Observation of a Monovacancy in the Metastable State of the *EL*2 Defect in GaAs by Positron Annihilation

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(Received 24 August 1990)

A monovacancy defect is observed by positron-lifetime and Doppler-broadening experiments in semi-insulating GaAs after photoquenching the *EL*2 defects. The monovacancy exhibits the same thermal and optical recoveries as the metastable state of *EL*2 and its concentration is proportional to that of the *EL*2 defect. It is concluded that the metastable state of the *EL*2 defect involves the monovacancy. The results indicate that the monovacancy or its immediate surroundings is negatively charged.

PACS numbers: 61.70.Bv, 71.55.Eq, 78.70.Bj

The *EL*2 defect is a native midgap donor in GaAs which compensates the residual acceptors. Because of the technological importance of semi-insulting GaAs this defect has been the object of extensive theoretical and experimental investigations. However, the atomic nature of *EL*2 is still a matter of controversy.[1]

A most interesting property of *EL*2 is its metastability. The metastable state $EL2^*$ can be populated by illumination with 1.2-eV photons at low temperatures. This state is electrically as well as optically inactive.[1] It can be turned back to the stable state either by annealing at temperatures above 120 K or by illuminating with 0.7-1.5-eV photons with temperatures in the 70-120-K range. There are so far no direct experimental observations of the metastable state.

In this Letter we report the first experimental results on the atomic structure of the metastable state $EL2^*$. Our positron-annihilation measurements give direct evidence that $EL2^*$ contains a monovacancy. The data further suggest that the monovacancy or its immediate surroundings is negatively charged.

Positron annihilation is a method to study vacancy defects in metals and semiconductors.[2] Neutral and negative vacancies trap positrons: This manifests itself as an increase of the positron lifetime and as a narrowing of the line shape of the Doppler-broadened annihilation radiation. In GaAs, positrons have been used to characterize As vacancies in as-grown *n*-type materials[3-5] and Ga vacancies after electron irradiation.[6] Until now, no correlation between positron parameters and the *EL*2 defect has been found.

In this work, positron-lifetime and Doppler-broadening experiments at $T = 25$-300 K were carried out in an optical cryostat. All the measurements as well as the thermal annealings of the samples were performed in darkness. The positron-lifetime experiments were done in a conventional way with a time resolution of 230 ps (FWHM).[2,3] The positron source was 40 μCi of ^{22}NaCl on a 1.5-μm-thick Al foil. During 4 h, $\sim 2\times10^6$ counts were collected for a lifetime spectrum. After source corrections (212 ps with 5.4%, 450 ps with 2.5%, and 1700 ps with 0.12%), the lifetime spectra were analyzed with one or two exponential decay components. From the decomposed lifetimes τ_i and intensities I_i, the average positron lifetime was calculated as $\tau_{\text{av}} = \sum I_i \tau_i$. The Doppler broadening of the annihilation radiation was recorded by a Ge detector with an energy resolution of 1.2 keV. The shape of the 511-keV line was characterized by the conventional parameter *S*, defined as the relative area of the 1.4-keV-wide central region.[2,7] Typically, 5×10^6 counts were collected in the 511-keV line to determine accurately the value of *S*.

Two undoped semi-insulating ($n < 10^{11}$ cm^{-3}) liquid-encapsulated Czochralski-grown GaAs samples with *EL*2 concentrations of 1.0×10^{16} cm^{-3} (sample *A*) and 2.5×10^{16} cm^{-3} (sample *B*) were used for the experiments. In infrared-absorption measurements the samples showed the well-known characteristics of the metastability of *EL*2. After illumination at 25-80 K, the optical absorption by *EL*2 became very small, indicating the complete photoquenching of the stable state ($EL2 \rightarrow EL2^*$). The thermal recovery of the infrared absorption corresponding to the regeneration of the stable state ($EL2^* \rightarrow EL2$) was observed at 120 K. The normalized absorption coefficient (1 for the state with *EL*2 and 0 with $EL2^*$) of sample *B* is shown at the top of Fig. 1.

