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LETTER TO THE EDITOR

Correlation between the EL2 defect and the metastable vacancy observed by positron annihilation in SI GaAs

C Le Berre†, C Corbel†, M R Brozel‡, S Kuisma§, K Saarinen§ and P Hautojärvi§

† INSTN, CE-Saclay, 91191 Gif-Sur-Yvette Cédex, France
‡ Department of Electronics and Electrical Engineering, UMIST, Manchester M60 1QD, UK
§ Laboratory of Physics, TKK, 02150 Espoo, Finland

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Abstract. We have performed positron lifetime experiments on semi-insulating (SI) GaAs in darkness at 20 K, before and after illumination with light of photon energy 1.32 eV. EL2 concentrations have been measured by infrared absorption (FTIR). After illumination, positrons detect a metastable vacancy whose trapping rate correlates with the total EL2 concentration. We conclude that this vacancy is included in the metastable configuration of EL2 (EL2*). This correlation allows us to propose a value of $(3.0\pm0.3)\times10^{16}$ s^{-1} for the positron trapping coefficient at EL2* at 20 K.

The so-called EL2 defect in GaAs and related compounds has been extensively studied because of its high technological interest [1]. Being a midgap donor compensating the net concentration of residual shallow acceptors, it is responsible for the high resistivity of undoped substrates. The presence of an optically induced metastable configuration (EL2*) is the most unusual aspect of this defect. EL2 signals can be persistently bleached by photoexcitation with 1–1.3 eV light at low temperature ($T < 100$ K). EL2 is now well characterized optically and electrically but its atomic configuration has been a matter of controversy over several years. On the basis of EPR experiments [2, 3], the defect has been related to the As antisite. Two models have been generally discussed, which find some support from experiments or calculations [4]: the isolated antisite As_{Ga} [5] and the antisite coupled with an As interstitial As_{Ga}–As_i [6]. An important question is whether the metastability can be explained in terms of the isolated antisite model. The theoretical papers [5] have shown that the metastability could originate from a displacement of the As antisite along the [111] direction, induced by illumination, to an interstitial position, the configuration V_{Ga}–As_i being separated from the antisite position by an energy barrier.

Positron annihilation has been used to check whether a vacancy is optically generated in the bleaching process. Early experiments have shown the generation of a metastable vacancy in SI GaAs [7]. More recently, a thorough study has shown the same photoexcitation properties for EL2 and this metastable vacancy [8].

We have now performed infrared absorption measurements (FTIR) and positron lifetime experiments on a set of undoped SI GaAs crystals. The results show that the total EL2 concentration is directly proportional to the positron trapping rate at the metastable vacancy. This has allowed us to give a value at 20 K for the positron trapping coefficient at the metastable vacancy involved in the atomic structure of EL2*.

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Five samples were cut from five different undoped SI GaAs wafers, grown by the liquid encapsulated Czochralski (LEC) method. They were supplied by Johnson Matthey and Maspec. The total and neutral EL2 concentrations were measured at 300 K, using Martin's calibration [9] for $[EL2^0]$ and Silverberg's calibration [10] for $[EL2]_{total}$. This last measurement is made at 1.03 eV, where the EL2 photoionization and photoneutralization cross sections, σ_n^o and σ_p^o, are equal. In this special case, the absorption coefficient α is proportional to the total EL2 concentration:

$$a(h\nu,\,t) = \sigma_n^o(h\nu)\big[EL2^0\big](t) + \sigma_p^o(h\nu)\big[EL2^+\big](t)$$
$$a(1.03\text{ ev},\,t) = \sigma_n^o(1.03\text{ eV})[EL2]_{tot}(t) = \sigma_p^o(1.03\text{ eV})[EL2]_{tot}(t).$$

Table 1 shows that EL2 concentrations in the present samples vary from 10^{16} cm^{-3} to 3×10^{16} cm^{-3}.

Table 1. EL2 concentrations and lifetime spectra decompositions in the five SI GaAs crystals, before and after illumination at 20 K. In crystals A and C, τ_2 has been fixed to 258 ps to reduce the statistical scattering of the decomposition.

