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LETTER TO THE EDITOR

Vacancies and voids in deformed GaAs studied by positron lifetime spectroscopy

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Abstract. Positron lifetime experiments show the formation of voids in deformed n-type GaAs. In addition, the concentration of monovacancies is increased from the native population by a factor of three to six, depending on the deformation and annealing conditions of the material. The strong temperature dependency of the positron lifetime spectrum also indicates that the concentration of negative ions in deformed GaAs is increased compared to the as-grown material. We attribute this to the formation of Ga antisite defects during deformation.

Because positrons in solids are repelled by positive ion cores, open-volume defects act as attractive centres, where positrons can get trapped. Due to the reduced electron density in these defects, the lifetime of the trapped positrons increases in comparison with the annihilations in the perfect crystal. Consequently, positron lifetime measurements give direct information on the vacancy-type defects on an atomic scale (Hautojärvi 1979, Brandt and Dupasquier 1983).

Positron lifetime experiments in deformed metals have shown the formation of dislocations, vacancies, vacancy clusters and larger voids during deformation (Hautojärvi 1979, Brandt and Dupasquier 1983). Each of these defects gives a specific positron lifetime, from which the defect species can be distinguished. However, the situation is more complicated in semiconductors, because the defect charge has an additional effect on the trapping properties of the positron. Only the negative or neutral vacancies act as trapping centres, whereas the positive vacancies repel positive positrons (Puska *et al* 1989, Corbel *et al* 1988). At low temperature positrons can become bound to shallow Rydberg states around negative ions, where the annihilation characteristics are close to those in the bulk (Saarinen *et al* 1989). In addition to vacancies, positrons can thus give information also on the negative-ion-type defects in semiconductors, for example residual impurities, antisites and interstitials. In as-grown n-type GaAs, positrons have revealed both native vacancies (Corbel *et al* 1988) and negative ions (Saarinen *et al* 1989) at high concentrations.

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Table 1. The samples studied in this work, their degrees of deformation, temperatures and heat treatment temperatures, the measured average positron lifetimes at 300 K, and the corresponding trapping rates at monovacancy defects (κ_{vac}) and voids (κ_{void}).

Sample	Deformation	Annealing temperature	τ_{ave} (ps)	κ_{vac} (ns^{-1})	κ_{void} (ns^{-1})
(1) GaAs(Si)	—	—	241	2.5 ± 0.2	—
(2) GaAs(Si)	6%/500 °C	500 °C	277	2.7 ± 0.2	1.1 ± 0.1
(3) GaAs(Si)	8%/500 °C	400 °C	321	9.3 ± 0.2	5.5 ± 0.2
(4) GaAs(Se)	—	—	244	2.3 ± 0.2	—
(5) GaAs(Se)	5.9%/300 °C	—	321	12.7 ± 0.2	6.0 ± 0.2
(6) GaAs(Se)	12.3%/500 °C	625 °C	338	8.9 ± 0.2	6.7 ± 0.2
(7) GaAs(Se)	12.9%/500 °C	—	348	14.7 ± 0.2	11.5 ± 0.2

In this letter, we investigate the effects of deformation on the defect structure in n-type GaAs. We show that during deformation large vacancy clusters or voids are formed in the lattice. In addition, the monovacancy concentration is increased by a factor of three to six, depending on the deformation conditions. Positron lifetime measurements at low temperature indicate that as the deformation increases so does the concentration of the negative ions. We suggest that this is due to the formation of Ga_{As} antisite defects.

Our GaAs samples were LEC-grown n-type crystals doped with Si or Se atoms. The carrier concentrations at 300 K were $n = 2 \times 10^{18}$ cm^{-3} and $n = 7 \times 10^{17}$ cm^{-3} for the Si- and Se-doped materials, respectively. The samples (approximately $13 \times 4 \times 4$ mm^3) were deformed by uniaxial compression along a ⟨123⟩ axis at 500 °C in an argon atmosphere. The dislocation density after the deformation was typically 10^7–10^8 cm^{-2}. The samples and their different deformation and annealing treatments are listed in table 1.

