Native Vacancies in Semi-Insulating GaAs Observed by Positron Lifetime Spectroscopy under Photoexcitation

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We have performed positron lifetime experiments under monochromatic illumination in undoped semi-insulating GaAs. A negative vacancy, identified as the Ga vacancy, is observed in darkness. Illumination with 1.42 eV photons below 150 K reveals another type of vacancy, identified as the As vacancy. The As vacancy has a negative charge state above the ionization level at 50 ± 5 meV below the conduction band. This level offers a microscopic explanation to the optical near-band-edge absorption. The concentrations of both Ga and As vacancies are between 10^{15} and 10^{16} cm^{-3}.

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The influence of intrinsic points defects on the electronic and optical properties of high-purity undoped GaAs is known to be particularly significant. The As-antisite-related *EL*2 defect which can compensate residual acceptors in undoped semi-insulating (SI) GaAs has been extensively studied [1]. However, the role of other elementary defects such as the Ga and As vacancies in undoped SI GaAs is unclear, because the identification of the defects has proved to be difficult.

Positron annihilation is a powerful method to study vacancies [2]. In *n*-type GaAs positron lifetime spectroscopy has revealed As vacancies at concentrations of 10^{17} cm^{-3} [3]. Positrons have also been found to be sensitive to the different charge states of the vacancy defects [3-5]. However, positive vacancies have so far escaped observation due to the Coulomb repulsion preventing positron annihilation at positive centers.

In this work we have developed a new technique to observe vacancies in excited charge states. In analogy with optical deep-level transient spectroscopy and electron paramagnetic resonance measurements under illumination, we have combined positron lifetime experiments with *in situ* monochromatic illumination. The technique is applied to study native vacancies in SI GaAs.

We report the first observation of two different native vacancies in SI GaAs. A negative vacancy, identified as the gallium vacancy, is observed in darkness. Another type of vacancy is revealed under illumination and identified as the As vacancy. It has an ionization level at 50 meV below the conduction band. When the level is occupied the vacancy is negative. This As vacancy level gives a microscopic explanation to the near-band-edge absorption [6]. The vacancy concentrations of 10^{15}-10^{16} cm^{-3} are close to those of residual impurities and *EL*2 defects, indicating that the native vacancies play a role also in the compensation of SI GaAs.

The positron lifetime experiments were performed in a conventional way with a time resolution of 230 ps (FWHM) [2-4]. The positron source was 30 μCi of ^{22}NaCl deposited on a 1.5 μm thick Al foil. About 2×10^6 counts were collected to each lifetime spectrum. The positron source was sandwiched between two identical sample pieces of $5\times5\times0.4$ mm^3. The sandwich was mounted in an optical cryostat allowing the illumination of the sample during the positron experiments at 20-300 K. The illumination was performed from both sides of the source-sample sandwich using two monochromators with identical photon fluxes. After subtracting positron annihilations in the source (210 ps with 5.4% and 450 ps with 1.9%), the lifetime spectra were analyzed with one or two exponential components. The average positron lifetime was calculated as $\tau_{\rm av} = \sum I_i \tau_i$ from the decomposed lifetimes τ_i and intensities I_i [2-4]. Three undoped SI GaAs samples grown by the liquid-encapsulated Czochralski method were studied. Their resistivities were 10^7-10^8 Ωcm and the *EL*2 concentrations were 4.6×10^{16} cm^{-3} (sample 1), 3.0×10^{16} cm^{-3} (sample 2), and 1.5×10^{16} cm^{-3} (sample 3).

Positrons get trapped at neutral or negative vacancies. The trapping rate κ is proportional to the vacancy concentration c by $\kappa = \mu c$, where μ is the positron trapping coefficient [2,7]. The electron density at vacancies is reduced compared to bulk and consequently the lifetime of trapped positrons is longer than that of free positrons. The increase of the average lifetime $\tau_{\rm av}$ above the free positron lifetime τ_b is thus a clear indication that vacancies exist in the sample. For negative vacancies this increase is magnified at low temperatures due to the strong increase of μ, whereas positron trapping at neutral vacancies is independent of temperature [7,8].

At 300 K the positron lifetimes in darkness vary from 231 to 233 ps in the three samples. These values are close to the lifetime $\tau_b = 231$ ps for free positrons in GaAs [3], which indicates that only a few vacancies are detected at room temperature. This is in good agreement with our earlier observations on as-grown SI GaAs [3,4].