				Before illumination—20 K		After illumination—20 K		
Crystal	$[EL2]_{tot}$ (cm^{-3})	$[EL2^0]$ (cm^{-3})	$EL2^+$ (%)	$\bar{\tau} \pm 0.8$ (ps)	τ_2 (ps)	$\bar{\tau} \pm 0.8$ (ps)	$\tau_2 \pm 5$ (ps)	I_2 (%)
A (M195)	3×10^{16}	2.6×10^{16}	13	240.2	258	244.0	244	99.0±0.2
B (M196)	2.3×10^{16}	2×10^{16}	13	242.8	258±5	244.8	245	98.8±0.2
C (JM105)	1.04×10^{16}	0.97×10^{16}	7	239.6	258	242.9	247	95.0±2.0
D (JM121)	1.04×10^{16}	0.91×10^{16}	13	241.4	256±5	244.8	246	95.0±3.0
E (JM123)	1.2×10^{16}	0.92×10^{16}	23	238.6	260±5	241.8	245	95.5±3.0

The positron lifetime spectra were recorded in darkness at 20 K, by using a fast–fast coincidence spectrometer with an FWHM of 220 ps [11]. About 2×10^6 counts were collected for each spectrum. After source and background corrections, the lifetime spectra were analysed with one or two exponential components. The average lifetime was calculated as $\bar{\tau} = \sum_i I_i \tau_i$ from the decomposed lifetimes τ_i and their intensities I_i. A first series was recorded after cooling in darkness. A second one was recorded after 1 h of illumination with (1.32 ± 0.05) eV (940 ± 40) nm light obtained from LEDs, with an intensity of 2.9 mW cm^{-2}.

Because of its sensitivity to open volumes, charge states and concentrations of the defects, positron annihilation is a powerful method to study vacancy type defects in semiconductors [11]. Positrons are repelled by positive ion cores and positive vacancies, but they can localize at negative or neutral defects. The electron densities at vacancies are reduced compared to those in the lattice. Therefore, the lifetime of positrons trapped at vacancies is longer than that of positrons delocalized in the lattice. The positron trapping rate K is proportional to the defect concentration C: $K = \mu C$, where μ is the positron trapping coefficient [12].

Before illumination, the average positron lifetime at 20 K varies from 239 ps to 243 ps in the five samples (see table 1). The lifetime spectra decompositions show that we have two different kinds of crystal. For crystals A, B and C, the spectra can be decomposed into two components. The average value of the longest component τ_2 is 258 ± 5 ps, with an intensity varying from 60% to 90%. For crystals D and E, the lifetime spectra decomposition is impossible at 20 K. The average lifetimes are all above the lifetime $\tau_b = 230$ ps measured for free positrons at 20 K [13], indicating that positrons are trapped at vacancies in all crystals. A study of the lifetime spectra as a function of temperature up to 300 K [14] shows that, in crystals A, B and C, positrons are trapped by a vacancy type defect characterized by the lifetime 258 ± 5 ps. The two-component decompositions are in good agreement with a trapping model [11] involving only this defect. The same study shows that crystals D and E contain negative ions in addition to the vacancies with a lifetime 258 ps, the two defects competing for positron trapping at low temperatures [14]. The vacancies are shown to be negatively charged [14] on the basis of the temperature dependence of their positron trapping coefficient [12]. According to calculations of ionization levels [15], Ga vacancies are generally negative when the Fermi level stands at midgap whereas As vacancies are positive. Hence, the observed vacancies are identified as Ga vacancies. The positron trapping rate at the Ga vacancy before illumination, $K_{V_{Ga}}$, has been calculated using the one-defect trapping model [11] in crystals A, B and C. Table 2 shows that the calculated values are in the range 1–3 $\times 10^9$ s^{-1}.

Table 2. Trapping rates and annihilation fractions at 20 K after illumination. Calculations are made from equations (1), (2) and (3), using the trapping model including two defects with lifetimes $\tau_{V_{Ga}} = 258$ ps and $\tau_{V^*} = 244$ ps. τ_2 and I_2 values are adjusted by the amount $\Delta\tau_2$ and ΔI_2 within their experimental error bars in order to keep the experimental and calculated average lifetimes equal, i.e. $\bar{\tau}_{exp} - \bar{\tau}_{calc} \leqslant 0.8$ ps, 0.8 ps being the experimental error on the average lifetime.

