

Microscopic nature of thermally stimulated current and electrical compensation in semi-insulating GaAs

S. Kuisma,^{a)} K. Saarinen, and P. Hautojärvi

Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

Z.-Q. Fang and D. Look

Physics Department, Wright State University, Dayton, Ohio 45435

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In this work undoped semi-insulating (SI) GaAs grown by vertical gradient freeze and liquid encapsulated Czochralski methods was studied by near-infrared absorption (NIRA), thermally stimulated current (TSC) and positron annihilation techniques. The positron experiments reveal both gallium and arsenic vacancies, as well as gallium and arsenic antisites, in the samples. By comparing the results from the TSC and positron measurements, the following relations are found in the defect concentrations: trap T_2 correlates with the arsenic antisite and trap T_5 with the arsenic vacancy. The ionized fraction of the arsenic-antisite-related $EL2$ defect is obtained from NIRA measurements. The positive charge of these ionized $EL2$ defects correlates with the net negative charge, $3[V_{Ga}^{3-}] + 2[Ga_{As}^{2-}] - [V_{As}^+]$, related to the gallium vacancies and antisites and arsenic vacancies detected in positron measurements. The intrinsic defects may thus contribute significantly to the electrical compensation in SI GaAs. © 1997 American Institute of Physics. [S0021-8979(97)01008-6]

I. INTRODUCTION

Undoped semi-insulating (SI) GaAs has been studied extensively due to its technological significance. The native arsenic-antisite-related donor $EL2$ ¹ mainly controls the semi-insulating properties of undoped SI GaAs. Impurities like carbon are known to play a role in compensation as well, and more and more evidence indicates that other native defects, such as the gallium antisite defect Ga_{As} and the gallium and arsenic vacancies, exist in SI GaAs and contribute to electrical compensation and carrier recombination.²

The conventional optical and electrical measurements give mostly indirect information about the atomic structure of defects in semiconductors. For example, DLTS (deep level transient spectroscopy) and TSC (thermally stimulated current) techniques give information on activation energies and capture cross sections of carrier traps. Defects can be characterized by these properties, but the actual identification is not straightforward.

In earlier TSC measurements it has been observed that the activation energy of the dark conductivity in undoped SI GaAs is usually dominated by one of three different centers; their activation energies are 0.75 eV, 0.42 eV, and 0.15 eV. The defect related to the activation energy of 0.75 eV has been associated to the $EL2$ defect, but the origin of the other levels is not clear.

In this work, in addition to TSC measurements, as-grown GaAs samples were studied by positron annihilation spectroscopy. Positrons are sensitive to vacancy defects and negative ions in semiconductors, and it is possible to distinguish between the signals arising from these different defects. In as-grown SI GaAs, defects related to the Ga and As vacancies, as well as to As_{Ga} and Ga_{As} antisites, have been

observed in positron studies.³⁻⁶ It is interesting to note that positron experiments have revealed ionization levels ($-/0$) at $E_C - 0.05$ eV and ($0/+$) at $E_C - 0.14$ eV for the As vacancy, whereas a carrier trap with a similar activation energy of 0.15 eV has been found by TSC. Positron spectroscopy may thus provide an atomic scale identification of the defects detected in TSC measurements.

Only some years ago it was assumed that the deep donor $EL2$ was the only intrinsic defect taking part in the electrical compensation of undoped GaAs. When the purity of undoped GaAs was improved, it was realized that the low impurity concentrations by themselves no longer explained compensation, and other intrinsic defects had to be included in more realistic compensation models. In this work electrical compensation is studied by comparing the defect concentrations obtained from positron results to the acceptor concentrations from near-infrared absorption measurements.

The effect of growth method on the nature and concentration of the point defects will also be studied, since the TSC experiments have revealed different traps in SI GaAs materials grown either by the vertical gradient freeze (VGF) or the high and low pressure Czochralski techniques (HP-LEC or LP-LEC).

II. EXPERIMENTAL METHODS

A. Electrical and optical measurements

In the thermally stimulated current method the sample being studied is cooled down to low temperature in darkness. After a long enough illumination time to completely fill the electron traps or to reach a steady state under illumination, the illumination is turned off, and the sample is heated at a linear rate β in the dark. The measured current contains a component contributed by the carriers thermally emitted from the traps. The maxima of the current as functions of the

^{a)}Electronic mail: sirpa.kuisma@hut.fi

temperature depend on the energies of the individual traps, E_T , and on their carrier capture cross sections, σ_T . The concentration of a particular trap is proportional to the area of the current peak associated with it.

In this work the samples were cooled down with liquid nitrogen to temperatures of about 80 K in a Bio-Rad DL4600 system, and 1.45-eV illumination was used to fill the traps. Since the linear heating rate affects the temperatures at which the current maxima occur, various linear heating rates were used. Based on a theoretical analysis,⁷ the trap specific parameters E_T and σ_T were calculated from

$$E_T/k_B T_m = \ln(T_m^4/\beta) + \ln(1.7 \times 10^{16} \sigma_T/E_T), \quad (1)$$

where T_m is the temperature of the current maximum and k_B Boltzmann's constant. An Arrhenius plot of $\ln(T_m^4/\beta)$ vs $1/T_m$ can be used to obtain E_T and σ_T .

The concentration of a certain trap, N_T , can be estimated from the peak area A , i.e., from the total charge released by the trap

$$N_T = A/eVG, \quad (2)$$

where e is the electron charge, V volume of the sample, and G the photoconductivity gain.⁸ To determine G , the photocurrent was measured at 83 K < T < 300 K under a weak 1.13-eV illumination with a photon flux of $3.3 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$.

To study the electrical compensation in GaAs, near-infrared absorption (NIRA) measurements were conducted at room temperature. The native $EL2$ defect dominates the infrared absorption in as-grown undoped SI GaAs at photon energies 0.7–1.4 eV. For these photon energies the absorption coefficient is $\alpha = N_{EL2}[f\sigma_n + (1-f)\sigma_p]$, where N_{EL2} is the total concentration of $EL2$ and f is the occupation number of $EL2$. The quantities σ_n and σ_p are the electron and hole photoionization cross sections of $EL2$, and their photon energy dependencies are known.⁹

By measuring the IR absorption at room temperature for two photon energies, both the total concentration of $EL2$ and the ionized fraction can be determined.¹⁰ Being the dominant donor defect close to the Fermi level in SI GaAs, the ionized fraction of $EL2$, i.e., the concentration of $EL2^+$, is equal to the net negative charge related to the other defects in SI material: $[EL2^+] = \sum_i |q_i| [A_i^-] - \sum_j |q_j| [D_j^+]$, where the acceptors A_i (charge q_i) and donors D_j (charge q_j) have their ionization levels far below or above the Fermi level. In this work absorption was measured at three photon energies: 0.7, 1.03, and 1.13 eV. The absorption at 0.7 eV is not related to $EL2$,¹ and it was used for normalization.