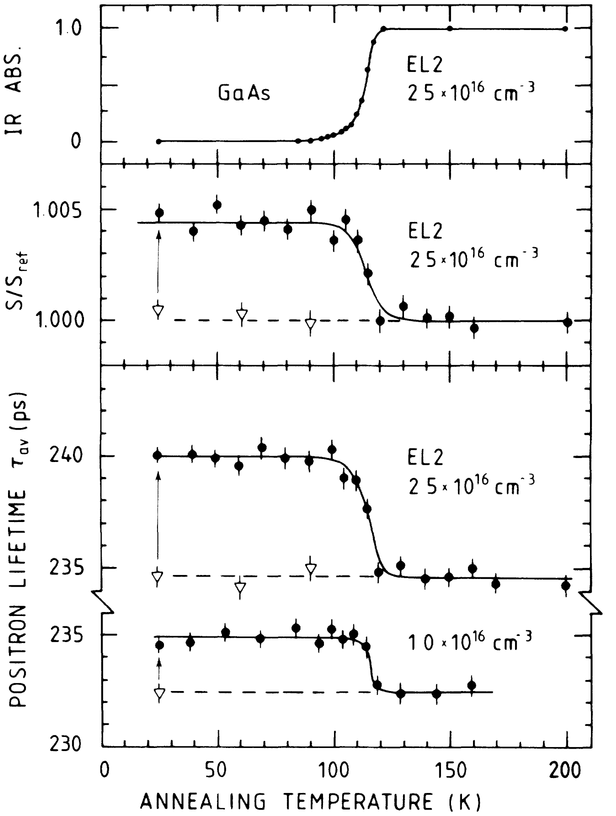

FIG. 1. The average positron lifetime τ_{av} and annihilation line-shape parameter S in semi-insulating GaAs as functions of isochronal annealing temperature after 1.2-eV illumination at 25 K. The illumination transforms $EL2$ into the metastable state and corresponding changes in positron parameters are indicated by arrows. The open triangles with dashed lines below 100 K represent the reference levels where $EL2$ is in the stable state. The normalized infrared absorption coefficient is shown in the top panel. All measurements have been made in darkness at 25 K.

Before illumination the positron lifetime τ_{av} at 25 K is 232 ps (sample A) and 234 ps (sample B). These values as well as the reference values S_{ref} for the line-shape parameter are nearly temperature independent in the range 25–300 K. The lifetime values agree with those of 230–235 ps reported earlier for delocalized positrons in semi-insulating GaAs.[3-5] Thus, before illumination, practically no positron trapping at vacancy-type defects is observed.

Figure 1 shows the positron results after 1-h illumination of the samples at 25 K with 1.2-eV photons. The low level of the infrared absorption at the top of Fig. 1 confirms that the $EL2$ defect has transformed to the metastable state. Compared to the reference levels, the illumination induces increases in both the average positron lifetime τ_{av} and the line-shape parameter S. The increases of τ_{av} and S are larger in sample B (5.5 ps and 0.43%, respectively), with the higher $EL2$ concentration of $[EL2]=2.5\times10^{16}$ cm^{-3}, than in sample A (2.5 ps and 0.13%), with $[EL2]=1.0\times10^{16}$ cm^{-3}.

The effects of 10-min isochronal annealings on the positron parameters measured at 25 K are shown in Fig. 1. At annealing temperatures of 30–100 K no changes are observed: Both the average lifetime and the S parameter remain at the higher values obtained after illumination at 25 K. At 100–120 K the positron parameters show abrupt decreases to the levels before illumination in both the samples. After annealings above 120 K the average lifetime τ_{av} and the line-shape parameter S stay at the reference levels obtained before illumination.

When the positron parameters have the higher values between 25 and 100 K, infrared absorption in Fig. 1 remains low indicating that $EL2^*$ stays populated. The increase in infrared absorption, i.e., the transformation $EL2^* \rightarrow EL2$, occurs exactly at the same temperature as the recovery of the positron parameters to the reference levels.

We have studied in more detail the kinetics of the 120-K recovery by simultaneous positron-lifetime and infrared-absorption measurements in sample B. The time for the 50% recovery was determined during isothermal annealings at 120, 115, 110, and 106 K. Both techniques gave consistent recovery times and the same apparent activation energy of 0.37 ± 0.02 eV, in good agreement with the reported values for the $EL2^* \rightarrow EL2$ thermal recovery.[1,8]

After photoquenching, the stable state of $EL2$ can also be optically regenerated using 0.9–1.4-eV light at temperatures 70–140 K.[1] We have performed the $EL2^* \rightarrow EL2$ optical recovery at 80 K in sample B with a 10-W halogen lamp and a heat-absorbing filter of about 1% transmittance for 1.4-eV photons. During 32-h illumination the average positron lifetime at 25 K decreased continuously from $\tau_{av}=240$ to 234 ps, which is the reference level observed at 25 K before illumination.

To summarize our experimental findings, we observe increases in positron lifetime τ_{av} and line-shape parameter S after $EL2$ is transformed into the metastable state. The increase is higher at higher $EL2$ concentration. The increased values of τ_{av} and S are stable as long as the metastable state $EL2^*$ is retained in the sample. The positron parameters recover thermally at 120 K and optically under 1.4-eV photon illumination at 80 K in perfect correspondence with the $EL2^* \rightarrow EL2$ transformation. We thus associate the increased values of the positron lifetime and annihilation line-shape parameter to the metastable state $EL2^*$.