Crystal	τ_2 ($\Delta\tau_2$) (ps)	I_2 (ΔI_2) (%)	$K_{V_{Ga}}$ (10^9 s^{-1})	$K^*_{V_{Ga}}$ (10^9 s^{-1})	K_{V^*} (10^9 s^{-1}	f_{bulk} (%)	$f_{V_{Ga}}$ (%)	f_{V^*} (%)	$\bar{\tau}_{calc}$ (ps)	$\bar{\tau}_{exp}$ ($\Delta\bar{\tau}$) (ps)
A	245.1	99	2.1	1.9	22.15	15	7	78	243.2	244.0
(M195)	(1.1)	(0)								(0.8)
B	246.3	98.6	3.2	2.9	14.97	20	13	67	244.5	244.8
(M196)	(1.3)	(0.2)								(0.3)
C	247.0	97	1.9	1.8	6.65	34	14	52	242.1	242.9
(JM105)	(0.)	(2)								(0.8)
D	249.0	97.2	—	3.7	6.53	30	25	45	244	244.8
(JM121)	(3)	(2.2)								(0.8)
E	246.5	97.5	—	1.8	8.15	30	13	57	242.1	241.8
(JM123)	(1.5)	(2)								(0.3)

After illumination, we observe a persistent increase of 2–4 ps in the average lifetime. All spectra can be decomposed in two components, even those of crystals D and E. In table 1, the values for τ_2 vary from 244 ps to 247 ps depending on the crystals, and their intensities are all very close to 100%. However, the one-defect trapping model is never verified, indicating that there are two defects at least. After warming up the crystals above 100 K, the average lifetime and the decomposition recover to those measured before illumination [7, 8].

The increase of the average lifetime and decrease of τ_2 show that a metastable vacancy defect is generated by the illumination. After illumination, the positron trapping is thus due to both the Ga vacancy and the metastable vacancy in crystals A, B and C as well as in crystals D and E. The successful decomposition of positron lifetime in crystals D and E indicates that the negative ions are probably partly neutralized after illumination. The long lifetime τ_2 =244–247 ps is a superposition of two lifetimes: one for the positron trapping at the Ga vacancy, $\tau_{V_{Ga}} = 258$ ps, and one for the positron trapped at the metastable vacancy, τ_{V^*}. Its intensity I_2 is the sum of their respective intensities, $I_{V_{Ga}}$ and I_{V^*}:

$$\begin{cases} \tau_2 = \left(I_{V_{Ga}}\tau_{V_{Ga}} + I_{V^*}\tau_{V^*}\right)/\left(I_{V_{Ga}} + I_{V^*}\right) \\ I_2 = I_{V_{Ga}} + I_{V^*}. \end{cases} \tag{1}$$

In our previous work [8], a lifetime $\tau = 245 \pm 3$ ps was found for the metastable vacancy. In table 1, the lowest value of τ_2 observed after illumination is 244 ps, with an intensity $I_2 = 99\%$. Thus, equation (1) shows that τ_{V^*} is slightly shorter or equal to 244 ps. In the following, we will attribute the value $\tau_{V^*} = 244$ ps to the metastable vacancy. It is then possible to calculate the intensities $I_{V_{Ga}}$ and I_{V^*} from equation (1), and the positron trapping rates at both defects, $K^*_{V_{Ga}}$ (the star means after illumination) and K_{V^*}, using the two-defect trapping model. We can write

$$\begin{cases} K^*_{V_{Ga}} = \left[I_{V_{Ga}}\left(\lambda_b - \lambda_{V_{Ga}}\right) + I_{V_{Ga}} I_{V^*}\left(\lambda_{V_{Ga}} - \lambda_{V^*}\right)\right]/\left(1 - I_{V_{Ga}} - I_{V^*}\right) \\ K_{V^*} = \left[I_{V^*}\left(\lambda_b - \lambda_{V^*}\right) + I_{V_{Ga}} I_{V^*}\left(\lambda_{V^*} - \lambda_{V_{Ga}}\right)\right]/\left(1 - I_{V_{Ga}} - I_{V^*}\right) \end{cases} \tag{2}$$