B. Positron annihilation

In this work the positron lifetime experiments were performed in a conventional way.¹¹ Two identical sample pieces were sandwiched with a 30 μCi positron source. The time differences between the 1.275-MeV gamma emitted simultaneously with the positron in the β^+ decay and the annihilation gamma were recorded with a fast-fast lifetime spectrometer. The positron source was carrier-free $^{22}\text{NaCl}$ deposited on a 1.5 μm thick Al foil. The sample sandwich was mounted in an optical cryostat which enabled illumination of

the samples before or during the measurements. The cryostat was cooled with a closed-cycle He cryocooler, and it was possible to make measurements between 20 and 300 K. The illuminations were performed with monochromatic light obtained from a 250 W halogen lamp via a monochromator. Details of the experimental set-up can be found in Ref. 4.

Time resolution of the lifetime spectrometer was 240 ps (FWHM), and 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 material, the measured positron lifetime spectrum was analyzed with one or two exponential components

$$n(t) = n_0 [I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)] \quad (3)$$

convoluted with the Gaussian resolution function of the spectrometer. Here n_0 is the total number of annihilation events and I_i the intensity of the decay mode with positron lifetime τ_i . The average positron lifetime is defined by

$$\tau_{av} = I_1 \tau_1 + I_2 \tau_2. \quad (4)$$

The average lifetime is insensitive to the decomposition procedure and coincides with the center of mass of the lifetime spectrum.

In a perfect semiconductor crystal positrons are delocalized in the lattice and annihilate with a free positron lifetime τ_b . If there are vacancy defects present in the material, positrons get trapped to localized states at neutral and negative vacancies.¹² In vacancies the electron density is lower than in the bulk, and thus positrons annihilate with a longer lifetime τ_v . The lifetime τ_v can be used to identify vacancies with different open volumes.

Positrons can also get trapped at Rydberg states around negative ions: this enables the detection of negative-ion-type defects in semiconductor materials. These negative ions are shallow traps for positrons, since the binding energy for positrons is less than 0.1 eV. At higher temperatures positrons start to thermally escape from the Rydberg states,¹³ e.g., in GaAs the thermal escape begins at 100 K.¹⁴ Positrons trapped at negative ions annihilate with the same lifetime as free positrons.¹⁴

Concentrations of the defects trapping positrons can be estimated from the trapping rate κ which is proportional to the defect concentration c , $\kappa = c\mu/N$. Here μ is the defect specific trapping coefficient, and N is the atomic density of the material. For neutral vacancies μ_v is temperature independent, and its value is typically 10^{15} s^{-1} .¹⁵ For negative vacancies μ_v is roughly $2 \times 10^{15} \text{ s}^{-1}$ at 300 K, and it increases by an order of magnitude when temperature decreases to 20 K.^{6,12,15} The trapping coefficient at positive vacancies is several orders of magnitude smaller because of the Coulombic repulsion and, consequently, no trapping at positive vacancies occurs before the positron annihilates.

According to the trapping model,¹⁶ the average positron lifetime is a superposition of the free positron lifetime, the lifetimes at vacancy defects i and lifetime at the Rydberg states around negative ions $\tau_{st} = \tau_b$

$$\tau_{av} = \eta_b \tau_b + \sum_{i=1}^k \eta_{vi} \tau_{vi} + \eta_{st} \tau_b, \quad (5)$$

TABLE I. Total $EL2$, neutral $EL2^\circ$, and ionized $EL2^+$ concentrations determined from NIRA results and presented in units of 10^{15} cm^{-3} . Relative accuracy of the concentrations is 10%.

| Sample | $[EL2]$ | $[EL2^\circ]$ | $[EL2^+]$ |
|--------|---------|---------------|-----------|
| VGF | 14 | 13 | 1.1 |
| HP-LEC | 17 | 15 | 1.9 |
| LP-LEC | 13 | 10 | 2.9 |

where η_b , η_{vi} , and η_{st} are the fractions of positrons annihilating in the defect-free bulk, at vacancies and at the negative ions. In practice, positron trapping can be detected by measuring the average positron lifetime τ_{av} . The increase in τ_{av} above τ_b is a clear indication of vacancy defects in the sample. If the vacancies are negative, the trapping is enhanced at low temperatures, and the average lifetime increases as temperature decreases. The trapping fractions η can be expressed in terms of positron trapping rates which can be calculated from the average positron lifetime. If there are both vacancies and negative ions present in the sample, the positron trapping rates at both these defects can be determined by measuring the average lifetime as a function of temperature.^{17,18}

C. Samples

In this work semi-insulating undoped VGF, LP-LEC, and HP-LEC GaAs materials were studied. The VGF GaAs samples were cut from wafers manufactured by American Xtal Technology, and the HP-LEC and LP-LEC samples were from Freiburger and Texas Instruments, respectively. Materials grown by these three techniques generally differ in the following aspects: the $EL2$ concentration, which is mainly controlled by the melt stoichiometry and the pressure in the puller; the dislocation density, which is dependent on the temperature gradient at the solid-liquid interface; and the thermal history experienced by the GaAs ingot after crystal growth, either in the growth chamber or during additional post-growth annealing. These post-growth annealings can strongly affect the formation of point defects and the uniformity of the electrical properties of the ingot. Usually VGF GaAs has much lower dislocation density and lower $EL2$ concentration than the more As-rich LEC material. The carbon concentrations of these samples are in the range of $10^{14} - 10^{15} \text{ cm}^{-3}$.

The size of the samples was $6 \times 6 \times 0.6 \text{ mm}^3$. Four indium contacts on the corners, alloyed at 425°C for a few minutes in forming gas, were used in the TSC measurements. Positron measurements required two identical samples, and two adjacent samples cut from the same wafer were used.