The positron lifetime experiments were performed in a conventional way using a fast–fast spectrometer with a time resolution 230 ps (FWHM) (Hautojärvi 1979, Brandt and Dupasquier 1983). Two identical sample pieces were sandwiched with a 15 μCi positron source, which was prepared by evaporating a carrier-free $^{22}NaCl$ solution deposited onto a thin (0.89 mg cm^{-2}) nickel foil. A liquid-nitrogen cryostat was used to vary the sample temperature between 85 and 600 K.

After the subtraction of the annihilations in the source material, the lifetime spectra were analysed with two or three exponential decay components. From the lifetimes τ_i and intensities I_i the positron average lifetime is calculated as

$$\tau_{ave} = \sum I_i \tau_i.$$

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

The positron trapping rates κ_i were calculated from the lifetimes and intensities using the positron trapping model with one, two or three defect types (West 1979). In the trapping model, longer lifetimes are defect-specific and correspond to positrons annihilating as trapped at vacancy-type defects. The shortest experimental positron lifetime τ_1 is a superposition of annihilations in the bulk (lifetime τ_b) and trapping at vacancies

$$\tau_1^{-1} = \tau_b^{-1} + \sum \kappa_i.$$

The trapping rates κ_i can be calculated from the lifetime decompositions (τ_i, I_i), and

they depend on the defect concentration c_i via the relation $\kappa_i = \mu_i c_i$. Hence the defect concentration can be obtained from the positron data, provided that the trapping coefficient μ_i is known. Even when this is not the case, relative changes in the defect concentration c_i can be obtained directly from κ_i.

Before deformation, the average lifetime at room temperature was between 240 and 244 ps in both Si- and Se-doped reference samples. Two lifetime components were needed to decompose the spectra at all temperatures. The longer component was constant, $\tau_2 = 260$–270 ps, and it corresponds to positron annihilation in a native vacancy defect. The value $\tau_2 = 260$ ps is typical for heavily n-type (10^{18} cm^{-3}) as-grown GaAs, and it has previously been assigned to a defect involving a monovacancy, namely V_{As}^{2-}, by Corbel *et al* (1988). Because positron lifetime is insensitive to the atomic surroundings of a vacancy defect, it cannot be used to distinguish between isolated vacancies and those bound to other defects such as impurities or antisites (Corbel *et al* 1988).

Above 200 K, the lower lifetime τ_1 in the reference GaAs sample closely followed the one-defect trapping model (West 1979). Below 200 K, shallow positron traps with a lifetime close to the bulk value $\tau_b = 230$ ps were found in addition to the vacancy defects, and the average lifetime was decreased to 234 ps at 85 K. This behaviour has previously been discussed by Saarinen *et al* (1989), and it is explained by a weak positron localisation at a Rydberg state around a negative ion. When the temperature is increased, the positron is thermally detrapped from the Rydberg state and the average lifetime is increased due to the increased fraction of annihilations in the vacancy defects. A detrapping analysis (Saarinen *et al* 1989, Manninen and Nieminen 1981) of the Si-doped reference sample yielded values of $E_b = 63 \pm 10$ meV for the positron binding energy, and $c_{st} = (2 \pm 1) \times 10^{17}$ cm^{-3} and $\kappa_{st} = 15.7$ ns^{-1} for the concentration of the negative ions and the rate of positron trapping by the Rydberg states, respectively. These values are in good agreement with the hole binding energies to acceptor atoms and with typical acceptor concentrations in heavily n-type GaAs, and they also coincide with the values we have previously obtained (Saarinen *et al* 1989).

In deformed GaAs, the positron average lifetime at 300 K has increased from the reference level 240 ps to 277–348 ps, depending on the degree of deformation and temperature (table 1). The average lifetime has in fact been raised to higher values than the lifetime τ_2 of the trapped positron in as-grown material. This is a clear sign that a large number of vacancy-type defects have been created during the deformation, and also that more extended defects than monovacancies have been formed.

