of three years. Despite these facts, the positron lifetime results measured at different times are accurate within 1 ps.

The Doppler broadening of the annihilation radiation was recorded simultaneously with some lifetime experiments by a high-purity Ge gamma detector with an energy resolution of 1.2 keV. Typically 10^7 counts were collected in the 511 keV annihilation line. The shape of this line was described by the conventional parameters S and W.[3] The S parameter (the valence annihilation parameter) is the relative number of annihilation events in the 1.4 keV wide central region of the peak and it represents mainly positron annihilation with the low-momentum valence electrons. The W parameter (the core annihilation parameter) is calculated from the tail of the peak at the energy range of ±(2.55–4.08 keV) from the centroid, and only annihilations with the core electrons fall in the energy window of the W parameter. The S and W parameters can be used to determine the R parameter as $R=(S-S_b)/(W_b-W)$ where S_b and W_b correspond to defect-free reference material. The R parameter is independent of the vacancy concentration and it characterizes the type of the vacancy in the studied material.[9]

III. EXPERIMENTAL RESULTS

A. Measurements in darkness

The positron lifetime as a function of the measurement temperature in darkness was measured in all the samples. The results of the samples 4 and 6 and the free positron lifetime as a reference level are shown in Fig. 1. The reference level was obtained in Zn-doped reference sample which is free of positron trapping.[10,11] The average positron lifetime at 300 K in SI GaAs is very near the free positron lifetime, namely between 232 and 234 ps in all the samples. When the measurement temperature decreases positron lifetime increases and at temperatures $T<100$ K the average positron lifetime is clearly longer than the free positron lifetime in GaAs. The results in darkness at the lowest measurement temperature of 25 K are between 232 and 241 ps (Table I).

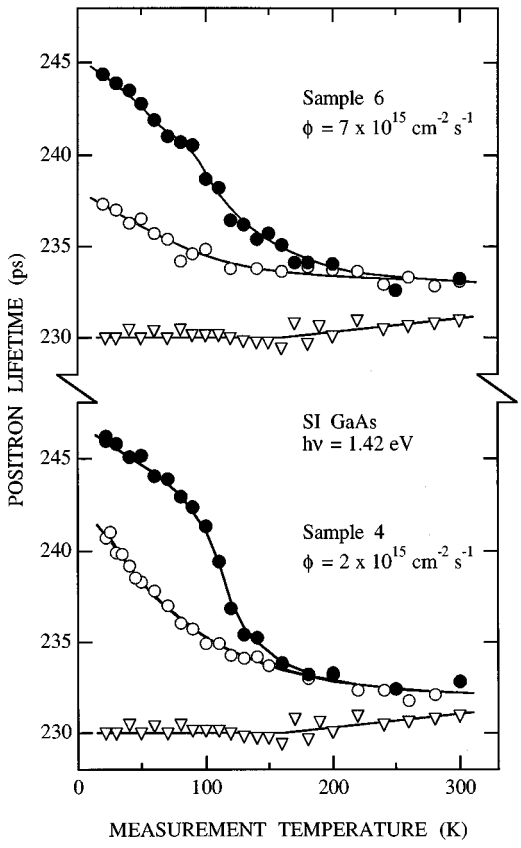

FIG. 1. The average positron lifetime as a function of the measurement temperature in undoped semi-insulating GaAs, samples 4 and 6. The results obtained in darkness are marked with open circles and under $h\nu=1.42$ eV illumination with filled ones. The reference level corresponding to defect-free material is measured in p-type GaAs and is marked with open triangles.

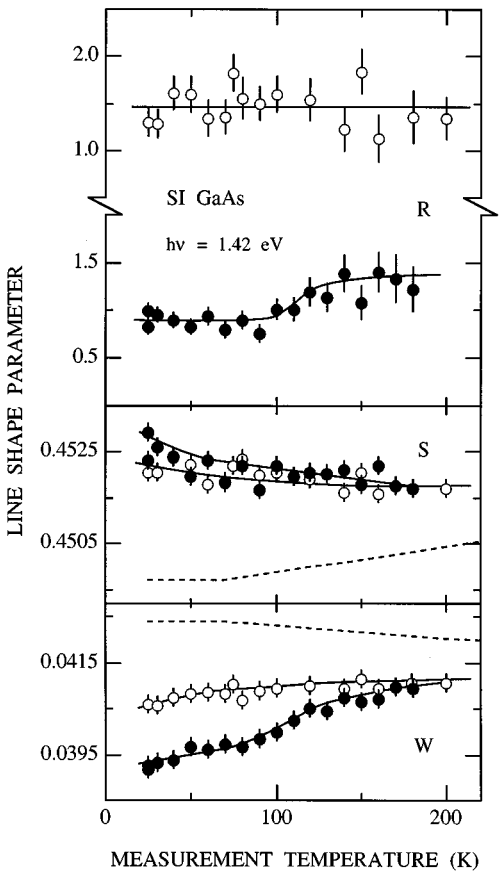

FIG. 2. The valence annihilation parameter S, the core annihilation parameter W, and the defect-specific parameter R as functions of the measurement temperature in undoped SI GaAs sample 1. The results obtained in darkness are marked with open circles and under $h\nu=1.42$ eV illumination with filled ones. The reference levels corresponding to defect-free material are marked with dashed lines.

In samples 1–4, 6, and 7 the spectra measured at temperatures below 80 K can be decomposed into two components. The shorter lifetime is $\tau_1=150$–200 ps and the second component is $\tau_2=250$–260 ps with the intensity of 50%. At temperatures above 80 K and in sample 5 it is difficult to decompose the spectra probably because the average lifetime is very near the free positron lifetime.

The Doppler broadening of the annihilation radiation was recorded simultaneously with lifetime experiments in samples 1 and 4. The results for sample 1 are shown in Fig. 2. In darkness the S parameter decreases from 0.4521 to 0.4518 and the W parameter increases from 0.0398 to 0.0411 as temperature increases from 25 to 300 K. The parameters S_b and W_b are shown with dashed line in Fig. 2. The temperature coefficients of S_b and W_b are 0.122%/100 K and -0.665%/100 K when compared to the room temperature values, respectively. The R parameter is independent of temperature and its value is $R=1.5\pm0.2$ and $R=1.2\pm0.2$ in samples 1 and 4, respectively.

B. Measurements under photoexcitation

1. The increase of positron lifetime under illumination

Under illumination with 1.42 eV light the positron lifetime is clearly longer than in darkness. This effect is demonstrated in Fig. 1 for samples 4 and 6. The increase of τ_{av} depends on temperature, being the largest at $T<100$ K, and at about $T\approx150$ K the average lifetime is the same in darkness and under illumination. When the illumination is removed, typically 50%–70% of the increase of τ_{av} disappears instantly. However, a persistent increase of 1–4 ps is detected at 25 K even if the illumination is switched off. This effect can be removed by annealing the sample at 120 K.

The effect of the illumination on the average lifetime has been studied earlier in samples containing the $EL2$ defect.[6,12] The $EL2$ defect possesses a metastable state to which it can be photoquenched by illumination with 1.15 eV photons. This metastable state anneals out at 120 K. The positron annihilation results show that the metastable state of $EL2$ contains a vacancy and this causes an increase in the average lifetime at temperatures $T<60$ K after illumination.[6,12] The persistent increase of τ_{av} detected in this work can thus be associated to the metastable state of the $EL2$ defect. However, the increase of τ_{av} *under illumination* is much larger than the persistent part of it. Furthermore, the previous positron results show that the effect due to the metastable state of $EL2$ can only be detected at temperatures below 60 K

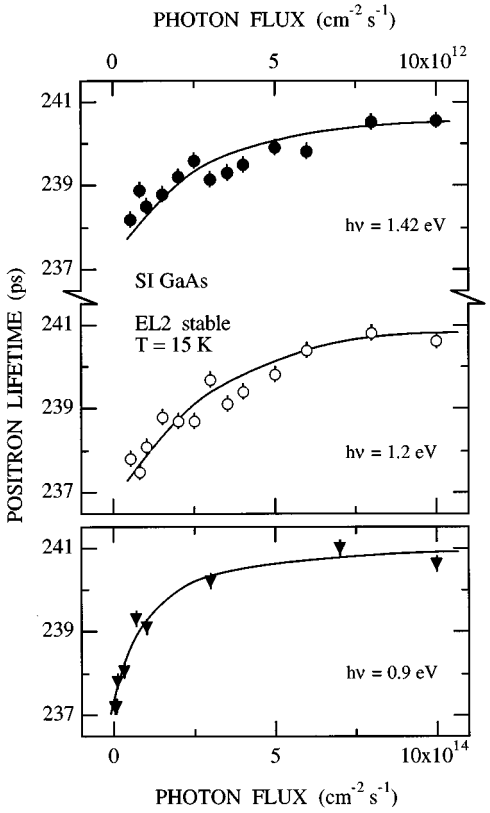

FIG. 3. The average positron lifetime in SI GaAs (sample 1) under illumination as a function of the photon flux. Before the measurements the *EL*2 defect has been in the stable state. The measurement temperature is 15 K. The photon energies used for the illuminations are marked in the figure. Note the different scaling in bottom and top axis.

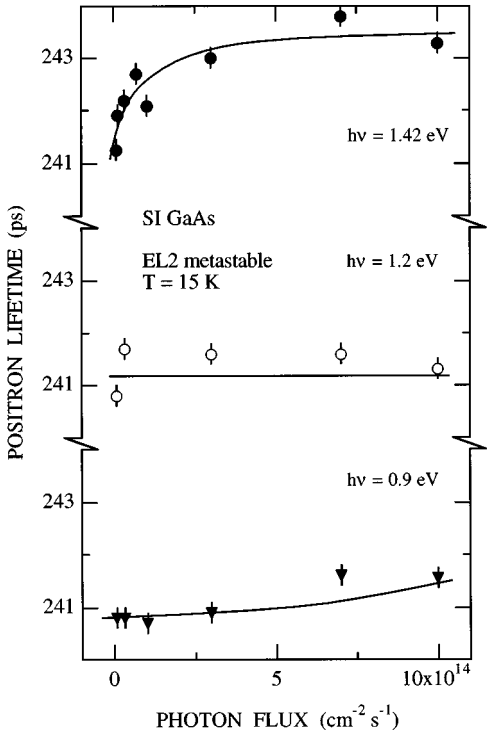

FIG. 4. The average positron lifetime in SI GaAs (sample 1) under illumination as a function of the photon flux. Before the measurements the *EL*2 defect has been converted into the metastable state. The measurement temperature is 15 K. The photon energies used for the illuminations are marked in the figure.

whereas the illumination effect in Fig. 1 is observed up to 150 K.