When a sample is cooled down to low temperatures, the positron lifetime increases as shown for sample 1 in Fig. 1. The values at 20 K are 237, 239, and 231 ps in samples 1, 2, and 3, respectively. These lifetimes are clearly above the free positron lifetime of 228 ps at 20 K. The shape of the difference $\tau_{\rm av}(T) - \tau_b(T)$ is the same in all

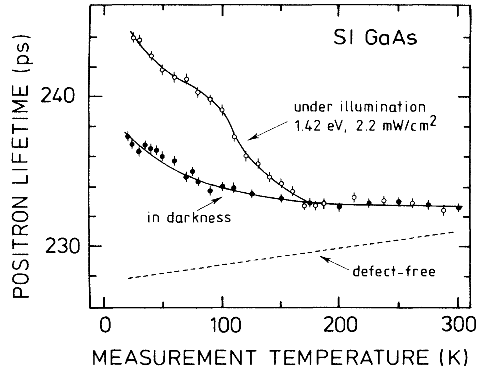

FIG. 1. Positron average lifetime as a function of measurement temperature in undoped semi-insulating GaAs sample 1. The figure shows the results obtained in darkness and under illumination with 1.42 eV photons at the intensity of 2.2 mW/cm^2. The free positron lifetime corresponding to defect-free material is indicated with the dashed line (Ref. [3]).

three samples. Hence, the increase of τ_{av} at low temperatures shows that the samples contain vacancy defects and that the charge of those defects is negative.

In samples 1 and 2 the lifetime spectra measured in darkness at 20-80 K can be decomposed into two components. The first lifetime is $\tau_1 = 150$-200 ps and the second component is $\tau_2 = 250$-260 ps with a typical intensity of 50%. The decompositions are in good agreement with the so-called one-defect trapping model [2], and the lifetime values τ_2 thus characterize the open volume of the defects present in the sample. The value of $\tau_2 = 250$-260 ps is typical for monovacancies in GaAs [3,4,9]. We can thus conclude that at low temperatures positrons detect negative vacancies in as-grown SI GaAs. No evidence of positron trapping around negative ions is observed, since no increase of τ_{av} due to thermal positron detrapping at 100-150 K is seen [10,11].

We identify the vacancies assuming that they are isolated and using their negative charge as a fingerprint. In thermal equilibrium, the Fermi level stays at midgap in SI GaAs at all temperatures. According to theoretical calculations As vacancies are positive and Ga vacancies are negative in SI GaAs [12]. Since positrons repel positive defects [7], Ga vacancies are the only candidates responsible for positron trapping.

The concentration of the Ga vacancies can be determined from the average positron lifetime using the one-defect trapping model [2-4]. In electron-irradiated GaAs the positron trapping coefficient of $\mu = 1.4\times10^{15}$ s^{-1} has been estimated for negative Ga vacancies at 300 K [11]. The scaling of this trapping coefficient with the temperature dependence determined from Fig. 1 yields a value of $\mu = 1.5\times10^{16}$ s^{-1} at 20 K. From the positron trapping rates calculated in the one-defect trapping model [2], we get the Ga vacancy concentrations of 5×10^{15} cm^{-3} for sample 1, 7×10^{15} cm^{-3} for sample 2, and 1×10^{15} cm^{-3} for sample 3.

To summarize, positrons detect negative vacancies in undoped SI GaAs, when the experiment is performed in darkness. Because of their negative charge, the defects are identified as Ga vacancies or complexes involving V_{Ga}. Their concentration in SI GaAs is typically $(1$-$7)\times10^{15}$ cm^{-3}.

The positron lifetime results under illumination in sample 1 can be seen in Fig. 1. The data in Fig. 1 show clearly that the positron average lifetime increases under illumination compared to the values in darkness. The amount of the increase at 20 K is 7 ps in sample 1, 4 ps in sample 2, and less than 1 ps in sample 3. The data in Fig. 1 show further that the effect of illumination becomes smaller when temperature increases, until it finally disappears above 180 K.

The increase of τ_{av} under illumination is most effective at the photon energies of 1.4-1.5 eV. This 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} under illumination (Fig. 1) does not have the well-known metastability of *EL*2 [1,13], which further indicates that the effect is not linked to the *EL*2 defect.