In contrast to the case for the reference samples, three components were necessary to decompose the lifetime spectra in all deformed samples. At room temperature, as seen in figure 1, the second lifetime τ_2 is close to 260 ps with the intensity I_2 typically about 60%. The third lifetime τ_3 is in all samples between 480–500 ps, and its intensity varies from sample to sample ranging between 20 and 40%. Because the two lifetime components τ_2 and τ_3 are much larger than the bulk lifetime 230 ps, they both represent positron annihilations as trapped at open-volume lattice defects. Thus, two different types of vacancy defect are present in the samples after deformation, corresponding to the two lifetimes $\tau_2 = 260$ ps and $\tau_3 = 490$ ps, respectively.

The lower defect lifetime $\tau_2 = 260$ ps is the same as in the as-grown samples, and we can therefore directly relate it to monovacancies in the Ga or As sublattice. The longer lifetime $\tau_3 = 490$ ps has never been observed in as-grown GaAs, and thus it has been formed during the deformation. The lifetime value 490 ps is much larger than expected for mono- or divacancies in GaAs (Corbel *et al* 1988, Puska and Corbel 1988), therefore

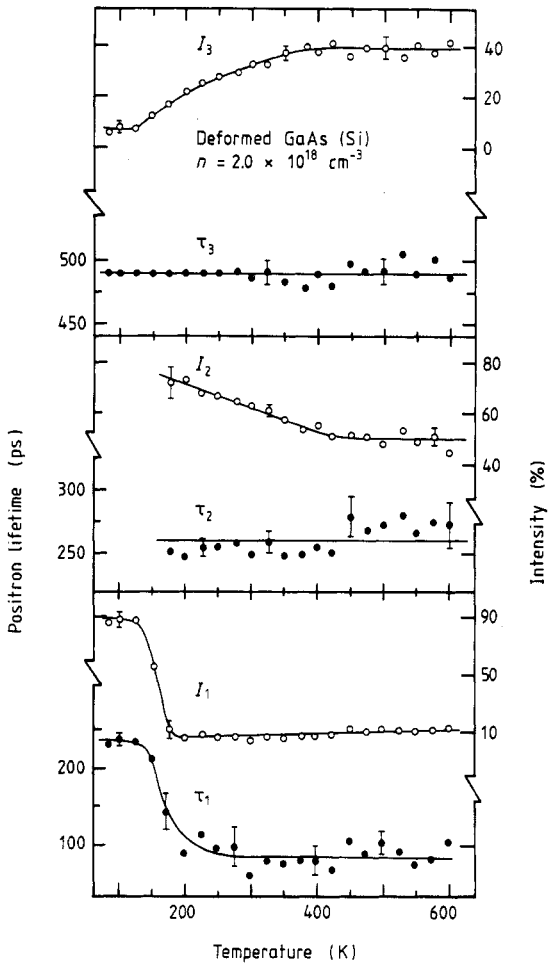

Figure 1. Decompositions of the lifetime spectra in deformed Si-doped GaAs sample 3 ($n = 1.5 \times 10^{18}$ cm^{-3}). The results below 250 K are based on fits with $\tau_3 = 490$ ps fixed.

suggesting that it comes from large vacancy clusters. As 490 ps is a typical value found for voids ($R > 10$ Å) in metals (Hautojärvi 1979, Brandt and Dupasquier 1983), we conclude that small voids with a positron lifetime of 490 ps are formed in the deformation of GaAs. Unfortunately, the positron lifetime in voids is insensitive to their sizes, and thus we have no information on the radius of the voids in GaAs.