III. RESULTS OF THE OPTICAL AND ELECTRICAL MEASUREMENTS

From the near-infrared absorption the total concentration of the native $EL2$ defect as well as the ionized fraction of $EL2$ can be determined. In the SI GaAs samples studied here, the $EL2$ concentrations were approximately $1.5 \times 10^{16} \text{ cm}^{-3}$, and the ionized fraction was roughly 15%. The results are presented in Table I.

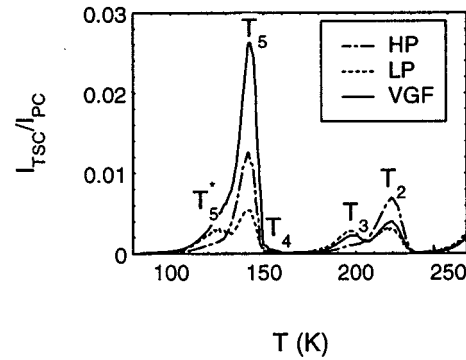


FIG. 1. Normalized thermally stimulated current as a function of temperature in the VGF, LP-LEC, and HP-LEC SI GaAs samples. The heating rate was 0.3 K/s .

The thermally stimulated current measurements of these samples revealed at least six traps: T_2 at 220 K , T_3 at 200 K , T_4 at 155 K , T_5 at 140 K , T_5^* at 123 K , and T_6^* at 93 K ($\beta = 0.3 \text{ K/s}$). The current peak heights were quite different for these traps, indicating different defect concentrations. Above 240 K the TSC signal is due to the dark current with the activation energy of 0.77 eV , indicating control by $EL2$.

The TSC spectra were measured with various heating rates β , and the average trap depth E_T and capture cross section σ_T for the traps were calculated with Eq. (1): 0.63 eV and $1.9 \times 10^{-13} \text{ cm}^2$ for T_2 , 0.50 eV and $1.1 \times 10^{-13} \text{ cm}^2$ for T_3 , 0.35 eV and $1.9 \times 10^{-14} \text{ cm}^2$ for T_5 , and 0.15 eV and $1.8 \times 10^{-17} \text{ cm}^2$ for T_6^* . The data for trap T_6^* are actually obtained from 1 MeV electron-irradiated HP-LEC GaAs, since the peak height of T_6^* was quite low in the as-grown material. Properties of the traps T_2 , T_5 , and T_6^* are further discussed in Sec. V.

To estimate the concentrations of the traps, the TSC results have to be normalized with the photocurrent measured under 1.13-eV illumination. The normalized thermally stimulated current (NTSC) spectra of the samples are presented in Fig. 1. The normalization can affect the relative peak heights of the TSC spectrum rather drastically; e.g., trap T_6^* seems dominant in the TSC spectrum (not shown), but it almost vanishes in the NTSC spectrum (Fig. 1). Concentrations of the traps were estimated by the total charge being released from the trap [Eq. (2)], and they are presented in Table II.

The photocurrent measured under 1.13-eV illumination decreased as a function of temperature and showed two activation energies: 79 meV for $T > 135 \text{ K}$ and approximately

TABLE II. Concentrations of traps T_2 , T_3 , T_5 , and T_6^* determined from TCS results and presented in units of 10^{15} cm^{-3} . Relative accuracy of the concentrations is 10%.

| Sample | $[T_2]$ | $[T_3]$ | $[T_5]$ | $[T_6^*]$ |
|--------|---------|---------|---------|-----------|
| VGF | 1.5 | 0.61 | 4.4 | |
| HP-LEC | 2.5 | 0.27 | 2.4 | |
| LP-LEC | 1.0 | 0.78 | 1.1 | < 0.3 |

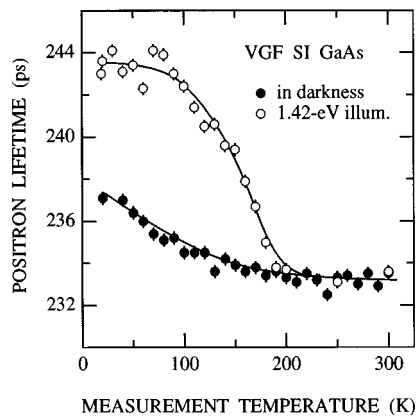


FIG. 2. The average positron lifetime as a function of the measurement temperature in VGF SI GaAs. The solid circles indicate the values in darkness and the open circles the average lifetime under 1.42-eV illumination.

55 meV for $T < 135$ K. The activation energy of 79 meV is close to the thermal activation energy of the electron capture cross section for $EL2$.¹⁹ However, it seems that at temperatures lower than 135 K another carrier lifetime mechanism dominates the photocurrent.

IV. POSITRON RESULTS

A. Gallium vacancies and antisites

When the average positron lifetime was measured in darkness at 300 K, the value was about 2 ps above the free positron lifetime $\tau_b = 231$ ps in all the samples of this study. In VGF GaAs the average positron lifetime increased monotonously as temperature decreased (Fig. 2). In HP-LEC GaAs the average positron lifetime was almost independent of temperature; a slight increase in τ_{av} took place at $T < 80$ K, and at $T = 80$ –100 K there was a local minimum in the average positron lifetime (see Fig. 3). The same features could be more clearly observed in the data obtained in LP-LEC GaAs, where the minimum of τ_{av} was situated at $T = 50$ K, and the increase in the average positron lifetime

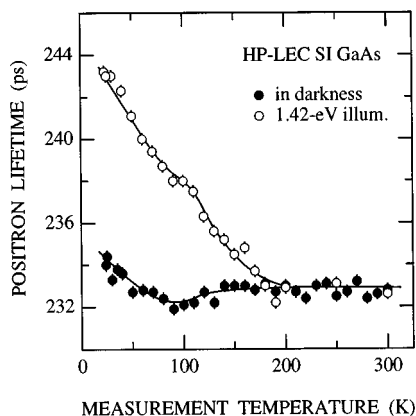


FIG. 3. The average positron lifetime as a function of the measurement temperature in HP-LEC SI GaAs. The solid circles indicate the values in darkness and the open circles the average lifetime under 1.42-eV illumination.