When negative or neutral vacancies are present, positrons get trapped at them with a trapping rate κ (Refs. 2 and 9). The trapping rate κ is proportional to the vacancy-defect concentration c by $\kappa=\mu c/n_A$, where μ is the positron-trapping coefficient and n_A the atom density.[2] Because of the reduced electron density in vacancy-type defects, the lifetime of trapped positrons increases and the electron-positron momentum distribution narrows, resulting in an increase in the average positron lifetime and in the line-shape parameter S, respectively.[2] Hence, increased experimental values of positron lifetime and S parameter are clear signs that vacancy-type defects exist in a sample. The increase of τ_{av} and S when $EL2$ is transformed into the metastable state $EL2^*$ is thus a direct evidence that a vacancy-type defect is present in the atomic configuration of $EL2^*$.

After illumination at 25 K, the lifetime spectra measured in sample B ($[EL2]=2.5\times10^{16}$ cm^{-3}) can be decomposed into two components with lifetimes of $\tau_1=214\pm10$ ps and $\tau_2=\tau_{def}=255\pm8$ ps and an intensity of $I_2=(62\pm12)\%$. The decomposition thus indicates that the vacancy-type defect in $EL2^*$ is characterized by the lifetime τ_{def} of about 255 ps. The characteristic S-parameter value due to trapped-positron annihilation at $EL2^*$ can also be estimated. In Fig. 1 the S parameter after illumination is $S/S_{ref}=1.0043$ in sample B. This value is the superposition of the annihilations in the bulk (S_{ref}) and at the $EL2^*$ defects (S_{def}). From the lifetime measurements the fraction of positrons annihilating as trapped is $(\tau_{av}-\tau_{ref})/(\tau_{def}-\tau_{ref})=23\%$. These values give us $S_{def}/S_{ref}=1.018\pm0.003$.

The positron lifetime $\tau_{def}=255\pm8$ ps is a typical value observed previously for monovacancies in GaAs.[3-5] In n-type material, native vacancies attributed to the As sublattice have been found to trap positrons with lifetimes of 257 ± 3 and 295 ± 3 ps, depending on the position of the Fermi level.[3] Positron traps with $\tau_2=260$ ±3 ps have also been observed after 1.5-3-MeV electron irradiation of semi-insulating GaAs, and the defects have been attributed to monovacancies in the Ga sublattice.[6] The change of 1.8% in the S parameter estimated for positrons trapped at $EL2^*$ is close to the values of 1.9% and 2.2% which we have determined for V_{Ga} in electron-irradiated and for V_{As} in as-grown GaAs, respectively. Hence, both positron-lifetime and Doppler-broadening measurements indicate that positron traps at $EL2^*$ defects are of the monovacancy type.

The trapping rate κ at the monovacancy defects can be calculated from the trapping model.[2] For samples A and B with $EL2$ concentrations of 1.0×10^{16} and 2.5×10^{16} cm^{-3} we get $\kappa_A=0.5\times10^9$ s^{-1} and $\kappa_B=1.4\times10^9$ s^{-1}. The ratio $\kappa_B/\kappa_A=2.8$ is in reasonable agreement with the ratio of the $EL2$ concentrations in the two samples, thus giving further support to the association of the monovacancy to the $EL2^*$ defect.

Information on the charge of a vacancy defect can be obtained by measuring the temperature dependence of the positron-trapping coefficient μ. Positron trapping at neutral vacancies is temperature independent from both a theoretical[9] and an experimental[10] basis, and values of 10^{15} s^{-1} have been estimated for μ.[9,10] On the contrary, trapping to negative vacancies has been found to increase strongly at low temperatures, reaching values of the order of 10^{17} s^{-1} at 20 K in Si.[9,10]