In this work our main purpose is to study the illumination-induced increase of τ_{av} which is not persistent and can only be observed under illumination. However, we shall see that the *EL*2 defect plays an important role also in the detection of this effect. The influence of *EL*2 is twofold: (i) the metastable state of *EL*2 behaves itself as a positron trap at $T \leqslant 60$ K[6,12] and (ii) the transformation of *EL*2 between the stable and metastable states has a large influence on the population of the energy levels in the gap.

2. Photon flux and photon energy effects at 25 K

The effects of the photon flux and energy on the average positron lifetime were studied further in sample 1. In the experiments of Fig. 3 the photon flux is so small that no photoquenching of the *EL*2 defect takes place, i.e., *EL*2 is in the stable state. Increase in the average lifetime is observed under illumination with 0.9–1.5 eV photons. The increase is most efficient with 1.2–1.4 eV photons and only a photon flux of 1×10^{13} cm^{-2} s^{-1} is needed to obtain the saturation effect. With 0.9 eV photons a clearly larger flux of 1×10^{15} cm^{-2} s^{-1} is required to obtain the maximum increase in positron lifetime.

Figure 4 shows the positron lifetime as a function of the photon flux in the case where *EL*2 has been photoquenched to the metastable state before measurements. A photon flux of 1×10^{15} cm^{-2} s^{-1} is needed to obtain the full increase in the average lifetime under illumination with 1.4 eV photons. This flux is roughly 100 times larger than required for the same effect when *EL*2 is in the stable state (Fig. 3). Furthermore, after photoquenching practically no effects are observed under illumination with 0.9 and 1.2 eV photons (Fig. 4) although 1.2 and 1.4 eV illuminations induce the increase in the average lifetime with equal efficiency in the conditions where *EL*2 defect is in the stable state (Fig. 3).

To study the effect of photon energy on the average lifetime the photon flux was kept constant at different photon energies over the experiment under illumination. The constant photon flux was chosen so that the illumination effect in τ_{av} is not in saturation under illumination with any photon energy at $h\nu \leqslant 1.4$ eV. When *EL*2 remains in the stable state in the experiment (Fig. 5), the increase of τ_{av} is largest at photon energies $h\nu = 1.2$–1.4 eV, and at $h\nu = 0.9$ eV the effect is clearly smaller. When *EL*2 is photoquenched to the metastable state before the experiment under illumination, the increase of τ_{av} is only detected with photon energies $h\nu > 1.35$ eV (Fig. 5). The photon flux required to detect the effect is now also much larger than in the case in which *EL*2 remains stable (see also Figs. 3 and 4). Notice that the shape of the spectrum of τ_{av} vs $h\nu$ is different depending on the state of *EL*2. When *EL*2 is in the stable state, τ_{av} is constant under illumination with $h\nu = 1.2$–1.5 eV. However, when *EL*2 is in the metastable state, τ_{av} increases rapidly with the photon energy in the range $h\nu = 1.2$–1.5 eV.

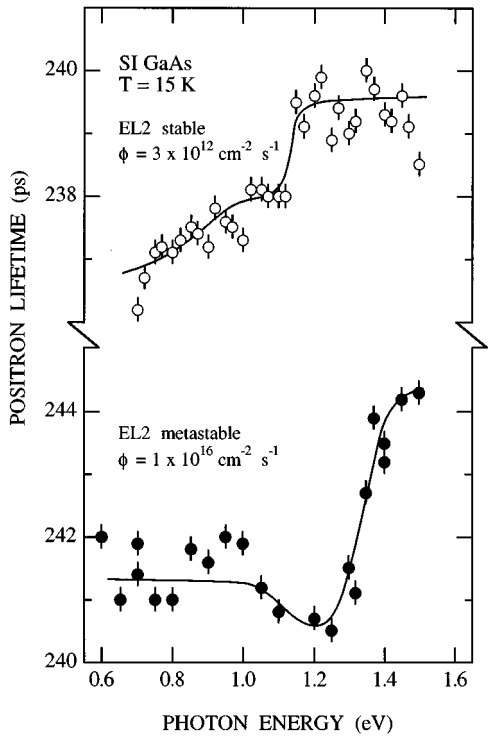

FIG. 5. The average positron lifetime in SI GaAs (sample 1) under illumination as a function of the photon energy. In the data of the top panel the *EL*2 defect remains in the stable state over the experiment. In the data of the bottom panel *EL*2 is deliberately converted into the metastable state before the measurements. The measurement temperature is 15 K and the photon fluxes used for the illuminations are marked in the figure.

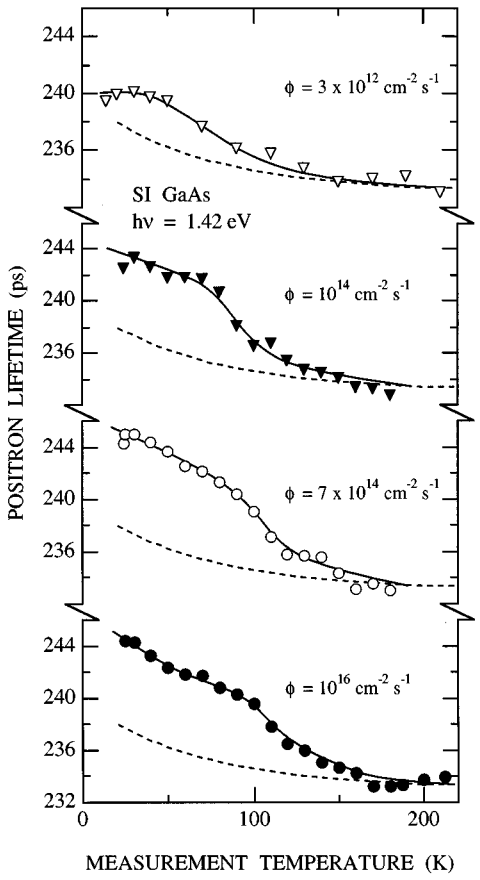

FIG. 6. The average positron lifetime in SI GaAs (sample 1) under $h\nu=1.42$ eV illumination as a function of the measurement temperature. The different photon fluxes used for the illuminations are marked in the figure. The dashed lines in the figure represent the reference level obtained in darkness.

3. Temperature dependence of the 1.42 eV illumination effects

The influence of 1.42 eV-photon illumination on the average positron lifetime as a function of temperature was studied in all the samples. Figure 1 shows the results of the measurements under illumination for samples 4 and 6. It is observed that under illumination the average lifetime at low temperatures is clearly longer than in darkness. The maximum increase of τ_{av} at 25 K is 7 ps in samples 1 and 6, and less than 1 ps in sample 5. The longest average lifetimes measured under illumination are presented in Table I. The average lifetime decreases slightly with temperature when $T<100$ K, but above 100 K the decrease of the average lifetime becomes much more rapid. At temperatures above 180 K no change in the average lifetime due to illumination is observed.

The temperature at which the average positron lifetime under illumination begins to decrease steeply depends on the intensity of the illumination. The effect of intensity on the average lifetime was studied in samples 1, 3, 4, and 7 and in all these samples the effect was qualitatively the same. Figure 6 shows the results in sample 1 for four different photon fluxes and for $h\nu=1.42$ eV. In the experiment under $\phi=10^{14}$–10^{16} cm^{-2} s^{-1} illuminations *EL*2 is converted to the metastable state before the first measurement. In the experiment with the lowest flux $\phi=3\times10^{12}$ cm^{-2} s^{-1} practically all *EL*2 defects are in the stable state over the whole positron lifetime curve. For illumination fluxes $\phi=3\times10^{12}$, 1×10^{14}, 7×10^{14}, and 1×10^{16} cm^{-2} s^{-1} the level of $\tau_{av}=239$ ps is reached at 60, 80, 100, and 110 K, respectively. At temperatures below 60 K the average lifetime does not depend on the intensity used for illumination when photon flux is greater than 10^{14} cm^{-2} s^{-1}.

The changes in the Doppler broadening spectra were measured simultaneously for samples 1 and 4 under 1.42 eV illumination. Results of the measurements of sample 1 are shown in Fig. 2. Compared to the values in darkness the *S* parameter increases and the *W* parameter decreases. Both *S* and *W* coincide with the values measured in darkness above 180 K. The *R* parameter depends on temperature; below 90 K its value is $R=0.9\pm0.1$ and above 120 K $R=1.4\pm0.1$. In sample 4 the *R* parameter increases similarly from 0.9 ± 0.1 to 1.3 ± 0.1.

4. The temperature dependence of positron lifetime versus photon energy

The temperature dependence of the average positron lifetime under illumination depends on the photon energy used for the illumination. This effect was studied in samples 1, 3, 5, and 6 with photon energies $h\nu=0.9$, 1.15, and 1.4 eV and the photon flux was $\phi=7\times10^{14}$ cm^{-2} s^{-1}. The results in sample 1 are shown in Fig. 7 and in samples 3, 5, and 6 the

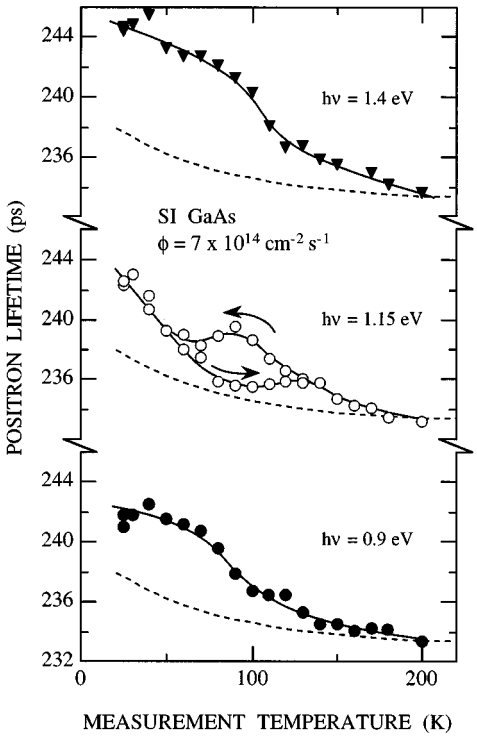

FIG. 7. The average positron lifetime in SI GaAs (sample 1) under illumination as a function of the measurement temperature. The different photon energies are marked in the figure, and the photon flux is the same in all the measurements. Under $h\nu=1.15$ eV illumination there is some hysteresis in the temperature dependence of the average lifetime and the arrows indicate the direction of the temperature change.