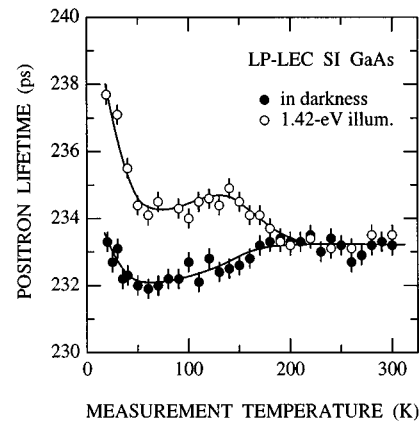


FIG. 4. The average positron lifetime as a function of the measurement temperature in LP-LEC SI GaAs. The solid circles indicate the values in darkness and the open circles the average lifetime under 1.42-eV illumination.

continued up to 180 K (Fig. 4). The lifetime spectra measured in the VGF GaAs sample can be decomposed into two components: the longer lifetime component is $\tau_2 = 250 \pm 10$ ps. In LP-LEC and HP-LEC GaAs samples the decomposition of the lifetime spectrum is not feasible at any temperature.

The decompositions of the lifetime spectra follow the trends discussed in detail in Ref. 6. When the average positron lifetime increases monotonously as temperature decreases like in the VGF GaAs sample (Fig. 2), the decomposition is feasible for the spectra measured at $20 \text{ K} < T < 300 \text{ K}$. It is most reliable at low temperatures where the increase in τ_{av} is largest.⁶ When there is a local minimum in the average lifetime at $T \approx 50$ K like in the HP-LEC and LP-LEC GaAs samples (Figs. 3 and 4), the decomposition is more difficult and possible only for some data measured at $T > 150$ K.⁶ In both these cases, however, the longer lifetime component is the same, $\tau_2 \approx 260$ ps. Similarly as in Ref. 6, it can be concluded that the lifetime component $\tau_2 \approx 260$ ps is present in all the samples and remains constant as a function of temperature.

The data in the VGF sample show that positron trapping at vacancies in SI GaAs is enhanced at low temperatures. Since the Fermi level stays near midgap in SI GaAs, the equilibrium charge states of different defects do not change as functions of temperature. The fact that positron trapping increases at low temperatures, while the concentration of vacancies trapping positrons is constant, shows that the vacancies trapping positrons are negative.^{3,4,12} The value $\tau_v = \tau_2 \approx 260$ ps indicates that the vacancies are monovacancies.

According to calculations,²⁰ the ionization levels of arsenic vacancies in GaAs are in the upper half of the energy gap, and as they are unoccupied in SI GaAs, the arsenic vacancies are positively charged. Ga vacancies are negative in SI GaAs, since their ionization levels are near the valence band maximum.²⁰ Thus the vacancies observed in darkness in VGF GaAs are negative Ga vacancies or V_{Ga} -related complexes.

TABLE III. Positron trapping rates at Ga vacancies, Ga antisites, As vacancies and As antisites presented in units of 10^9 s^{-1} . Relative accuracy of the trapping rates is 10%.

| Sample | $\kappa(V_{\text{Ga}})$ 300 K | $\kappa(\text{Ga}_{\text{As}})$ 30 K | $\kappa(V_{\text{As}})$ 80 K | $\kappa(\text{As}_{\text{Ga}})$ 30 K |
|--------|----------------------------------|---|---------------------------------|---|
| VGF | 0.35 | 5.7 | 6 | 10 |
| HP-LEC | 0.29 | 16 | 5 | 12 |
| LP-LEC | 0.38 | 29 | 2 | 6.5 |

In the LEC GaAs samples the average positron lifetime at room temperature is 233 ps indicating that some trapping at vacancies takes place. When temperature decreases the average lifetime remains constant to $T \approx 180 \text{ K}$, and then it decreases until a local minimum is reached. This temperature dependence of τ_{av} indicates that positrons are trapped both at shallow traps and at vacancies in the LEC GaAs sample.

At these shallow traps the positron lifetime is the same as in defect free bulk, i.e., $\tau_{\text{st}} = \tau_b$, and the increase in positron lifetime at $50 \text{ K} < T < 180 \text{ K}$ is due to the thermal detrapping of positrons from the shallow traps, where the binding energy for positrons is roughly 50 meV.^{13,14} The detrapped positrons are able to get trapped at vacancies, and the average lifetime increases. Also at temperatures $T < 50 \text{ K}$ the average lifetime increases, indicating that the vacancies are able to compete with the negative shallow traps for trapping positrons. The vacancies in LEC GaAs samples are thus negative as in VGF GaAs. Similarly, they are attributed to Ga vacancies or V_{Ga} -related complexes.

The shallow positron traps in LEC GaAs samples are negatively charged intrinsic defects which do not have open volume. According to calculations,²⁰ gallium antisites are the only intrinsic ion-type defects which are negative in SI GaAs. Positron lifetime experiments thus reveal negative gallium antisites or defects related to Ga_{As} in LEC GaAs.

The concentrations of Ga vacancies in these samples can be estimated by calculating the positron trapping rates at 300 K. At room temperature the possible negative ions do not trap positrons, and thus the trapping is due to Ga vacancies. The positron trapping rate at Ga vacancies can be estimated with Eq. (5) since the free positron lifetime ($\tau_b = 231 \text{ ps}$ at 300 K), positron lifetime at the Ga vacancy ($\tau_v = 260 \text{ ps}$), and the average lifetime in darkness are known.^{4,6} The results are presented in Table III. The positron trapping rates at gallium vacancies, and thus the vacancy concentrations, are practically the same in all the samples.

The temperature dependence of the trapping coefficient $\mu(V_{\text{Ga}})$ has been determined earlier.^{4,6} This temperature dependence can be used to calculate the trapping rate $\kappa(V_{\text{Ga}}, 30 \text{ K})$, and, consequently, the trapping rate at negative ions at 30 K can be estimated using the trapping model, where Ga vacancies and negative ions are taken into account as positron traps. The trapping rates at negative ions at 30 K are presented in Table III. The positron trapping rate at Ga antisites is clearly smaller in the VGF GaAs than in the two LEC GaAs samples.

Concentrations of Ga vacancies and Ga antisites can be compared when the positron trapping coefficient is taken into account: the factor κ_v/μ_v is proportional to the defect con-

centration. For Ga vacancies the trapping coefficient is $\mu(V_{\text{Ga}}, 300 \text{ K}) = 1.4 \times 10^{15} \text{ s}^{-1}$ and for Ga antisites $\mu(\text{Ga}_{\text{As}}, 30 \text{ K}) = 9 \times 10^{15} \text{ s}^{-1}$.^{17,18} In VGF GaAs there are twice as many Ga antisites as Ga vacancies, and in the LEC GaAs samples there are roughly 10 times more Ga antisites than Ga vacancies.