The 1.42 eV illumination effects have been investigated further in sample 1 as functions of the light intensity (0-5 mW/cm^2) and temperature (20-300 K). Up to the intensity of 5 μW/cm^2 there is no effect. At higher intensity, the behavior of positron lifetime depends on temperature. At 20-70 K, positron lifetime increases monotonically as a function of the light intensity in the range 5-30 μW/cm^2, whereafter it saturates. The saturation value of τ_{av} depends on temperature. For example, at 20 K, τ_{av} increases from 237 to 244 ps at 5-30 μW/cm^2 and remains at 244 ps at higher intensities up to 5 mW/cm^2. Above 100 K, positron lifetime increases with the light intensity, but shows no saturation in the range of $I = 0$-5 mW/cm^2. For the highest intensity of $I = 5$ mW/cm^2, the illumination effect can be induced up to 180 K.

The lifetime spectra measured under illumination can be decomposed into two components. The values of τ_2 are scattered between 250 and 265 ps. No temperature dependence of τ_2 is seen in the range 20-200 K. The decompositions are in good agreement with the one-defect trapping model [2]. This means that all positron traps present in the sample induce the same lifetime, and the defects trapping positrons under illumination can be characterized with the value $\tau_2 = 255 \pm 5$ ps. There is no evidence of positron trapping at negative ions. The value of $\tau_2 = 255 \pm 5$ ps is typical for monovacancies in GaAs [3,4,9].

The increase of positron average lifetime under illumination shows that more positron trapping at vacancies takes place than in darkness. This means that some vacancies are converted to more efficient positron traps by capturing electrons under illumination. In a semi-insulating sample, the ionization levels of the vacancies located below the midgap are occupied by electrons. The levels populated under illumination are thus located above the midgap. As mentioned above, no ionization levels are expected in the upper half part of the gap for Ga vacancies, whereas they are expected for As vacancies. It is thus natural to identify the defects seen under illumination to As vacancies or complexes related to the As vacancies.

The positron trapping rate at the As vacancies can be calculated from the lifetime data under illumination using the positron trapping model [2]. At the temperature range 20–70 K, the positron trapping rate increases as a function of the 1.42 eV light intensity from 5 to 30 μW/cm^2, whereafter it saturates at a value independent of the intensity. This behavior shows that for the intensities greater than 30 μW/cm^2, the occupation of the vacancy ionization levels under illumination is entirely determined by the optical transitions. At the temperature range 20–70 K (see Fig. 1), the saturation value of τ_{av} and correspondingly the positron trapping rate decrease as temperature increases. This behavior is similar to that obtained for the Ga vacancies in darkness, and it is a clear indication of the negative charge of the vacancies. Thus we conclude that the As vacancies revealed under illumination are in a negative charge state.

Arsenic vacancies have been previously detected by positron lifetime spectroscopy in *n*-type GaAs [4,5]. Positron lifetimes of 257 and 295 ps have been determined for negative and neutral charge states of V_{As}, respectively [4,5]. In this work, both under illumination and in darkness the positron lifetimes fall in the range of $\tau_2 = 255 \pm 5$ ps. No indications of the longer lifetime 295 ps are found, and the experiments are thus consistent with the conclusion that the As vacancies are negatively charged.

Above 70 K, the positron trapping rate depends on the light intensity and its temperature dependence becomes much steeper than for a negative vacancy. To investigate this steep part in more detail, we calculate the concentration of photoinduced negative As vacancies as a function of measurement temperature for different 1.42 eV illumination intensities. We assume that the positron trapping at the Ga vacancies remains the same as in darkness. For both negative V_{Ga} and V_{As} we use the same temperature-dependent value of $\mu(T)$ obtained from the $\tau_{av}(T)$ curve measured in darkness (Fig. 1) and scaled to the value of $\mu = 1.4 \times 10^{15}$ s^{-1} at 300 K [11]. The concentration of V_{As}^- for sample 1 is shown in Fig. 2. At low temperatures of 20–70 K the concentration of the negative As vacancies is independent of the light intensity and saturates at the value of $[V_{As}^-] = 1.3 \times 10^{16}$ cm^{-3}. Above 70 K, $[V_{As}^-]$ decreases, until above 150 K the vacancies are no longer detected. The relation between the light intensity and the decrease of $[V_{As}^-]$ is clear: The stronger the photon flux, the higher the temperature needed to decrease the vacancy concentration from the plateau value. This type of behavior shows that at $T > 70$ K the thermally activated emission of electrons from the As vacancy ionization level to the conduction band starts to compete with the optical transitions. The spontaneous electron emission rate is $g_e = c_e \gamma N_c(T) \exp(-E_d/kT)$, where $c_e = \sigma_e v_e$ is the electron capture coefficient, v_e is the electron thermal velocity, γ is the degeneracy factor of the ionization level, $N_c(T)$ is the effective density of states of the conduction band, and E_d is the ionization energy to the conduction band [14].