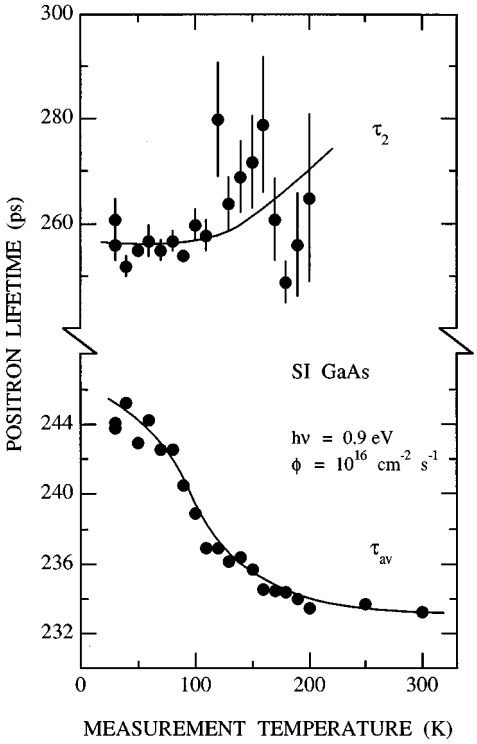

FIG. 8. The average positron lifetime and the second lifetime component τ_2 in SI GaAs (sample 7) as functions of the measurement temperature under $h\nu=0.9$ eV illumination. The photon flux is marked in the figure. Above 200 K the lifetime spectra have one component and only the average positron lifetime is shown in the figure.

results are qualitatively similar. During the experiments with 1.15 and 1.4 eV photons the *EL*2 defect is completely converted to the metastable state within the first 2–3 experimental data points at 20–30 K in Fig. 7. In the experiment under 0.9 eV illumination about 20% of *EL*2 remain in the stable state over the whole positron lifetime curve of Fig. 7.

For 0.9 eV photons the increase in $\tau_{\rm av}$ compared to the values in darkness is about 5 ps in the temperature range 20–50 K. The average positron lifetime decreases steeply as temperature rises from 50 to 100 K and above 150 K no illumination effect can be observed. The temperature dependence of the average lifetime is fully reversible as a function of temperature. For 1.4 eV photons the behavior of $\tau_{\rm av}$ is similar; the increase of $\tau_{\rm av}$ is about 7 ps and the average lifetime decreases steeply at 90–180 K.

Illumination with 1.15 eV photons results in a different behavior in $\tau_{\rm av}$. The average lifetime decreases very steeply already at low temperatures (20–100 K). At higher temperature $\tau_{\rm av}$ increases again up to 120 K and above 120 K it decreases again. Above 150 K the illumination has no effect on the average lifetime. In the temperature range 50–120 K the average lifetime curve is not reversible: $\tau_{\rm av}$ is longer when the temperature decreases although the shape of the curve remains similar.

The lifetime spectra measured under illumination with 0.9 and 1.42 eV photons can be decomposed into two components (Figs. 8 and 9). In all the samples the values of τ_2 are 255–260 ps under both 0.9 and 1.42 eV illuminations and in the range of 20–100 K only a weak temperature dependence is perhaps seen in the data under 1.42 eV illumination. At 100–150 K the lifetime τ_2 increases slightly from 257 to 280 ps when temperature increases.

IV. POSITRON TRAPPING AT VACANCY DEFECTS

In a perfect crystal positrons are delocalized and annihilate with a free positron lifetime τ_b. In the presence of vacancy defects positrons get trapped at them. Because the electron density is lower in a vacancy defect than in the bulk, positrons annihilate in defects with a lifetime τ_V which is always longer than τ_b. The lifetime τ_V depends on the open volume of the defect, thus τ_V can be used to identify different defects.

The concentration of the vacancies which trap positrons can be estimated from the positron trapping rates. The trapping rate κ_V at a vacancy is proportional to the concentration of the vacancy defects $\kappa_V=\mu_V c_V$, where c_V is the concentration of the vacancies and μ_V is the positron trapping coefficient. In semiconductors the vacancies can have different charge states depending on the position of the Fermi level. For neutral vacancies the trapping coefficient is independent of the temperature and its value is typically 1×10^{15} s^{-1}.[13–15] For negative vacancies μ_V is roughly 2×10^{15} s^{-1} at 300 K and it increases by an order of magnitude when temperature decreases to 20 K.[13–16] The trapping coefficient at positive vacancies is several orders of magnitude smaller because of

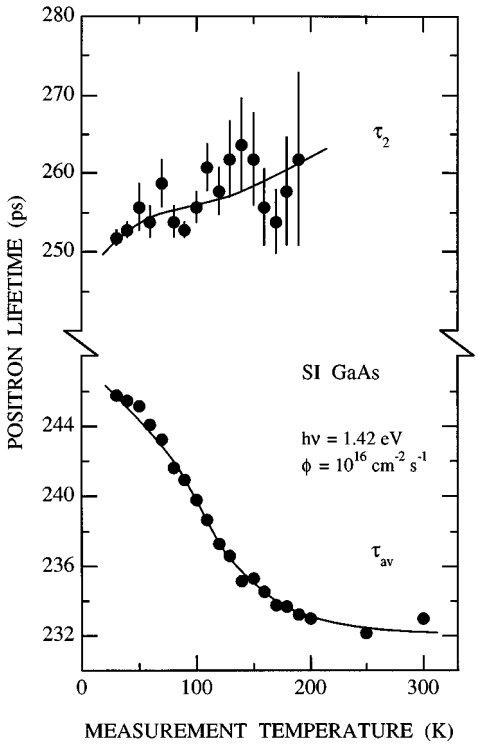

FIG. 9. The average positron lifetime and the second lifetime component τ_2 in SI GaAs (sample 7) as functions of the measurement temperature under $h\nu=1.42$ eV illumination. The photon flux is marked in the figure. Before the experiment the *EL*2 defect was converted into the metastable state. Above 200 K the lifetime spectra have one component and only the average positron lifetime is shown in the figure.

the Coulombic repulsion and thus no trapping occurs.

The average positron lifetime $\tau_{\rm av}$ is a superposition of the free positron lifetime τ_b and of the lifetimes τ_{Vi} in the different vacancy defects V_i

$$\tau_{\rm av}=\eta_b\tau_b+\sum_i \eta_{Vi}\tau_{Vi}, \tag{1}$$

where η_b and η_{Vi} are the fractions of positron annihilation events in the bulk and at the vacancies V_i, respectively. Similar equations can be written for the line shape parameters S and W. According to the positron trapping model[17] the fractions η_b and η_{Vi} are related to the trapping rates by the following equations:

$$\eta_b=\lambda_b \Big/ \left(\lambda_b+\sum_i \kappa_{Vi}\right), \tag{2a}$$

$$\eta_{Vi}=\kappa_{Vi} \Big/ \left(\lambda_b+\sum_i \kappa_{Vi}\right), \tag{2b}$$

where $\lambda_b=\tau_b^{-1}$ is the positron annihilation rate in the bulk and κ_{Vi} is the positron trapping rate at the vacancy type i.

When vacancies with $\tau_{Vi}>\tau_b$ are present, positron trapping rates and trapping fractions are greater than zero, $\kappa_{Vi}>0$ and $\eta_{Vi}>0$, and the average positron lifetime is longer than the value in bulk $\tau_{\rm av}>\tau_b$ through Eq. (1). Thus vacancy defects can be detected by measuring the average positron lifetime. If the measured $\tau_{\rm av}$ increases compared to its earlier value, more positron trapping at vacancies takes place in the sample than previously.

In the case of negative vacancies the positron trapping is strongly temperature dependent. A model to explain the positron trapping at negative vacancies with two different processes has been presented by Puska *et al.*[15] The positron can get trapped at the negative vacancy either directly or by a two-state capture mechanism via a Rydberg state. Assuming that positron trapping to a negative vacancy is characterized by the trapping through the Rydberg precursor state it is possible to write the positron trapping coefficient as

$$\mu_V=\frac{\mu_R}{1+\dfrac{\mu_R}{N\eta_R}\left(\dfrac{m_+k_BT}{2\pi\hbar^2}\right)^{3/2}e^{-E_R/k_BT}}. \tag{3}$$

Here $N=4.4\times10^{22}$ cm^{-3} is the number of atoms per cubic centimeter in GaAs, $m_+\approx1.0\times m_e$ is the effective mass of the positron, E_R is the positron binding energy at the Rydberg state, and η_R is the transition rate from the Rydberg state to the ground state at the vacancy. The transition coefficient from the free-positron state to the Rydberg state is temperature dependent, $\mu_R\propto T^{-1/2}$. Experimental estimations for parameters E_R, μ_R, and η_R exist for vacancies in Si[18] and GaAs[16].

V. IDENTIFICATION OF NATIVE DEFECTS

A. Ga vacancies

Results of the measurements in darkness show that the average positron lifetime in darkness is longer than the free positron lifetime in GaAs. This indicates that there are vacancy type defects present in the as-grown SI GaAs samples. At 300 K the average positron lifetime is close to the bulk lifetime $\tau_b=231$ ps which indicates that only few vacancies are detected at room temperature. This is in good agreement with the earlier observations on as-grown SI GaAs.[10,16,19] No evidence of positron trapping around negative ions is observed since no increase of $\tau_{\rm av}$ due to thermal positron detrapping at 100–150 K is detected.[20,21]

The Fermi level in SI GaAs stays at the midgap and the vacancies do not change their charge states when temperature changes. The increase of the average positron lifetime as temperature decreases is thus due to the temperature dependence of the positron trapping coefficient at defects. Since positron trapping at neutral defects is independent of temperature, the increase of $\tau_{\rm av}$ in darkness at low temperatures indicates that the observed vacancies are negatively charged.

The second lifetime component τ_2 is about 250–260 ps which is a typical value for monovacancies is GaAs.[10,19,22] According to theoretical calculations the As vacancies are positive and the Ga vacancies negative in SI GaAs.[23] Since positive defects repel positrons, the negative Ga vacancies are the only defects able to trap positrons in as-grown SI GaAs in darkness. We thus associate the vacancies with negative gallium vacancies. The positron experiments are unable to identify, however, whether the Ga vacancies are isolated or bound to a defect complex.