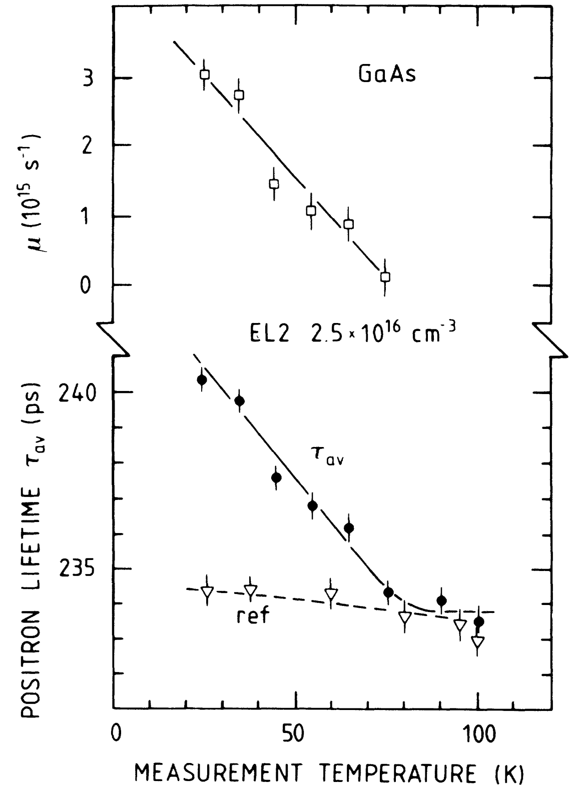

FIG. 2. Average positron lifetime τ_{av} and positron-trapping coefficient μ at the metastable state of $EL2$ in semi-insulating GaAs as functions of measurement temperature. Before measurements the sample has been illuminated by 1.2-eV photons to transform $EL2$ into the metastable state. The dashed line represents the reference level where $EL2$ is in the stable state.

Figure 2 shows the positron lifetime τ_{av} as a function of measurement temperature after photoquenching of $EL2$ at 25 K. The positron-trapping coefficient μ, also given in Fig. 2, is calculated from the average lifetime using the one-defect trapping model with $\tau_{def}=255$ ps and $[EL2]=2.5\times10^{16}$ cm^{-3}. The positron lifetime τ_{av} and trapping coefficient μ in Fig. 2 show a strong decrease as a function of temperature between 25 and 80 K. At 80-100 K, τ_{av} reaches the reference level of 234 ps and the positron trapping is almost completely removed. This strong decrease of μ with temperature is typical for negatively charged vacancies.[9,10] This suggests that the charge of the monovacancy involved in $EL2^*$ is negative, or a neighboring atom is negatively charged. In both cases, a temperature-dependent build-up of the positron wave function in the vacancy region is expected.[9]

However, the absolute level $\mu=3\times10^{15}$ s^{-1} of the trapping coefficient at 25 K is small compared to values of $\sim10^{17}$ s^{-1} obtained previously for isolated negative monovacancies in Si at 20 K.[10] A possible explanation for this difference is that the monovacancy involved in $EL2^*$ is a part of a larger defect complex, the total charge of which is neutral instead of negative. Finally, it should be noted that the temperature dependence of the trapping coefficient shown in Fig. 2 could be partly influenced by positron trapping at Rydberg states around negative acceptors,[7] which can also change their charge state at 25–100 K due to thermal ionization. However, the decrease of μ in Fig. 2 is so strong that the 6-ps change of τ_{av} would require an acceptor concentration of more than 10^{17} cm^{-3} (Ref. 6). In our samples the concentration of acceptors is at the typical level of 10^{15}–10^{16} cm^{-3}.

To summarize the properties of $EL2^*$ revealed by positron-annihilation experiments, we conclude that (i) $EL2^*$ involves a monovacancy either in the Ga or As sublattice and (ii) the monovacancy or its immediate surroundings is negatively charged.

Several atomic models have been proposed for the $EL2$ defect and for its transition to the metastable state. There is general agreement with the arsenic antisite defect $\mathrm{As_{Ga}}$ is present in the stable state of $EL2$ (Ref. 1), but it is not clear whether the antisite is isolated or bound to another defect such as an interstitial or vacancy. Although no direct observation of the metastable state $EL2^*$ has been made so far, most models of $EL2^*$ are based on atomic displacements induced by electronic transitions during the $EL2 \rightarrow EL2^*$ transformation.[1] The models include, e.g., movement of the isolated $\mathrm{As_{Ga}}$ to an interstitial position, $\mathrm{As_{Ga}} \rightarrow V_{\mathrm{Ga}}\mathrm{As}_i$ (Ref. 11), transformation of the antisite-vacancy pair $\mathrm{As_{Ga}}$-V_{As} to a Ga vacancy (Ref. 12), metastable change in the position of the As interstitial in the antisite-interstitial pair $\mathrm{As_{Ga}}$-As_i (Ref. 13), and transformation in the divacancy-antisite complex from the V_{As}-V_{Ga}-$\mathrm{As_{Ga}}$ configuration to V_{As}-$\mathrm{As_{Ga}}$-V_{Ga} (Ref. 14). Our positron results strongly support the $EL2$ models, which relate a monovacancy to the metastable state $EL2^*$.

In summary, we have observed positron trapping at a monovacancy defect when the $EL2$ defect is in the metastable state. The monovacancy concentration is proportional to the $EL2$ concentration. The monovacancy exhibits the same thermal and optical recovery as the metastable $EL2^*$ defect. Thus we conclude that the monovacancy is involved in the atomic configuration of the metastable state of $EL2$. We suggest that the monovacancy or its surroundings is negatively charged.

We are grateful for discussions with R. M. Nieminen, M. J. Puska, and C. Schwab.

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