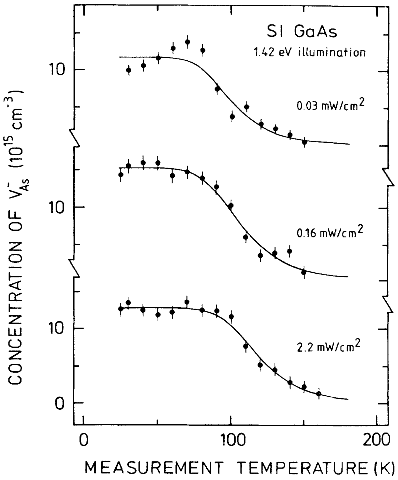

FIG. 2. The measured concentration of negative As vacancies as a function of temperature. The experiments have been performed under illumination with 1.42 eV photons and using the three different light intensities shown in the figure. The solid lines are fits of Eq. (1) with the ionization level of As vacancies located at 50 ± 5 meV below the conduction band.

We can analyze the data in Fig. 2 by assuming that the concentration of V_{As}^- above 70 K is controlled by the electron emission g_e from the ionization level and the optical transitions between the bands and the vacancy level. Assuming further that the electron capture cross section σ_e is independent of temperature, we can write the fraction of negative vacancies as

$$[V_{As}^-]/[V_{As}] = A/[1 + B\Phi^{-1} v_e(T) N_c(T) \exp(-E_d/kT)] , \tag{1}$$

where A and B are constants and Φ is the photon flux. The expression (1) is independent of the number of ionization levels in the gap, and it assumes that the thermal electron emission occurs only from the highest level of V_{As}. In the simple case of one ionization level we have $A = (1 + \sigma_e^0/\sigma_h^0)^{-1}$ and $B = A\gamma\sigma_e/\sigma_h^0$, where σ_e^0 and σ_h^0 are the optical electron and hole generation cross sections of the ionization level, respectively.

The solid lines in Fig. 2 are the fits of Eq. (1) to the experimental data with the ionization energy E_d and the constants A and B as free parameters. The fitted functions reproduce well the trends observed in the data: When the intensity increases, the decrease of $[V_{As}^-]/[V_{As}]$ from the saturation level is shifted to higher temperatures and takes place over a wider range of temperature. The fitted ionization energy for sample 1 in Fig. 2 is $E_d = 55 \pm 5$ meV. The same analysis gives $E_d = 49 \pm 5$ meV for sample 2.

The observed thermal ionization energy of $E_d = 50$ meV is much smaller than the band gap (1.52 eV at 20 K) or the photon energy of 1.42 eV used to populate the $V_{\rm As}^-$ state in this work. For such a case, the optical cross section σ_e^o is usually very small, because the defect level and the conduction band do not overlap effectively in k space [15,16]. Taking $\sigma_e^o \ll \sigma_h^o$ [$A \approx 1$ in Eq. (1)] the observed concentration of $[V_{\rm As}^-] \approx 10^{16}$ cm^{-3} becomes the *total* concentration of As vacancies. Hence, the experiments in this work show that the concentration of As vacancies in semi-insulating GaAs is typically 10^{16} cm^{-3}.