The positron trapping rate κ_V to the gallium monovacancies can be calculated through Eqs. (1) and (2). In this cal-

culation we use the positron lifetime at the vacancy $\tau_V=260$ ps (Refs. 19 and 20) and the annihilation rate in the perfect lattice is obtained from the experimental data in Fig. 1. The positron trapping rate can be modeled with Eq. (3) using the value of $\mu_V=1.4\times10^{15}$ s^{-1} at 300 K (Ref. 20) in $\kappa_V=\mu_V c_V$. The parameters E_R, μ_R, and η_R can be determined as fitting parameters. For the data of this work the fit is in excellent agreement with the data in all samples in the temperature range $T=30$–300 K. The average factor between the trapping coefficients at 30 K and at 300 K is 9 ± 1. In the fits the positron binding energy is typically $E_R=15$ meV. The positron trapping coefficient at the Rydberg state is $\mu_R=1.1\times10^{16}$ s^{-1} at 30 K and the transition rate to the ground state is 3.0×10^{11} s^{-1}. These values are reasonable compared with the theoretical and experimental values calculated for positron trapping at negative vacancies in Si.[15,18] However, the binding energy $E_R=15$ meV is slightly smaller than the earlier estimates for V_{Ga} in GaAs.[16]

From the trapping rate at the gallium vacancy the concentration of V_{Ga} can be estimated. The concentrations are between 1 and 12×10^{15}cm^{-3} in the samples which have been studied in this work (see Table I). These values are in agreement with earlier results on undoped SI GaAs samples.[16] The V_{Ga} concentrations are less than those typically found for the *EL*2 defect, but they are equal to or larger than the usual impurity concentrations in LEC GaAs.

B. Arsenic vacancies

1. Identification of the vacancies

Under illumination the average positron lifetime increases compared to the values measured in darkness. This indicates that more positron trapping takes place in the sample. Hence some vacancies which do not trap positrons in darkness are converted into positron traps under illumination. The effect of illumination on the average positron lifetime is strongest at photon energies 1.4–1.5 eV (Fig. 5). This energy range is outside the photoexcitation peak (1.1–1.2 eV) of the metastable state of the *EL*2 defect.[1] The increase of τ_{av} shows no metastability as *EL*2 does[1,12] and it is observed independently of whether *EL*2 is in the stable or in the metastable state. These facts indicate that the increase of τ_{av} is not produced by the *EL*2 defect.

When the spectra measured under illumination are decomposed, the second lifetime τ_2 is scattered between 250 and 260 ps (Figs. 8 and 9). This value is close to the positron lifetime at V_{Ga} detected in darkness. Under illumination both the Ga vacancies and the illumination-induced vacancies may trap positrons. The lifetime τ_2 is a superposition of lifetimes in the Ga vacancies and in the illumination induced vacancies.[6,10] Furthermore, the decompositions of the spectra are in good agreement with the one trap model and no sign of positron trapping at negative ions[20,21] is detected. We can conclude that the positron lifetime at the vacancy which traps positrons under illumination is about the same as that at the Ga vacancies, i.e., 250–260 ps. This value indicates that the defect has the size of a monovacancy. Notice that the positron trapping at the metastable state of the *EL*2 defect has no influence on the measured τ_2 above 60 K since this trapping can only be detected at $T<60$ K.[6]

In a semi-insulating sample the defect ionization levels which are located below midgap are occupied by electrons. The levels populated under illumination are thus located above the midgap. For the Ga vacancies no ionization levels are expected in the upper half of the gap whereas the As vacancies have their ionization levels above the midgap.[23] It is thus natural to identify the defects observed under illumination as As vacancies which convert from positive to neutral or negative charge state under illumination. We can conclude that under illumination positrons are trapped at both Ga monovacancies and As monovacancies. However, positron experiments give no information whether these defects are isolated or parts of a defect complex.

2. Charge state of the As vacancies

The positron trapping rate κ_V at the As vacancy can be calculated using Eqs. (1) and (2). Here we assume a three trap model, i.e., Ga vacancies, As vacancies and the metastable state of the *EL*2 defect trap positrons under illumination.[6] Earlier, positron lifetimes of 257 and 295 ps have been obtained for negative and neutral As vacancies, respectively.[10] Lifetime $\tau(V_{\mathrm{As}})=257$ ps is chosen for the As vacancy because it is closer to the lifetimes obtained from the decompositions of the spectra and there is no indication of the longer lifetime of 295 ps. We assume that the trapping rate at Ga vacancies under illumination is the same as in darkness, i.e., illumination does not change the occupation of the ionization levels of the Ga vacancies. We further assume that the metastable state of *EL*2 traps positrons similarly under illumination as after illumination in the dark and we use the lifetime of 245 ps for the positrons trapped at the metastable state of the *EL*2 defect, *EL*2*.[6]

At the temperature range 20–70 K the positron lifetime and consequently the positron trapping rate increase as functions of the 1.42 eV photon flux from 2×10^{13} to 10^{14} cm^{-2} s^{-1}, and thereafter they saturate at values which are independent of the illumination intensity (Figs. 3 and 4). It can be estimated (see Sec. VI B 1) that at these temperatures and for the photon flux $\phi>10^{14}$ cm^{-2} s^{-1} the occupation of the As vacancy ionization levels under illumination is mainly controlled by optical transitions and not by the thermal escape of electrons or by the hole capture. Thus the occupation of the ionization levels is independent of the temperature and the number of As vacancies trapping positrons is constant at $T=20$–70 K.

Figure 10 shows the positron trapping rate at As vacancies as a function of temperature under 1.42 eV illumination with the photon flux $\phi=10^{16}$ cm^{-2} s^{-1}. In the temperature range 20–70 K the trapping rate $\kappa(V_{\mathrm{As}})$ decreases strongly with temperature and above 100 K the decrease of the trapping rate is even faster. Below 70 K the temperature dependence of $\kappa(V_{\mathrm{As}})$ is similar to that observed for the Ga vacancies in darkness. It shows that the positron trapping is enhanced at low temperatures which is a clear indication that the As vacancies are negative. This conclusion is also supported by the lifetimes $\tau_2=250$–260 ps which are very close to the value 257 ps determined for the negative As vacancy in *n*-type GaAs whereas the longer values of 295 ps is associated with the neutral As vacancy.[10]

Above 70 K the trapping rate $\kappa(V_{\mathrm{As}})$ decreases much faster than expected for a negative vacancy. The steep decrease and the temperature at which it starts depend on the

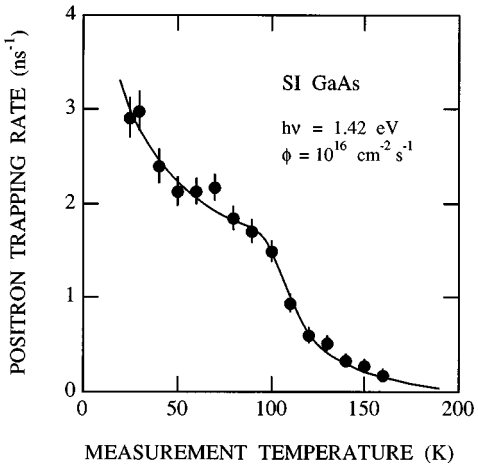

FIG. 10. The positron trapping rate at arsenic vacancies in SI GaAs (sample 1) as a function of the measurement temperature. The trapping rate has been calculated from the lifetime results measured under illumination with the photon energy $h\nu=1.42$ eV and photon flux $\phi=10^{16}$ cm^{-2} s^{-1}.

illumination intensity. This decrease of the positron trapping will be studied further in Sec. VI.

3. Concentration of negative As vacancies

The positron trapping rate κ_V at the As vacancy can be used to estimate the concentration of the negative As vacancies if the trapping coefficient μ_V is known. Here we assume that the absolute value and the temperature dependence of the trapping coefficient μ_V at the As vacancy are the same as for μ_V at the Ga vacancy. Since both vacancies are negative, this is a reasonable approximation.

As will be explained in the Sec. VI, the positron trapping rate at As vacancies depends both on the illumination flux ϕ and on the measurement temperature T because both these parameters change the concentration of As vacancies in the negative charge state. However, the trapping rate at V_{As} is almost independent of ϕ and T in the range $\phi>10^{14}$ cm^{-2} s^{-1} and $T\leqslant 70$ K and it can thus be used to estimate the total As vacancy concentration. Rigorously, the concentration of the negative As vacancies determined this way is the lower limit of the total As vacancy concentration since some of the As vacancies may not be in the negative charge state due to photoionization or hole capture processes. The negative As vacancy concentrations of all the samples are listed in Table I. Typically the values are $[V_{\mathrm{As}}]=10\times10^{15}$ cm^{-3}. When the V_{As} concentrations are compared between samples, it should be kept in mind that the error estimates in Table I take into account only the statistical error in the positron lifetime measurements. The absolute numbers are accurate to about 30%.

C. Line shape parameters for vacancy defects

The Doppler broadening measurements can be analyzed by calculating the line shape parameters S_V and W_V for the Ga and the As vacancies through equations similar to Eqs. (1)–(2). When calculating the line shape parameters for the Ga vacancy, the one trap model is used. The fractions η_b and $\eta(V_{\mathrm{Ga}})$ can be calculated using the positron lifetime measurements in darkness. For the Ga vacancy the results are $S_V/S_b=1.021\pm0.003$ and $W_V/W_b=0.83\pm0.01$ as the average of the values in samples 1 and 4. The R value for the Ga vacancy is 1.33 ± 0.15, respectively.