B. Arsenic vacancies

When the samples are illuminated with 1.42 eV photons, the average positron lifetime increases when compared to the values in darkness at temperatures $T = 20 - 180 \text{ K}$ (see Figs. 2–4). Under illumination the average positron lifetime decreases monotonously as a function of temperature and reaches the level measured in darkness at 200 K. The spectra measured at $T = 20 - 150 \text{ K}$ can be decomposed to two components, yielding $\tau_2 = 250 \pm 10 \text{ ps}$. Both the increase in the average positron lifetime under 1.42 eV illumination and values of τ_2 are similar to those found earlier.⁴

The increase in the average lifetime indicates that some vacancies are converted to more efficient positron traps under illumination. Additionally, the gallium vacancies may trap positrons similarly as in darkness. As discussed in detail in Ref. 4, the second lifetime component $\tau_2 \approx 255 \pm 10 \text{ ps}$ at this state of the sample is a superposition of the lifetimes at gallium vacancies and at the illumination-induced positron traps. The positron lifetime at the defects trapping positrons only under illumination is thus about the same as at the Ga vacancy, i.e. 250–260 ps, indicating that the open volume at these defects is that of a monovacancy.

According to calculations,²⁰ arsenic vacancies are positive in darkness. Under illumination some of them are converted to the negative charge state and thus start to act as positron traps.³ The optical processes related to this charge transfer have been studied in detail earlier.⁴ At 80 K the decrease in the average lifetime is due to the thermal emission of electrons from the As vacancy. According to the analysis of Refs. 3 and 4, the ionization level of V_{As} related to this transition is roughly 50 meV below the conduction band minimum.

Positron trapping rates at the arsenic vacancies can be estimated assuming that Ga vacancies and Ga antisites trap positrons similarly under illumination and in darkness.⁴ At low temperatures $T < 60 \text{ K}$ the metastable state of the $EL2$ defect can also trap positrons (see Sec. IV C), so there the three-trap model is not accurate.⁴ However, above 60 K the metastable $EL2^*$ is unable to trap positrons,⁵ and the trapping rate at the arsenic vacancies can be estimated there. In the calculation the positron lifetime of $\tau_v = 257 \text{ ps}$ at the As vacancy is used since this value is in agreement with the present and earlier⁴ decompositions of the lifetime spectra in SI GaAs, and this value has also been determined for negative As vacancy in n -type GaAs.²¹ The trapping rates at As vacancies at 80 K, before the beginning of the thermal escape of the electrons, are listed in Table III. VGF GaAs contains a little higher concentrations of As vacancies than HP-LEC GaAs, and in LP-LEC GaAs their concentration is somewhat lower.

In an earlier study on n -type GaAs, two ionization levels were found for the arsenic vacancies: $E_C - 50 \text{ meV}$ and

$E_C - 140$ meV.²¹ The 50 meV level corresponds to the charge transition $- \rightarrow 0$ and the 140 meV level to the transition $0 \rightarrow +$. Positron lifetimes in the different charge states are 257 ps and 295 ps, respectively.²¹ As explained earlier,⁴ in SI GaAs the concentration of As vacancies, when compared to the concentrations of other defects detected by positrons, is so small that positron trapping at the neutral As vacancy is not detected due to the small trapping coefficient $\mu(V_{As}^0)$.

C. Arsenic antisites

Metastability is one of the most fascinating properties of the native arsenic-antisite-related *EL2* defect. After illuminating undoped SI GaAs with, e.g., white light at temperatures $T < 80$ K, the infrared absorption and other signals related to the native *EL2* are lost. The defect is converted to an optically and electrically inactive state. This persistent metastable state can be transformed back to normal *EL2* by heating the sample at temperatures above 120 K. The metastability of *EL2* can be explained with a vacancy–interstitial model²² where the transition between the stable and metastable state is a change in the atomic configuration of the defect, $As_{Ga} \rightarrow V_{Ga} - As_i$.

The vacancy in the metastable state of both the native and electron-irradiation-induced As_{Ga} -related defects in GaAs traps positrons, and this enables the study of these defects by positron annihilation.^{5,18} This Ga vacancy is slightly smaller than an isolated Ga vacancy due to the arsenic interstitial in its neighborhood. The positron lifetime at the metastable state of *EL2* is $\tau(EL2^*) = 245$ ps.⁵

In this work the arsenic antisite concentrations were determined by converting the *EL2* defect completely into the metastable state with a long 1.15 eV illumination and then measuring the average positron lifetime as a function of the annealing temperature after the illumination. All the measurements were done at 30 K in darkness, and between the measurements the samples were annealed for 10 min at a higher temperature.

In all the samples the average positron lifetime after illumination was longer than the reference value in darkness. In Fig. 5 the increase in τ_{av} after illumination is marked with an arrow. After illumination the average lifetime decreased during isochronal annealing in two stages: first at 30–50 K and then at 120 K. The decrease in the average lifetime after annealing at 120 K was 3 ps in VGF and HP-LEC GaAs [Figs. 5(a) and 5(b)] and 2 ps in LP-LEC GaAs [Fig. 5(c)]. After illumination the second lifetime component is $\tau_2 = 247 \pm 7$ ps at all annealing temperatures below 100 K.

The increase in average positron lifetime after 1.15 eV illumination, the decrease in τ_{av} after annealing at 120 K, and the values of τ_2 are similar as observed and discussed in Ref. 5. Illumination with 1.15 eV photons converts the *EL2* defect to the metastable state, and the vacancy belonging to the atomic configuration of the metastable state is able to trap positrons. Consequently, the average positron lifetime increases. The decrease in τ_{av} after annealing at 120 K is due to the recovery of the metastable vacancy. The lifetime component $\tau_2 \approx 247$ ps is a superposition of the positron lifetimes

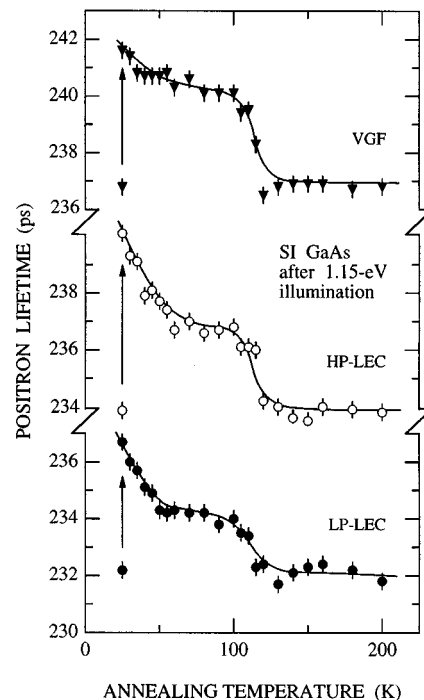


FIG. 5. The average positron lifetime as a function of the annealing temperature in SI GaAs. Before annealing the samples were illuminated with 1.15-eV light. The annealing time was 10 min and measurement temperature 30 K.

at the Ga vacancies and at the vacancy belonging to the metastable state of *EL2*.⁵ Similarly, as earlier,⁵ a positron lifetime of 245 ps at *EL2*^{*} can be extracted from this value of τ_2 using the positron trapping model.