Positron lifetime spectroscopy has earlier revealed native As vacancies in n-type GaAs at the concentration of $(5\text{–}10)\times 10^{16}$ cm^{-3} [3]. This concentration is by a factor of 5–10 larger than the values estimated above for SI GaAs. Further, the As vacancies n-type GaAs have $- \rightarrow 0$ ionization level at $E_c - 30$ meV and $0 \rightarrow +$ level at $E_c - 140$ meV [3]. Thus our finding that $V_{\rm As}$ is negative above $E_c - 50$ meV is in perfect agreement with the previous results in n-type GaAs. However, in Fig. 2 we see no evidence of positron trapping below $E_c - 50$ meV. This can be understood as the positron trapping coefficient at $T \approx 100$ K is an order of magnitude lower at a neutral vacancy than at a negative one [5,7].

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 [6,17]. This near-band-edge absorption has been attributed to an unidentified point defect center, but it is not associated to the $EL2$ defect [6]. The present positron experiments indicate that the ionization level of the As vacancy is situated close to the conduction band at about $E_c - 50$ meV and further that this level can be most effectively populated using 1.4–1.5 eV light. Therefore, our results provide a natural explanation for the near-band-edge absorption in GaAs: It results from the photoinduced electron transition from the valence band to the ionization level of the arsenic vacancy.

In semi-insulating GaAs the $EL2$ 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 [18]. In this work, we have shown that SI GaAs contains typically $10^{15}\text{–}10^{16}$ cm^{-3} Ga and As vacancies. Because these vacancy concentrations are comparable to those of impurities and $EL2$ defects, the native vacancies have a role in the compensation of SI GaAs.

To conclude, we have performed positron lifetime experiments on SI GaAs in darkness and under photoexcitation. A negative vacancy, identified as the Ga vacancy, is observed in darkness. Another type of vacancy is revealed by its photoexcited negative charge state under 1.42 eV illumination. The vacancy has an ionization level at $E_d = 50 \pm 5$ meV below the conduction band, and it is identified as the As vacancy. We further suggest that the As vacancy is responsible for the near-band-edge absorption seen in the earlier optical experiments [6,17]. The concentrations of both Ga and As vacancies in our samples fall typically in the range of $(5\text{–}10)\times 10^{15}$ cm^{-3}. This is roughly 1 order of magnitude less than our previous results of the As vacancy concentration in n-type GaAs [3], but comparable to the concentrations of residual impurities and $EL2$ defects in high-purity GaAs.

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[1] G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), Chap. 6.

[2] *Positrons in Solids*, edited by P. Hautojärvi, Topics in Current Physics Vol. 12 (Springer-Verlag, Heidelberg, 1979); *Positron Solid State Physics*, edited by W. Brandt and A. Dupasquier (North-Holland, Amsterdam, 1983).

[3] K. Saarinen, P. Hautojärvi, P. Lanki, and C. Corbel, Phys. Rev. B **44**, 10585 (1991).

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

[5] J. Mäkinen, P. Hautojärvi, and C. Corbel, J. Phys. Condens. Matter **4**, 5137 (1992).

[6] S. Tüzemen and M. R. Brozel, Appl. Surf. Sci. **50**, 395 (1991).

[7] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 10632 (1990).

[8] J. Mäkinen, C. Corbel, P. Hautojärvi, P. Moser, and F. Pierre, Phys. Rev. B **39**, 10162 (1989).

[9] M. J. Puska and C. Corbel, Phys. Rev. B **38**, 9874 (1988); K. Laasonen, M. Alatalo, M. J. Puska, and R. M. Nieminen, J. Phys. Condens. Matter **3**, 7217 (1991).

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

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

[12] G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985); M. Puska, J. Phys. Condens. Matter **1**, 7347 (1989); H. Xu and W. Lindefelt, Phys. Rev. B **41**, 5975 (1990).

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

[14] J. Bourgoin and M. Lannoo, *Point Defects in Semiconductors II* (Springer, Heidelberg, 1983), Chap. 6.

[15] J. I. Pankove, *Optical Processes in Semiconductors* (Prentice-Hall, Engelwood Cliffs, 1971), pp. 62–66.

[16] B. K. Ridley, *Quantum Processes in Semiconductors* (Clarendon, Oxford, 1988), pp. 200–202.

[17] J. Jiménez, A. Alvárez, J. Bonnafé, and L. I. Murin, Phys. Rev. B **39**, 13310 (1989).

[18] B. K. Meyer, K. Kambrock, D. M. Hofmann, and J.-M. Spaeth, in *Defect Control in Semiconductors*, edited by K. Sumino (Elsevier, Amsterdam, 1990).