The line shape parameters for the As vacancy can be estimated from the Doppler data measured under illumination at 50–100 K. At these temperatures only Ga and As vacancies act as positron traps because positron trapping at the metastable state of the *EL*2 defect is efficient only at 20–50 K.[6,12] The parameters S_V/S_b and W_V/W_b determined from the data in darkness can be used for the Ga vacancy. The fractions η_b, $\eta(V_{\mathrm{Ga}})$ and $\eta(V_{\mathrm{As}})$ were calculated using the lifetime measurements under 1.42 eV illumination. For the As vacancy we obtain the line shape parameters of $S_V/S_b=1.009\pm0.003$ and $W_V/W_b=0.88\pm0.01$. The R value for the As vacancy is 0.7 ± 0.1. These values are close to those we have determined previously for V_{As}^{-} in n-type GaAs.[24]

The parameters S_V/S_b and W_V/W_b are different for the vacancy detected only under illumination and for the one detected in darkness. Thus the increase in the S and W parameters under illumination is caused by a different vacancy than the one observed in darkness. Similarly, the R parameter (Fig. 2) shows that at $T>150$ K the vacancy trapping positrons under illumination is the same as in darkness. At lower temperatures the value of R under illumination decreases due to an additional, different positron trap. The larger value of W_V/W_b and the smaller value of S_V/S_b for the vacancy observed under illumination support the identification of that vacancy as V_{As} since the gallium atoms around the arsenic vacancy yield more core annihilations than the arsenic atoms surrounding the gallium vacancy.[25] Respectively, the vacancy detected in darkness is V_{Ga}.

VI. PHOTOEXCITED STATE OF THE ARSENIC VACANCY

The identification in the previous section shows that the native As vacancies are converted to efficient positron traps when electrons are transferred to their ionization levels under illumination. The electrons can be excited either directly from the valence band or they may originate from the capture of photoelectrons due to the excitation of other defect levels in the energy gap. The photoexcited electrons may escape from the ionization levels of the As vacancies to the conduction band via thermal emission. Electrons in the ionization level can also recombine with the holes in the valence band due to hole capture. In this section we investigate these optical and thermal processes of the As vacancy by studying the concentration of V_{As}^{-} as a function of the photon energy and flux, and the sample temperature.

A. Optical generation of negative As vacancies

1. Detection of As vacancies versus the metastability of EL2

To investigate the efficiency of the generation of the negative charge state of the As vacancy as a function of the photon energy and flux, we have calculated the positron trapping rate at V_{As}^{-} using the data of Figs. 3–5 and the positron trapping model (Sec. IV). We assume that the Ga vacancies trap positrons similarly under illumination as in darkness. We

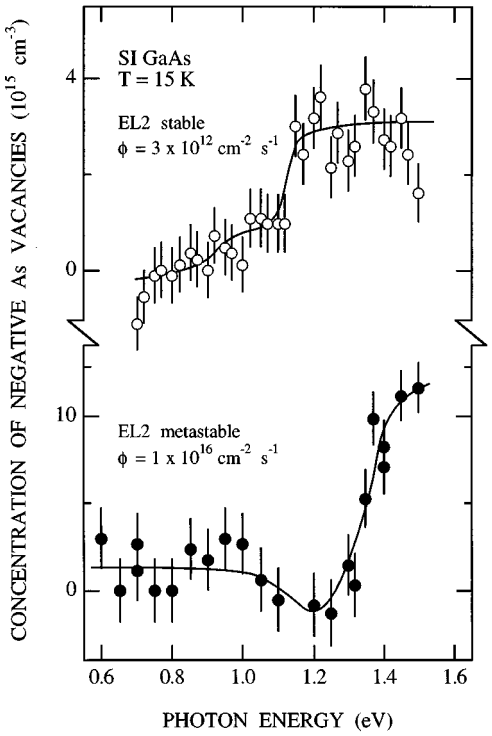

FIG. 11. Concentration of the negative arsenic vacancies in SI GaAs (sample 1) under illumination as a function of the photon energy. In the data of the top panel the *EL*2 defect remains in the stable state over the experiment. In the data of the bottom panel *EL*2 is deliberately converted into the metastable state before the measurements. The measurement temperature is 15 K and the photon fluxes used for the illuminations are marked in the figure.

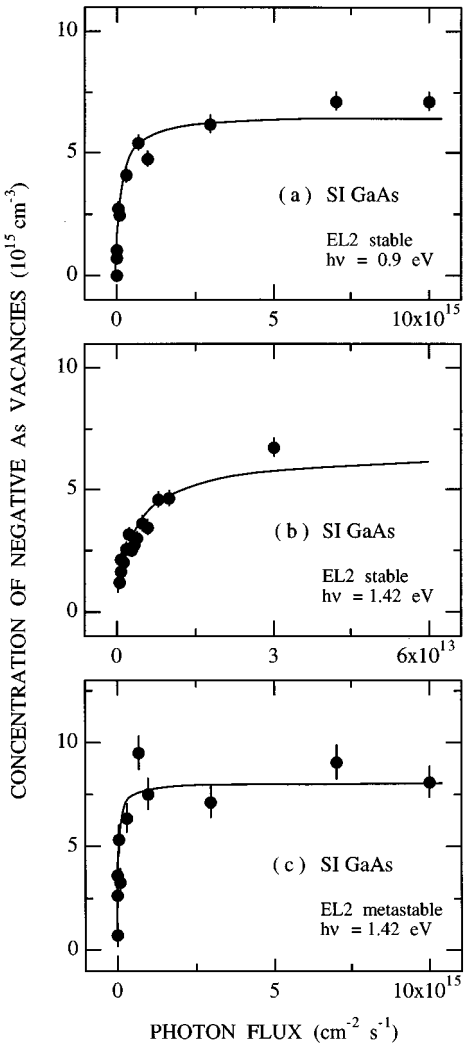

FIG. 12. Concentration of the negative arsenic vacancies in SI GaAs (sample 1) under illumination as a function of the photon flux. The photon energies used for the illuminations are marked in the figure. In the experiments of panels (a) and (b) the *EL*2 defect is in the stable state. In panel (c) *EL*2 is converted into the metastable state before the measurements. The measurement temperature is 15 K.

also take into account the metastable *EL*2* as a positron trap [$\tau(EL2^*)=245$ ps] in the cases where *EL*2 is transformed to this state under illumination. In the analysis we use Eqs. (1) and (2) with $\tau(V_{Ga})=260$ ps and $\tau(V_{As})=257$ ps to calculate the trapping rate at the Ga and As vacancies. The trapping rate at V_{As}^- under illumination is converted to the concentration of V_{As} in the negative charge state using $\kappa_V=\mu_V c_V$ with $\mu_V=1.1\times10^{16}$ s^{-1} at 15 K.

The concentration of negative As vacancies under illumination at 15 K is shown as a function of the photon energy and the photon flux in Figs. 11 and 12. When the *EL*2 defect is in the stable state, the negative charge state of the As vacancy can be generated efficiently with photons of $h\nu\geq0.9$ eV. At $h\nu\geq1.2$ eV the spectrum is almost flat (Fig. 11). The saturation effect can be obtained with a photon flux of $\phi=1\times10^{15}$ cm^{-2} s^{-1} (Fig. 12) with 0.9 eV photons and with 1.4 eV photons with as low a flux as $\phi=1\times10^{13}$ cm^{-2} s^{-1} (Fig. 12). When the *EL*2 defect has been first converted into the metastable state, the generation of the negative V_{As} depends strongly on the photon energy: the spectrum of Fig. 11 increases steeply at $h\nu\geq1.2$ eV, whereas at $h\nu\leq1.1$ eV no negative As vacancies are detected. The 1.4 eV photon flux of $\phi=1\times10^{15}$ cm^{-2} s^{-1} is needed to obtain the saturation effect in the photoexcitation of V_{As} (Fig. 12). This flux is two orders of magnitude larger than required to generate the same effect when the *EL*2 is in the stable state (Fig. 12). Both the shape of the photoexcitation spectrum of V_{As} and the photon flux needed for its generation depend thus strongly on the state of the *EL*2 defect in SI GaAs.

The different efficiency in the generation of the negative V_{As} can be explained in two ways. First, the optical process leading to the photoexcitation of V_{As} can depend strongly on the state of the *EL*2: when the *EL*2 defect is transformed to the metastable state, its ionization level is removed from the band gap, and it is no longer possible to excite photoelectrons to the conduction band by the optical ionization of the *EL*2 defect. For example, if the As vacancy becomes negative due to the trapping of photoelectrons emitted from the *EL*2, the excitation is possible only if the *EL*2 defect is in the stable state. Second, the recombination processes may also depend strongly on the state of the *EL*2. When *EL*2 is in the metastable state, the electrical compensation of undoped GaAs is lost. The *depopulation* rate of the optically excited charge state of the As vacancy may then be increased due to

the trapping of holes from the valence band. However, in the experiments we observe that the *shape* of the excitation spectrum of V_{As} is clearly different depending on the metastability of *EL*2 (Fig. 11). Since the hole trapping rate does not depend directly on the photon energy, it can only affect the photon flux needed to obtain the saturation population of V_{As}^{-} by decreasing the excitation efficiency (Fig. 12), but it does not have an influence on the shape of the excitation spectrum. We thus conclude that there are two different optical processes leading to the population of the negative As vacancy: the first one is efficient only when the *EL*2 defect is in the stable state and the second is independent of the state of *EL*2.

The absorption spectrum of semi-insulating GaAs has been studied in detail in many earlier works.[1] When the *EL*2 is in the stable state, the absorption at $h\nu \leqslant 1.4$ eV is due to the optical exchange of electrons between the conduction and the valence bands and the ionization levels of the *EL*2 defect. These optical processes generate photoelectrons which can recombine with the photoholes either directly or through a capture by the ionization levels of the defects in the band gap. In this work we observe that the As vacancy becomes negatively charged under 0.9–1.5 eV illumination when the *EL*2 defect is in the stable state. The shape of the generation spectrum of the As vacancy in Fig. 11 is roughly similar to the photoexcitation spectrum of electrons from the *EL*2 defect to the conduction band.[26] It is thus natural to associate the optical process populating the negative V_{As} to the capture of the photoelectrons emitted from the ionization level of the *EL*2 defect to the conduction band.

When the *EL*2 defect is in the metastable state, the optical absorption is zero at least for the photon energies below 1.4 eV. No photoelectrons or holes are thus created and consequently the negative charge state of the As vacancy can not be populated by the trapping of photoelectrons originating from the optical ionization of the *EL*2 defect. However, absorption near the band edge at $h\nu \geqslant 1.4$ eV has been reported even when the *EL*2 is in the metastable state.[5,27] According to the experiments of this work, the negative As vacancy is observed under illumination with the photon energy $h\nu \geqslant 1.4$ eV and the flux $\phi \geqslant 1\times10^{15}$ cm^{-2} s^{-1} when the *EL*2 defect is in the metastable state. As explained above, the optical process leading to the population of the negative V_{As} in this case is different from the one taking place when the *EL*2 defect is in the stable state. We attribute the process to the direct excitation of electrons from the valence band to the ionization level of the arsenic vacancy.