Positron trapping rates at the metastable *EL2*^{*} at 30 K can be calculated with the positron trapping model assuming that Ga vacancies and Ga antisites trap positrons at the same rate as that existing before illumination.⁵ The results are shown in Table III. In VGF and HP-LEC GaAs the positron trapping rates at arsenic antisites, and thus the As_{Ga} concentrations, are almost the same, and in LP-LEC about half the amount.

V. MICROSCOPIC NATURE OF THE THERMALLY STIMULATED CURRENT AND ELECTRICAL COMPENSATION

The earlier sections treated the properties of the traps detected in thermally-stimulated-current measurements and the identification of the defects observed by positrons. In this section the properties of these defects and traps are compared in order to associate the TSC traps to the arsenic and gallium vacancies and antisites observed by positrons. The effect of the intrinsic defects on the electrical compensation will be studied as well, since the ionized fractions of the *EL2* defect obtained from the NIRA experiments suggest that acceptor concentrations in these samples are larger than the impurity, i.e., carbon, concentrations, $[C_{As}] \approx 10^{14} - 10^{15} \text{ cm}^{-3}$.

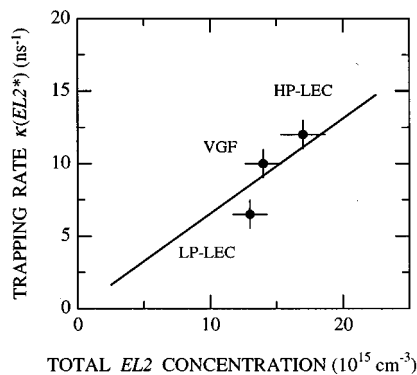


FIG. 6. Positron trapping rate at metastable vacancies vs the total $EL2$ concentration from NIRA experiments in SI GaAs. The samples are indicated in the figure.

A. Arsenic-antisite-related trap

In an earlier TSC study, As-rich melt was observed to favor higher concentrations of trap T_2 in GaAs.²³ The concentration of T_2 had a W-profile across the diameter of the LP-LEC GaAs wafers.²⁴ In addition to these properties, trap T_2 was quenchable with IR-light at 80 K; i.e., the trap disappeared after illumination from the TSC spectrum, and after annealing at 124 K the trap was recovered.²⁵ Many other traps exhibited the same quenching and recovery properties, and two possible explanations for this were suggested: either the traps were all related to the $EL2$ defect and were actually quenched themselves, or $EL2$ controlled the carrier lifetime and thus indirectly caused these traps to disappear from the TSC spectrum.

The metastable vacancy observed by positrons in this work was generated by illuminating the samples with 1.15 eV light at 30 K. After annealing the samples at 120 K for 10 min the vacancy signal was lost. In addition to these properties, the concentration of the metastable vacancy correlates with the total $EL2$ concentration in the present SI GaAs samples, just as was observed in an earlier positron study.²⁶ The correlation is shown in Fig. 6, where the positron trapping rate at metastable vacancies (Table III) is presented as a function of the total $EL2$ concentration determined from the NIRA measurements (Table II).

This correlation confirms that the metastable vacancy belongs to the atomic configuration of the metastable state of the $EL2$ defect, and it can be used as an indicator for As-rich conditions. The positron trapping coefficient at the metastable state $EL2^*$ can be calculated from the data in Fig. 6 by $\mu(EL2^*) = \kappa(EL2^*)N/[EL2]$. The result is $\mu(EL2^*) = 2.9 \pm 0.6 \times 10^{16} \text{ s}^{-1}$ at 25 K, in accordance with the earlier positron results.²⁶

Several of the properties of trap T_2 are similar to those of the native arsenic-antisite-related $EL2$ defect in undoped SI GaAs. Furthermore, if we compare the concentrations of the metastable vacancies estimated from positron measurements and those of T_2 from TSC results, the correlation is clear. In Fig. 7 this correlation is shown by presenting the positron trapping rate at metastable vacancies as a function

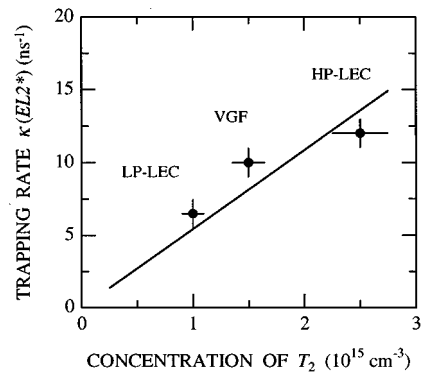


FIG. 7. Positron trapping rate at metastable vacancies vs the concentration of T_2 traps in SI GaAs. The samples are indicated in the figure.

of the T_2 concentration obtained from TSC measurements. The conclusion is that trap T_2 is present in As-rich conditions, and it is likely to be related to the arsenic-antisite defect due to the similarity of the properties of T_2 and $EL2$. However, the activation energy and concentration of trap T_2 are not the same as those of the $EL2$ defect, so this trap is evidently not identical to $EL2$.