where $\lambda_b = 1/\tau_b$ is the annihilation rate of the positron delocalized in the bulk of the crystal and $\lambda_{V_{Ga}} = 1/\tau_{V_{Ga}}$ and $\lambda_{V^*} = 1/\tau_{V^*}$ are the annihilation rates at the Ga vacancy and at the metastable vacancy, respectively. The positron annihilation fraction f_i in each state i can also be calculated from this model, leading to a theoretical average lifetime

$$\bar{\tau}_{calc} = \sum_i f_i \tau_i = f_b \tau_b + f_{V_{Ga}} \tau_{V_{Ga}} + f_{V^*} \tau_{V^*} \tag{3}$$

which can be compared to the experimental average lifetime $\bar{\tau}_{exp}$ given in table 2. For the trapping rate calculations, we have varied the experimental parameters within their error bars in order to keep the experimental and calculated average lifetimes equal, i.e. $\bar{\tau}_{exp} - \bar{\tau}_{calc.} \leqslant 0.8$ ps, 0.8 ps being the experimental error on the average lifetime. This criterion is a guarantee for the coherence of the analysis.

Trapping rates, annihilation fractions and calculated lifetimes are reported in table 2. This table shows that the positron trapping rate at the Ga vacancy is slightly lower after illumination than before. Calculations by Puska *et al* [12] have shown that the less negative a defect is, the lower the trapping coefficient is. If the Ga vacancy plays a role in the compensation mechanism, it can lose electrons when EL2 becomes metastable. In that case the trapping rate after illumination would be lower than before. Such a neutralization of Ga vacancies is a good explanation for our results.

The long illumination time of 1 h was chosen in order to convert all the EL2 centres into EL2*. Then, positrons are likely to detect the total EL2 concentration. Figure 1 shows the excellent correlation between the positron trapping rate at the metastable vacancy and the total EL2 concentration. This result allows us to conclude that the observed monovacancy is indeed involved in the metastable configuration of EL2. The trapping rate is proportional to the concentration of defects and the proportionality coefficient is the positron trapping coefficient at the defect, μ. The slope of the correlation line gives a value for the positron trapping coefficient at the metastable vacancy at 20 K: μ_{V^*} (20 K) = $(3.0 \pm 0.3) \times 10^{16}$ s^{-1}.

In summary, we have performed infrared absorption measurements (FTIR) and positron lifetime experiments on undoped SI GaAs in darkness at 20 K, before and after photoexcitation. Ga vacancies, and negative ions depending on the samples, are observed before illumination. A metastable vacancy, whose properties are those of EL2*, is revealed

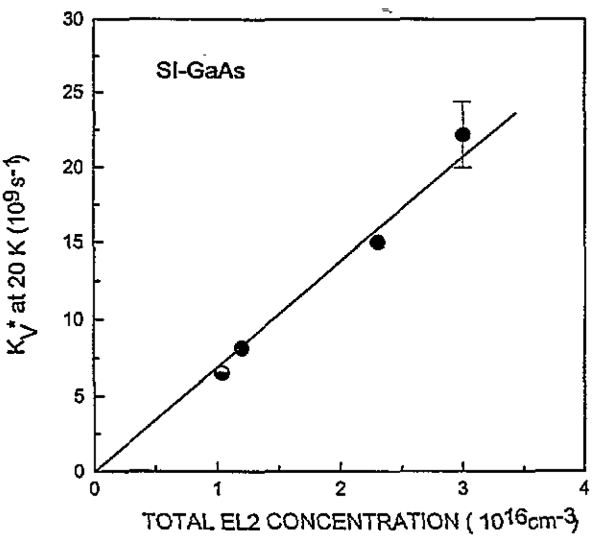

Figure 1. Positron trapping rate at the metastable vacancy at 20 K after illumination with light of energy of 1.32 eV and intensity of 2.9 mW cm^{-2}, as a function of the total EL2 concentration. The symbol ⊖ corresponds to both C and D crystals.

after illumination. Its positron trapping rate is proportional to the total EL2 concentration measured by FTIR, giving a value for the positron trapping coefficient at EL2*. This result definitively shows that the metastable vacancy seen by positrons is within the metastable configuration of EL2.

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