2. Occupation of the ionization level of the As vacancy at 15 K

The occupation of the ionization level of the As vacancy can be quantitatively studied by modeling the optical and thermal ionization processes of electrons and holes. In earlier studies on V_{As} two ionization levels, $-/0$ and $0/+$, have been observed.[10] The second lifetime component τ_2 in the measurements of this work is very near the positron lifetime at the negative As vacancy, $\tau_V = 257$ ps, and is independent of the measurement temperature. Thus positron trapping at neutral As vacancies, $\tau_V = 295$ ps, is not observed. The positron trapping coefficient at neutral vacancies $\mu(V_{As}^{0})$ at 30 K, e.g., is by a factor of 10 smaller than $\mu(V_{As}^{-})$ and this makes the detection of V_{As}^{0} difficult.[14,15] Because in this work the positrons are sensitive only to the negatively charged As vacancies we can for simplicity take into account only the highest ionization level of V_{As} and assume that only one electron is needed to change the charge state of the arsenic vacancy under illumination. If the $0/+$ ionization level was taken into account the results would remain practically unchanged. The following symbols are used in the models:

N_1	the total As vacancy concentration (cm^{-3}),
n_1	concentration of the occupied As vacancy levels (cm^{-3}),
N_2	*EL*2 concentration (cm^{-3}),
n_2	concentration of the occupied *EL*2 level, i.e., $EL2^0$ concentration (cm^{-3}),
Δn	increase of the free electron density compared to that in darkness,
Δp	increase of the free hole density compared to that in darkness,
$g_p^0 = \sigma_p^0 \phi$	optical electron transfer rate to an electron level from the valence band (VB),
$g_n^0 = \sigma_n^0 \phi$	optical electron transfer rate from an electron level to the conduction band (CB),
C	recombination factor between CB and VB,
$\sigma_n \langle v_n \rangle n$	electron capture rate from the CB to the electron level,
$\sigma_p \langle v_p \rangle p$	hole capture rate from the VB to the electron level, i.e., recombination rate.

When *EL*2 is in the stable state, it compensates the impurities and the intrinsic defects and the material is perfectly semi-insulating. All the electrons and the holes can then be assumed to be photoinduced, $n = \Delta n$ and $p = \Delta p$.

As explained in the previous section, at photon energies $h\nu < 1.2$ eV we can neglect the direct electron transition from the valence band to the ionization level of V_{As}. At the low measurement temperature of 15 K, thermal emission of electrons from the ionization levels in the gap can also be neglected. The rate equations describing the electron population of the conduction band, the ionization level of V_{As} and the *EL*2 level are then

$$\frac{d\Delta n}{dt} = -\sigma_{n1}\langle v_n \rangle (N_1 - n_1)\Delta n - \sigma_{n2}\langle v_n \rangle (N_2 - n_2)\Delta n + g_n^0 n_2 - C\Delta n \Delta p, \tag{4a}$$

$$\frac{dn_1}{dt} = \sigma_{n1}\langle v_n \rangle (N_1 - n_1)\Delta n - \sigma_{p1}\langle v_p \rangle n_1 \Delta p, \tag{4b}$$

$$\frac{dn_2}{dt} = \sigma_{n2}\langle v_n \rangle (N_2 - n_2)\Delta n - g_n^0 n_2 + g_p^0 (N_2 - n_2) - \sigma_{p2}\langle v_p \rangle n_2 \Delta p. \tag{4c}$$

In darkness the occupied *EL*2 states can be noted with n_2^t. The charge of the system remains the same before and under illumination, i.e., $N_2 - n_2^t = \Delta p + (N_2 - n_2) - \Delta n - n_1$.

The occupation of the vacancy level n_1 can be solved numerically from the steady state of the equations presented

above. We have used the following values: $\sigma^0_{p2}(0.9\ \text{eV})=4\times10^{-17}$ cm^2 and $\sigma^0_{n2}(0.9\ \text{eV})=1\times10^{-17}$ cm^2 for the optical cross sections related to the *EL*2 level,[27] $\sigma_{n2}=5\times10^{-19}$ cm^2 for the electron capture cross section of the *EL*2 level[28] and $C=2\times10^{-10}$ cm^{-3} s^{-1} for the recombination factor between the conduction band and the valence band.[29] The numerical solution indicates that both Δn and Δp increase linearly as a function of the illumination flux ϕ, when $\phi<10^{18}$ cm^{-2} s^{-1}. The occupancies of the n_1 and n_2 are then independent of the illumination flux which is in clear contradiction with the experimental results of Figs. 3 and 12.

The experimental data suggests rather that the recombination rate r of electrons from the As vacancy level is constant or depends much less on ϕ than Δn does. The constant recombination rate can be related to a recombination via an additional defect level or to a constant hole concentration p in the valence band.[30] The model of Eq. (4) can be modified by replacing the $-\sigma_{p1}\langle v_p\rangle n_1 p$ term in Eq. (4b) by $-rn_1$. The numerical solution of Eq. (4) shows that the effect of the electron and hole capture cross sections σ_{n2} and σ_{p2} can also be ignored in Eq. (4c) and the occupancy of the *EL*2 level can be written as $A=\sigma^0_{p2}/(\sigma^0_{p2}+\sigma^0_{n2})$. Also the band to band recombination rate can be excluded from the rate equations, since it has almost no effect on the carrier concentrations.

After these modifications the occupancy of the arsenic vacancy can be described by the following quadratic equation

$$rn_1^2-n_1\left[N_2\left(\sigma^0_{n2}\phi A+r\,\frac{\sigma_{n2}}{\sigma_{n1}}\,(1-A)\right)+rN_1\right]+\sigma^0_{n2}\phi A N_1 N_2=0. \tag{5}$$

The free parameters in the analysis are the ratio r/σ_{n1} and the total concentration of the arsenic vacancies N_1. The analysis shows that the saturation level of $[V^-_{\text{As}}]$ observed at $\phi>1\times10^{15}$ cm^{-2} s^{-1} is practically the *total* concentration of V_{As}, $[V^{\text{tot}}_{\text{As}}]=[V^-_{\text{As}}]$. The ratio r/σ_{n1} is optimized to a value 1.3×10^{16} cm^{-2} s^{-1}. The fit is not very sensitive to the value of A and small changes in its value do not affect the analysis. The fit of the solution of Eq. (5) is the solid line in Fig. 12(a).

When the *EL*2 is in the stable state and $h\nu\geq1.4$ eV, the previous model does not explain the measured data. Another way to populate the As vacancy levels has to be included in the analysis. As explained in Sec. VI A 1, at $h\nu\geq1.4$ eV the electrons can make a direct transition from the valence band to the As vacancy levels. If the optical hole generation rate related to the As vacancy level is described by $g^0_{p1}=\sigma^0_{p1}\phi$, the rate equation describing the arsenic vacancy level is

$$\frac{dn_1}{dt}=\sigma_{n1}\langle v_n\rangle(N_1-n_1)\Delta n+g^0_{p1}(N_1-n_1)-rn_1-\sigma_{p1}\langle v_p\rangle n_1\Delta p. \tag{6}$$

The conduction band and the *EL*2 level are treated as in the previous model. The optical cross sections related to the *EL*2 defect are $\sigma^0_{p2}(1.4\ \text{eV})=3\times10^{-17}$ cm^2 and $\sigma^0_{n2}(1.4\ \text{eV})=2\times10^{-16}$ cm^2,[27] yielding $A=0.13$. The values determined above for r/σ_{n1} and N_1 can be used to analyze the data of Fig. 12(b) because the vacancy concentration and the constant recombination process can be assumed to be the same. We have further assumed that the optical electron generation rate from the level of V_{As} is small compared to the optical hole generation rate. This assumption is based on the fact that the spectrum for the generation of the negative charge state of V_{As} suggests that the ionization level $-/0$ of V_{As} is close to the conduction band, possibly within 0.1 eV. As will be shown in Sec. VI B 2 the thermal ionization energy of V_{As} is also very small, about 60 meV. For such shallow levels the optical ionization rate is usually very small for photon energies close to the band gap energy since the ionization level and the conduction band do not overlap efficiently in k-space.[31,32] We can thus assume that $\sigma^0_{n1}\ll\sigma^0_{p1}$.

The solution of Eq. (6) can be fitted to the data of Fig. 12(b) with the quantities $\sigma^0_{p1}/\sigma_{n1}$ and $\sigma^0_{p1}/\sigma_{p1}$ as fitting parameters. When the ratio $\sigma^0_{p1}/\sigma_{n1}\geq2\times10^4$, the analysis of the data in Fig. 12(b) yields the ratio $\sigma^0_{p1}/\sigma_{p1}=10^{10}$ independently of $\sigma^0_{p1}/\sigma_{n1}$. In this case the ratio between the hole and the electron capture cross section is $\sigma_{p1}/\sigma_{n1}\leq2\times10^{-6}$. If we include only the constant recombination rate in the analysis, we can determine the ratio $\sigma^0_{p1}/\sigma_{n1}=3\times10^3$.

On the basis of the analysis presented above it is possible to compare the efficiency to excite the photoelectrons to the As vacancy level from the valence band directly or from the *EL*2 level via the conduction band. When the *EL*2 defect is in the stable state the fluxes needed to excite all As vacancies are $\phi=1\times10^{15}$ cm^{-2} s^{-1} and $\phi=1\times10^{13}$ cm^{-2} s^{-1} in the case of 0.9 and 1.4 eV photons, respectively (Fig. 12). According to the analysis under 1.42 eV illumination the net transfer rate of electrons from the *EL*2 level to the As vacancy level is practically the same as under 0.9 eV photon illumination since replacing σ^0_{n2} (0.9 eV) and σ^0_{p2} (0.9 eV) with σ^0_{n2} (1.4 eV) and σ^0_{p2} (1.4 eV) in Eq. (5) does not affect much the calculated values of Δn and n_1. The factor of 100 in the photon fluxes results mainly from the direct electron transfer from the valence band which is not possible under 0.9 eV illumination. The direct excitation process from the valence band is thus by a factor of 100 more efficient than the indirect transfer of electrons from the *EL*2 level via the conduction band.