B. Arsenic-vacancy-related traps

The T_6^* trap has been observed to have the activation energy 0.15 eV. This energy is likely related to a $(0/+)$ or $(+/++)$ transition of a center which is sometimes observed by temperature-dependent Hall-effect measurements in undoped GaAs.²⁷ The T_6^* trap is known to be an electron trap.²⁵ Electron irradiation was observed to increase the concentration of T_6^* , but the traps in the as-grown and electron-irradiated GaAs have different photoquenching properties.²⁷

The defect identified as the arsenic vacancy in positron experiments has an ionization level at $E_C - 50 \text{ meV}$, and the positron lifetime at this vacancy is roughly 260 ps. In n -type GaAs two ionization levels were found for the As vacancy, $E_C - 50 \text{ meV}$ and $E_C - 140 \text{ meV}$.²¹ These correspond to charge transitions $(-/0)$ and $(0/+)$. Positron lifetimes at these different charge states are 257 ps and 295 ps. Electron-irradiation-induced arsenic vacancies have been observed in n -type Te-doped GaAs.²⁸ Their ionization levels were the same as in as-grown n -type GaAs, and so was the positron lifetime in the defects. The similarity of the ionization levels and positron lifetimes indicates that the same basic defect is observed in these different materials.

In the present TSC measurements the minimum temperature of 80 K is too high for the detection of a 50 meV level, and thus the activation energies of the carrier traps and the observed $E_C - 50 \text{ meV}$ ionization level of the arsenic vacancy cannot be directly compared. Nevertheless, the arsenic vacancy has also an ionization level within 140 meV of the conduction band minimum, and this energy is almost equal to the activation energy of the T_6^* trap. Both of these defects are created by electron irradiation. However, in SI GaAs T_6^* is not observed in large concentrations, and therefore it is not possible to make a direct correlation between

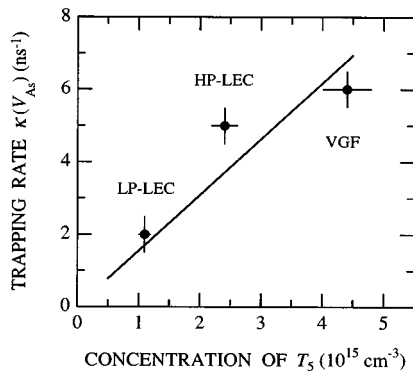


FIG. 8. Positron trapping rate at arsenic vacancies vs the concentration of T_5 traps in SI GaAs. The samples are indicated in the figure.

the concentrations of T_6^* and V_{As} . In any case, the similarity of their properties suggests that T_6^* is an arsenic-vacancy-related defect.

It is interesting to note that in an earlier study the arsenic vacancy has been observed to correlate with the reverse contrast absorption²⁹ which is caused by a nonradiative recombination center.³⁰ If the As vacancy is a recombination center in as-grown GaAs, it should not be observed in TSC measurements. In agreement with this statement, trap T_6^* is usually detected in very small concentrations in as-grown material. In electron-irradiated material, on the other hand, strong T_6^* signals are present and an accurate electron emission rate [$e_n(80 \text{ K}) = 0.004 \text{ s}^{-1}$] can be calculated from the TSC measurements. Thus, T_6^* is clearly a trap at 80 K in electron-irradiated GaAs; however, the T_6^* configurations may differ slightly in as-grown and electron-irradiated material.

The activation energy and capture cross section of trap T_5 are very close to those of the $EL6$ level observed with DLTS in VGF and LEC GaAs, more abundantly in less As-rich VGF material.³¹ In earlier TSC measurements the observed T_5 concentrations were so high that the trap was confidently assigned to intrinsic point defects.²³ In Fig. 8 the positron trapping rate at arsenic vacancies is presented as a function of the T_5 concentration in the samples studied in this work, and the observed concentrations of trap T_5 are found to correlate well with the concentration of arsenic vacancies.

However, the energy levels obtained from TSC measurement for trap T_5 and from positron measurements for the arsenic vacancy are different. A possible explanation for the good correlation between the concentrations is an arsenic-vacancy-related defect complex having energy levels both at $E_C - 0.05 \text{ eV}$ and $E_C - 0.35 \text{ eV}$. If the positron and TSC results are attributed to the same defect, the level at 0.35 eV should be such that it is not detected by positrons, e.g., the $(+/++)$ ionization level.

C. Compensation and intrinsic defects

Only some years ago it was assumed that the deep donor $EL2$ is the only intrinsic defect taking part in the electrical compensation of undoped SI GaAs. In addition to the $EL2$

defect, impurities like the carbon acceptor, C_{As} , whose concentration was typically 10^{16} cm^{-3} , were considered to contribute to the compensation. When the purity of undoped GaAs increased, it was realized that the low impurity concentrations did not always explain the compensation, and intrinsic defects had to be included into more realistic compensation models.³² Recently, more and more evidence has emerged that intrinsic acceptors contribute to the compensation and electrical properties of undoped SI GaAs.²

The native $EL2$ defect is related to the arsenic-antisite defect. In addition to this antisite defect, positron measurements reveal three different intrinsic defects in the present SI GaAs samples. In thermal equilibrium gallium vacancies and antisites are detected; both of these are negatively charged acceptors in SI GaAs. Under illumination positrons also detect As vacancies, which cannot be detected without illumination due to their positive charge state. All these defects should be taken into account in a compensation model.

The net negative charge related to the intrinsic defects compensated by the $EL2$ defect is $3[V_{Ga}^{3-}] + 2[Ga_{As}^{2-}] - [V_{As}^+]$, where the theoretically predicted charge states of the defects in SI GaAs have been taken into account.²⁰ The defect concentrations can be calculated from the positron trapping rate results. Factor κ/μ is proportional to the defect concentration, and for gallium vacancies and antisites the positron trapping coefficients μ are known: $\mu(V_{Ga}, 300 \text{ K}) = 1.4 \times 10^{15} \text{ s}^{-1}$ and $\mu(Ga_{As}, 30 \text{ K}) = 9 \times 10^{15} \text{ s}^{-1}$.^{17,18} For the arsenic vacancy, which according to the experimental results is negatively charged when trapping positrons,⁴ the trapping coefficient for the gallium vacancy, $\mu(V_{Ga}, 80 \text{ K}) = 7 \times 10^{15} \text{ s}^{-1}$, was used.⁴

The role of gallium and arsenic vacancies and gallium antisites in the electrical compensation can be studied by comparing their net negative charge $3[V_{Ga}] + 2[Ga_{As}] - [V_{As}]$ with the near-infrared absorption results. The NIRA measurements give information on the concentration of acceptors: $EL2$ is the main donor close to the Fermi level in SI GaAs and, consequently, the ionized fraction of $EL2$ is equal to the net negative charge in the other defects (see Sec. II A). In Fig. 9 the factor $3[V_{Ga}] + 2[Ga_{As}] - [V_{As}]$ has been presented as a function of the concentration of the ionized $EL2$ defects determined from NIRA measurements. The good correlation between these concentrations supports the conclusion that gallium and arsenic vacancies and gallium antisites are intrinsic defects which contribute significantly to the electrical compensation of undoped SI GaAs material.