When *EL*2 is in the metastable state, the ionization level of V_{As} can only be populated by a direct electron transition from the valence band. The transformation of *EL*2 to the metastable state induces changes to the compensation of impurities in the sample, resulting in a permanent hole concentration p_0. The rate equations describing the population of V_{As} and the valence band are then

$$\frac{dn_1}{dt}=g^0_{p1}(N_1-n_1)-\sigma_{p1}\langle v_p\rangle n_1(\Delta p+p_0), \tag{7a}$$

$$\frac{d\Delta p}{dt}=-g^0_{p1}(N_1-n_1)+\sigma_{p1}\langle v_p\rangle n_1(\Delta p+p_0), \tag{7b}$$

where we have assumed again that the thermal emission and capture rates of electrons between the vacancy level and the conduction band are negligible at the lowest measurement temperature of 15 K and that the optical electron generation rate from the level of the arsenic vacancy is small compared to the optical hole generation rate related to the same level.

Equation (7) and the conservation of charge $n_1=\Delta p$ can be reduced in the steady state to a quadratic equation for n_1 giving the occupation of the As vacancies under illumination as

$$n_1=\frac{1}{2\langle v_p\rangle}\left\{\left[\left(\langle v_p\rangle p_0+\phi\,\frac{\sigma_{p1}^0}{\sigma_{p1}}\right)^2+4\phi\langle v_p\rangle N_1\,\frac{\sigma_{p1}^0}{\sigma_{p1}}\right]^{1/2}-\phi\,\frac{\sigma_{p1}^0}{\sigma_{p1}}\right\}-\frac{p_0}{2}. \tag{8}$$

As fitting parameters we obtain the ratio of the optical generation and the hole capture cross sections $\sigma_{p1}^0/\sigma_{p1}$, the hole concentration p_0 and the concentration of the As vacancies N_1. The fit is the solid line in Fig. 12(c).

The analysis shows that when the photon flux is more than 1×10^{15} cm^{-2} s^{-1} practically all As vacancies are converted to the photoexcited state under illumination. At lower photon fluxes the recombination is competing with the optical generation rate, resulting in a partial occupation of the ionization level of the As vacancy. The fit yields the following values $\sigma_{p1}^0/\sigma_{p1}=4\pm4\times10^8$, $N_1=8.3\pm0.3\times10^{15}$ cm^{-3} and $p_0=2\pm4\times10^{15}$ cm^{-3}. Since the direct optical generation and all recombination processes are the same as in the case of Fig. 12(b) we can use the ratio $\sigma_{p1}^0/\sigma_{p1}=10^{10}$ and the fit to the data then yields $p_0=10^{16}$–10^{17} cm^{-3}. This order of magnitude is reasonable when compared to the total *EL*2 concentration in the studied samples.

The fluxes needed to excite all the As vacancies with 1.4 eV photons are $\phi=1\times10^{13}$ cm^{-2} s^{-1} and $\phi=1\times10^{15}$ cm^{-2} s^{-1} when the *EL*2 level is in the stable or the metastable state, respectively (Fig. 12). The ionization levels of the arsenic vacancies are thus more efficiently populated when the *EL*2 defect is in the stable state (Fig. 12). The analysis presented above indicates that in both these cases the direct photoexcitation from the valence band to the ionization level of $V_{\rm As}$ is the dominating generation mechanism. Since the optical generation of the As vacancies does not change, the more efficient population of the As vacancies is mainly related to the differences in the hole capture rates from the As vacancy. By comparing the photon fluxes one can state that the recombination rate of electrons in the $V_{\rm As}$ level is about 100 times larger when *EL*2 is in the metastable state than when it is in the stable state.

This difference can be related to the different compensation in the material, caused by the changes in the *EL*2 levels. When the *EL*2 defect is converted to the metastable state, the acceptors in the sample may emit holes to the valence band. The analysis above thus indicates that the free hole concentration under 1.42 eV illumination increases roughly by a factor of 100 when the *EL*2 defect is converted to the metastable state.

B. Thermal electron emission from the ionization level of the photoinduced As vacancy

1. Temperature dependence of the concentration of As vacancies

The experimental results of Sec. III B indicate that under illumination the behavior of the average positron lifetime as a function of temperature depends on the photon energy, on the photon flux, and on the metastability of the *EL*2 defect.

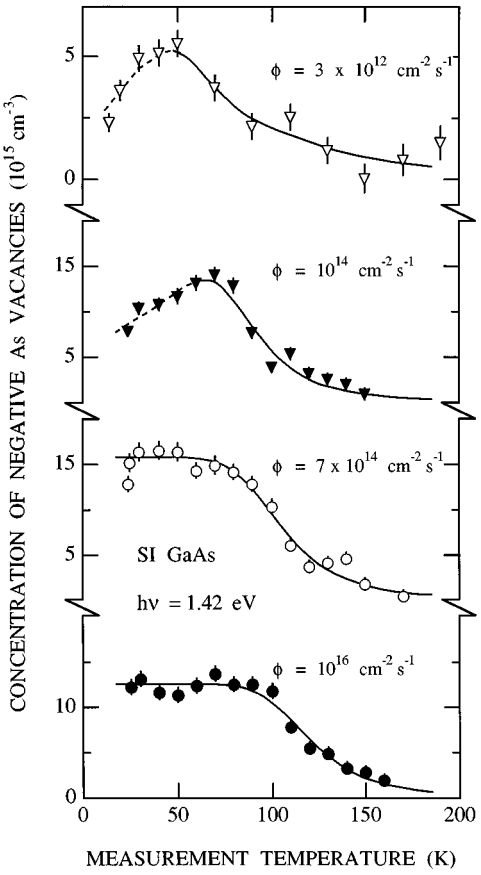

FIG. 13. Concentration of the negative arsenic vacancies in SI GaAs (sample 1) under $h\nu=1.42$ eV illumination as a function of the measurement temperature. The different photon fluxes used for the illuminations are marked in the figure.

According to the analysis of the previous section, the negative charge state of the As vacancy is detected at 15 K under illumination in the following conditions: (i) the *EL*2 defect is in the stable state, the photon energy is $h\nu\geqslant0.9$ eV and the flux $\phi\geqslant10^{15}$ cm^{-2} s^{-1}, and (ii) the *EL*2 defect is in the metastable state, the photon energy is $h\nu\geqslant1.35$ eV and the flux $\phi\geqslant1\times10^{15}$ cm^{-2} s^{-1}. In Fig. 7 the data under 0.9 and 1.4 eV illuminations have been measured under conditions (i) and (ii), respectively. These two curves are qualitatively similar; the average lifetime decreases rapidly at 70–120 K and the onset temperature of this effect depends on the illumination flux (Fig. 6). This decrease is much more rapid than expected for positron trapping at negative vacancies.

Figure 13 shows the concentration of negative As vacancies as a function of the measurement temperature under 1.42 eV light illumination. The concentration of $V_{\rm As}^-$ has been determined from the data of Fig. 6 similarly as in Sec. VI A 1 using the positron trapping model [Eqs. (1)–(2)] and the positron trapping coefficient $\mu_V=1\times10^{16}$ s^{-1} at 30 K. The metastable *EL*2 defect was taken into account as a positron trap in the curves measured under the photon fluxes $\phi=10^{14}$–10^{16} cm^{-2} s^{-1}. *EL*2 remains in the stable state and does not act as a positron trap over the whole experiment with the lowest photon flux of 3×10^{12} cm^{-2} s^{-1}.

The data under illumination with $\phi=10^{15}$–10^{16} cm^{-2} s^{-1} indicate that the concentration of the negative As vacancies

remains constant up to about 70 K when the temperature is increasing and then decreases towards zero. The constant level continues to higher temperatures under illumination with higher photon flux. As explained in Sec. VI A 2 at $T \leqslant 50$ K the concentration of the negative V_{As} saturates to the total As vacancy concentration when the photon flux is increased. However, above 70 K this type of saturation is not detected in the flux range of 10^{12}–10^{16} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. This behavior shows that above 70 K the thermally activated processes start to affect the population of the negative charge state of V_{As} in addition to the optical generation rate. The thermally activated processes may either involve emission of electrons or capture of holes. However, in Sec. VI A 2 the magnitude of the hole capture rate at 15 K was estimated to be much lower than the optical generation rate at photon fluxes above 10^{15} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$, and the hole capture coefficient usually decreases as a function of temperature.[31] Hence we attribute the decrease of $[V_{\mathrm{As}}^{-}]$ with temperature to the thermally activated emission of electrons from the ionization level of V_{As} to the conduction band.

When the photon flux is less than 10^{14} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ the concentration of negative As vacancies is not constant as a function of temperature under 1.42 eV illumination (Fig. 13). In these data the positron trapping rate at 25 K is not in saturation as a function of the photon flux. Hence the thermal capture and emission processes of photocarriers have influence on the concentration of negative V_{As} even at the lowest measurement temperature. The increase of $[V_{\mathrm{As}}^{-}]$ versus temperature may thus reflect the temperature dependence of the trapping of holes from the valence band changing the population of the ionization level of V_{As} under illumination. Another process affecting the concentration of negative As vacancies is the optical recovery of the metastable state of the *EL*2 defect. If *EL*2* recovers under illumination, it is possible to excite photoelectrons from its ionization level to the conduction band and the As vacancy may then be populated also by the trapping of photoelectrons as explained in Sec. VI A 1.

When the *EL*2 defect is in the metastable state, the negative charge state of V_{As} is not detected at 15 K under illumination with $h\nu \leqslant 1.35$ eV as explained in Sec. VI A 1. Figure 7 indicates that the temperature dependence of the average lifetime is in this case complicated under 1.15 eV illumination: at low temperatures τ_{av} decreases strongly, it increases and forms a local maximum at about 120 K and all illumination effects are removed at 150 K. At low temperatures $T<50$ K the second lifetime component is $\tau_2 \approx 245$ ps and it increases to about 260–270 ps at 120 K. The low temperature data at $T<50$ K are also metastable in the sense that the total photoeffect stays permanently in the sample even if the illumination is removed. This type of behavior is characteristic of the *EL*2 defect. Before the positron experiment *EL*2 was transformed to the metastable state which acts itself as a positron trap with a lifetime of 245 ± 3 ps.[6] Under illumination at $T<80$ K with $h\nu = 1.15$ eV only the strongly temperature dependent positron trapping at the metastable state of *EL*2[6] is thus seen in the experiment of Fig. 7.