Quantitatively, the defect concentrations determined from positron and NIRA experiments are, however, quite different. This discrepancy can be explained by the uncertainties in the analysis of both methods. For example, the experimental information available on the temperature dependence of positron trapping coefficient at negative ions in GaAs is limited. Despite these analysis uncertainties, the relative concentrations are accurately determined in both NIRA and positron experiments. To emphasize the good correlation between the relative defect concentrations, the net negative charge determined from positron measurements is presented in arbitrary units in Fig. 9.

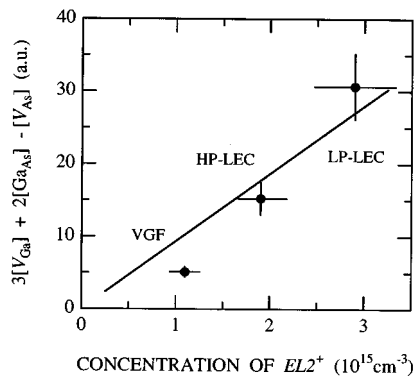


FIG. 9. Net negative charge related to gallium and arsenic vacancies and gallium antisites from positron measurements vs the concentration of the ionized $EL2$ defect obtained from NIRA measurements in SI GaAs. Due to the uncertainty of the absolute concentrations, the scaling on the vertical axis is arbitrary, but the relative concentrations are accurate.

It is interesting to note that although the TSC spectrum of LP-LEC GaAs shows low peak heights (Fig. 1), suggesting that this material contains only low concentrations of carrier traps and is of high quality, both NIRA and positron measurements show that LP-LEC GaAs has the largest acceptor concentrations. TSC and positron techniques thus give complementary information about defects in semi-insulating GaAs, and by using them together a more complete picture of the defects affecting the electrical properties of SI GaAs can be obtained.

D. Comparison between growth techniques and defect concentrations

When the point defect concentrations are compared to the growth technique of the SI GaAs material (see Table III), the following comments can be made. The Ga vacancy concentrations do not change much from sample to sample indicating that the growth technique and stoichiometry do not strongly affect the formation of Ga vacancies. The gallium antisite concentration, on the other hand, is smallest in the VGF GaAs sample, and in LP-LEC GaAs sample the concentration is higher by a factor of five. The arsenic vacancy concentration is largest in the VGF material, which is generally less As-rich than LEC materials, and lowest in the LP-LEC sample.

The concentrations of the As vacancies and Ga antisites, defects in the same sublattice, seem to anticorrelate in the present samples. The same effect, but not so clearly, can be noticed with the Ga vacancies and the As antisites; in the HP-LEC sample there are the most As antisites and the lowest concentration of Ga vacancies, while in the LP-LEC sample *vice versa*.

If stoichiometry were the only important factor, for example in Ga-rich material there should be more As vacancies and Ga antisites than in As-rich material, and their concentrations should correlate. The observed anticorrelation, however, can be associated with the fact that the position of the Fermi level (the chemical potential) in GaAs during crystal growth can favor the formation of either acceptor- or donor-

type intrinsic defects.³³ Since Ga antisites (acceptors) and As vacancies (donors) compete for the same sublattice sites, the defect whose formation is favored during crystal growth dominates, and the defect concentrations anticorrelate. This type of trend is also predicted by the theoretical calculations. According to Ref. 33, the formation energy of Ga_{As} is the lowest under conditions in which the formation energy of As vacancy is the highest. Similar anticorrelation also exists for As_{Ga} and the Ga vacancy.

VI. CONCLUSIONS

In this work undoped semi-insulating GaAs grown by the VGF, LP-LEC, and HP-LEC methods were studied by thermally stimulated current and positron annihilation techniques. TSC measurements revealed trap T_2 with an activation energy of 0.63 eV, T_5 with 0.35 eV, and T_6^* with 0.15 eV in all the samples studied here. Positron experiments were used to determine the concentrations of both gallium and arsenic vacancies, and gallium and arsenic antisite defects.

As-rich melt has earlier been found to favor T_2 , and this defect has similar quenching and recovery properties as those of the arsenic-antisite-related $EL2$ defect. Positron experiments detect a vacancy in the metastable state of $EL2$; $As_{Ga}^* = V_{Ga} - As_i$. Concentrations of trap T_2 and those of the metastable vacancies correlate. Trap T_2 is thus present under conditions similar to those which favor the $EL2$ defect and is most probably related to the arsenic-antisite defect because of its photoquenching properties.

In positron measurements arsenic vacancies were found. In correspondence with the T_6^* trap, the arsenic vacancies have ionization levels within 0.15 eV of the conduction band minimum. Both defects are also produced by electron irradiation.^{27,28} The concentrations of T_6^* in undoped as-grown SI GaAs are low when compared to the arsenic vacancy concentrations estimated from positron measurements. This disagreement is consistent with the assignment of arsenic vacancy as a nonradiative recombination center in SI GaAs. However, the particular configuration of T_6^* produced by electron irradiation is a trap, not a recombination center, below 80 K. Thus, T_6^* defects may exist with approximately the same energy, but with different carrier capture and emission properties.

The concentrations of trap T_5 are found to correlate with the arsenic vacancy concentrations. The observed energy levels of T_5 and the arsenic vacancy are, however, different: 0.35 eV vs 0.05 eV. A possible explanation for the good correlation between the concentrations is an **arsenic-vacancy-related defect** complex having both of these energy levels.

Positron experiments also revealed negative gallium antisites and gallium vacancies in undoped SI GaAs. Both these defects are acceptors in GaAs. When the arsenic vacancies, which are positive in thermal equilibrium in SI GaAs, are also taken into account, the net negative charge related to these defects correlates with the concentration of the ionized $EL2$ defects determined by the near-infrared-absorption measurements. This result suggests that these intrinsic point

defects contribute strongly to the electrical compensation of undoped GaAs.

The defect concentrations were compared according to the growth technique. The gallium vacancy concentrations were practically the same in all the samples. The defects in the same sublattice seem to anticorrelate in the present SI GaAs samples. This may indicate that, in addition to the stoichiometry, the chemical potential in GaAs affects the defect formation during crystal growth.

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