At 120 K the positron average lifetime under 1.15 eV illumination increases and forms a local maximum as a function of temperature. This behavior can be understood in the following way. The metastable state of the *EL*2 defect recovers at 120 K and the ionization levels of the stable *EL*2 appear again in the band gap. When *EL*2 is in the stable state, it is possible to excite photoelectrons from its ionization level to the conduction band and these electrons may be captured by the As vacancy. At 120 K the As vacancy is thus observed via the indirect process as explained in Sec. VI A 1. In the experiment a hysteresis in the temperature behavior of the average lifetime is also detected depending on whether temperature is increased or decreased in the range of 50–150 K (Fig. 7). This hysteresis can also be understood since the conversion of *EL*2 to the metastable state cannot occur at temperatures $T>85$ K.[33] At decreasing temperature *EL*2 is thus in the stable state when $T>85$ K and the As vacancy levels can be populated also with 1.15 eV illumination (Fig. 5). Below 70 K the *EL*2 is again converted to the metastable state and consequently As vacancies are not observed under 1.15 eV illumination.

2. Occupation of the As vacancy ionization level versus temperature

The temperature dependence of the occupation of the photoexcited As vacancies can be analyzed by modeling the electron transitions under illumination with rate equations. The population of the ionization level of As vacancy is then

$$n_1 = \frac{N_1}{1+(r/g)+(e/g)}, \tag{9}$$

where the generation rate g in the sum of the thermal capture $[g^t = \sigma_{n1}\langle v_n\rangle \Delta n]$ from the conduction band and of the direct optical transition rate $(g^0 = \sigma_{p1}^0 \phi)$ from the valence band. The thermal electron emission rate from the ionization level of V_{As} to the conduction band can be written as $e_n = \gamma \sigma_{n1} \langle v_n\rangle N_c \exp(-E_d/k_B T)$, where γ is a degeneration factor, N_C the effective density of conduction band states and E_d the energy difference between the vacancy ionization level and the conduction band minimum.[34] As explained in Sec. VI A 2 the hole capture rate plays no role in the occupation of the ionization level of V_{As} at 25 K. When temperature increases, the hole capture coefficient decreases.[31] We can thus neglect the hole capture rate in the analysis. The modified Eq. (9) becomes then

$$n_1 = \frac{N_1}{1+\dfrac{\gamma \sigma_{n1}\langle v_n\rangle}{g} N_c e^{-E_d/k_B T}}. \tag{10}$$

Assuming that the generation rate g and the electron capture cross section σ_{n1} do not vary strongly as functions of temperature, the temperature dependence of the population of the negative V_{As} is determined by the exponential term in Eq. (10). The fitted function reproduces well the observed trends in the measured data both as a function of temperature and illumination intensity. The fitted ionization energies are $E_d = 58 \pm 5$, 67 ± 5, 121 ± 25, 123 ± 25, 50 ± 9, and 60 ± 8 meV in samples 1–4, 6, and 7, respectively. The energy difference between the conduction band minimum and the arsenic vacancy ionization level is thus 60 ± 10 meV, indicating that the ionization level $-/0$ of the arsenic vacancy is located about 60 meV below the conduction band minimum in SI GaAs.

In Sec. VI A we concluded that the photons of $h\nu=1.4$–1.5 eV are able to populate the arsenic vacancy level by a direct optical excitation from the valence band. This result suggests that the ionization level of V_{As} is close to the minimum of the conduction band since the band gap of GaAs is 1.5 eV at 30 K. In good agreement with this conclusion the ionization level of the negative arsenic vacancy was found at about 60 meV below the conduction band by analyzing the temperature dependence of electron emission from the ionization level of the As vacancy (Fig. 13). The same ionization level of V_{As} at about 60 meV below the conduction band is thus able to explain the positron data as functions of temperature, photon energy and photon flux.

C. Relations to earlier optical, electrical, and positron annihilation experiments

In earlier positron experiments in *n*-type GaAs the $-/0$ ionization level of the native As vacancies has been detected at about 30 meV below the conduction band.[10] This level is close to that determined for V_{As} in the present work (E_C-60 meV) and the small difference in the ionization energy may be simply due to the experimental uncertainties. However, concentration of the native As vacancies in *n*-type GaAs is clearly at least an order of magnitude larger [$(5$–$10)\times10^{16}$ cm^{-3}] than determined in this work in undoped semi-insulating GaAs.

In the earlier positron lifetime measurements the ionization level $0/+$ of the As vacancy was observed at E_C-140 meV. In this work no clear signs of positron trapping at neutral vacancies were detected. The arsenic vacancies change their charge state to neutral when electrons thermally escape from the $-/0$ ionization level at temperatures above 100 K. At these temperatures the positron trapping coefficient μ_V at a neutral vacancy is by an order of magnitude lower than at a negative vacancy[14,15] which makes the detection of the V_{As}^0 difficult. However, in the decompositions of the lifetime spectra (Figs. 8 and 9) the second lifetime component τ_2 increases at $T=100$–200 K towards the value of $\tau_2=280$ ps. This effect may be a sign of positron trapping at V_{As}^0 where a positron lifetime of 295 ps has been detected earlier.[10]

In optical experiments on bulk GaAs a strong absorption of monochromatic light within 50 meV of the conduction band edge is observed below 150 K.[5,35] This near-band-edge absorption has been attributed to an unidentified point defect, but it is not associated with the *EL*2 defect.[5] Due to the spatial anticorrelation of E_g-50 meV absorption and the *EL*2 concentrations this absorption process is called the reverse contrast (RC). Other studies have shown that the defects giving rise to the RC absorption are the main nonradiative recombination centers in SI GaAs.[36] The present positron experiments indicate that the ionization level of the As vacancy is at about E_C-60 meV and that this level can be most efficiently populated with 1.4–1.5 eV light. This level can also be populated by the trapping of photoelectrons which is typical property of a recombination center. The concentration of V_{As} determined by positron experiments correlates with the magnitude of the RC absorption.[37] Therefore, it is natural to conclude that the near-band-edge absorption results from the photoinduced electron transitions from the valence band to the ionization level of the arsenic vacancy.

The optical cross section for the defect responsible for the RC absorption has been estimated to be $(1$–$7)\times10^{-15}$ cm^2.[37,38] Since we identify the RC absorption as the electron transfer from the valence band to V_{As} we can associate this cross section as σ_{p1}^0 in the notation of Sec. IV A 2. Using the ratios $\sigma_{p1}^0/\sigma_{n1}$, $\sigma_{p1}^0/\sigma_{\mathrm{p1}}$, and r/σ_{n1} obtained in that section, we get the following values: $\sigma_{n1}\approx10^{-19}$ cm^2, $r\approx3\times10^{-3}$ s^{-1}, and $\sigma_{p1}\approx10^{-24}$ cm^2 for the electron and hole capture cross sections and the total recombination rate at 15 K for the V_{As}. The estimate for r corresponds to the situation where *EL*2 is in the stable state. The value for σ_{n1} is reasonable compared to the electron capture cross section of the *EL*2 defect at the same temperature.[28]

In semi-insulating GaAs the *EL*2 defect is responsible for the compensation of the residual acceptor impurities. However, it has been verified that other unidentified intrinsic point defects also contribute to the compensation mechanism.[2] In this work we have shown that SI GaAs contains typically 10^{15}–10^{16} cm^{-3} Ga and As vacancies. Because these concentrations are comparable to those of the impurities and the *EL*2 defects, the native vacancies can have a role in the compensation of SI GaAs.

VII. CONCLUSIONS

We have performed positron lifetime and Doppler broadening measurements on semi-insulating GaAs in darkness and under photoexcitation. The possibilities of using monochromatic illumination together with positron spectroscopy have been examined by studying the excited charge states of vacancies in GaAs as a function of temperature ($T=15$–300 K), photon energy ($h\nu=0.6$–1.5 eV) and photon flux ($\phi=10^{12}$–10^{16} $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$). The technique is applied to study the elementary vacancies in GaAs and the correlation of their charge state under illumination to the metastability of the *EL*2 defect.

In the measurements in darkness the average positron lifetime is longer than in bulk GaAs and and it decreases strongly with temperature. The samples thus contain negatively charged native vacancies which we identify as gallium vacancies. Under illumination with photon energies 0.8–1.5 eV the average positron lifetime at 25 K increases compared to the values measured in darkness. This indicates that some vacancies are turned into more efficient positron traps by capturing electrons under illumination. The photoinduced vacancies are negative and they are identified as native arsenic vacancies. The $-/0$ ionization level of the As vacancies is determined to be at 60 ± 10 meV below the conduction band minimum.

Positron lifetime measurements as a function of the photon energy and the photon flux show that As vacancies can be populated by photoelectrons through two different optical processes depending on the metastability of the *EL*2 defect in GaAs. When the *EL*2 defect is in the stable state, photoelectrons excited to the conduction band in the optical ionization of the *EL*2 defect are partially trapped by the As vacancy. The As vacancy thus acts as a recombination center for the photoelectrons. When the *EL*2 defect is in the metastable state, another optical process converts the As vacancy to the negative charge state. In this case only photons with an energy close to the width of the band gap ($h\nu\geqslant1.35$ eV) are

able to excite electrons to the As vacancy. We associate this process with the direct transition of photoelectrons from the valence band to the ionization level of the As vacancy. This transition gives a microscopic explanation for the near-band-edge absorption seen in the previous optical experiments in undoped semi-insulating GaAs.[5,35]

The observed concentrations of the Ga and As vacancies are typically $(5–10)\times10^{15}$ cm^{-3}. This is roughly one order of magnitude less than the As vacancy concentrations observed in *n*-type GaAs,[10] but comparable to the concentrations of the residual impurities and of the *EL*2 defects in high-purity GaAs. The native Ga and As vacancies thus probably have a role also in the electrical compensation of undoped GaAs to highly resistive semi-insulating material.

It is concluded that photoexcitation enables the detection of vacancy defects which are otherwise inaccessible by positron spectroscopy due to their positive charge state. The positron experiments are able to yield new information on the photoexcited charge states of the As vacancies, e.g., the positions of their ionization levels in the band gap. Furthermore, the optical processes populating the excited charge states of the vacancy defects may be identified by positron lifetime measurements.

ACKNOWLEDGMENTS

We would like to thank J.-M. Spaeth, R. Fornari, Thomson SG and Outokumpu Semitronic for the samples, and R. M. Nieminen, J. Mäkinen, and M. J. Puska for the discussions.

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