Indications of lifetimes around 400 ps have also been found previously in deformed GaAs (Kuramoto *et al* 1973, Uedono *et al* 1985), and the long components have been attributed to positron trapping at dislocations formed in the deformation. We believe that in these earlier works the lifetime spectra were insufficiently decomposed with only two lifetime components, resulting in a mixing of the 260 ps and 490 ps lifetimes in the analysis of the experimental data. The long lifetimes of 400–500 ps in GaAs cannot be explained with positron trapping at dislocations, which in metals normally gives rise to positron lifetimes smaller than the lifetime at the monovacancies (West 1979 and references therein). In addition, using the positron specific trapping rate 5 cm^2 s^{-1} estimated in deformed Si (Dannefaer *et al* 1983), the rate of positron trapping to dislocations in our samples ($c = 10^7$–10^8 cm^{-2}) becomes very small (<0.5 ns^{-1}). We can

thus conclude that only effects related to the point defects and their agglomerates are seen in the positron lifetime experiments.

To compare the concentrations of monovacancies and voids in different samples at 300 K, we have calculated the positron trapping rates at both defects in table 1. For the deformed samples, a two-defect trapping model (West 1979) with defect lifetimes of 260 ps and 490 ps was used. To decrease the statistical error in the analysis of the lifetime spectra, the trapping rates in table 1 are calculated from the fits with the defect components 260 ps and 490 ps fixed.

In as-grown Si- and Se-doped GaAs the rate of positron trapping to vacancies is about 2.5 ns^{-1}. In all the deformed samples κ_{vac} is considerably higher, indicating that the monovacancy concentration has also increased in the deformation. For example, the 12.9% deformation of Se-doped GaAs at 500 °C has created a monovacancy concentration, which is about six times larger than in the as-grown sample. We thus conclude that the deformation increases the monovacancy concentration typically by a factor of three to six, depending on the degree of deformation, temperature and subsequent annealing heat treatment. Using the specific trapping rate $\mu_{vac} = 10^{15}\ s^{-1}$ (Puska *et al* 1989, Mäkinen *et al* 1989) the concentration of the monovacancies after deformation is about (3–6) $\times 10^{17}\ cm^{-3}$ in all samples.

The rate of positron trapping to voids shown in table 1 is typically 5 ns^{-1}. At 300 K the trapping is diffusion limited, and the trapping rate is $\kappa_{void} = 4\pi D_+ R c_{void}$ (Hautojärvi 1979). The positron diffusion constant in GaAs is $D_+ = 1.3\ cm^2\ s^{-1}$ (Saarinen *et al* 1989). If we assume arbitrarily a void radius R = 3–10 Å, we get an order-of-magnitude estimation for the void concentration $c_{void} \sim 10^{15}$–$10^{16}\ cm^{-3}$.

From table 1 some systematic trends in the vacancy and void concentrations can be deduced. The deformation and annealing temperatures in samples 2 and 3 are almost the same, and the only difference is the degree of deformation. We see from the positron trapping rates that when the deformation is increased from 6% to 8%, 5 times more voids and 3.5 times more monovacancies are created. Comparing trapping rates in samples 6 and 7, annealing at 625 °C can be seen to reduce both the vacancy and the void concentration by about 40%.

In n-type GaAs both As and Ga monovacancies can be negatively charged, whereas in p-type and semi-insulating material As vacancies are generally believed to be positive (Bourgoin *et al* 1988, Baraff and Schlüter 1985). Because our GaAs samples remained n-type after the deformation, both V_{As} and V_{Ga} are negative and thus possible candidates for positron traps. The positron lifetime is about 260 ps both in V_{Ga}^{3-} and in V_{As}^{2-} (Corbel *et al* 1989), and hence we cannot use the trapped positron lifetime to identify either the charge state of the vacancy or in which sublattice the monovacancies exist. However, positron lifetime experiments in electron irradiated GaAs have shown that the V_{Ga} anneal out at around room temperature (Corbel *et al* 1989), whereas in our measurements in deformed GaAs no irreversible changes were observed between 300 K and 600 K. This gives us an indirect argument that mainly arsenic vacancies contribute to the positron lifetime in deformed GaAs, and most Ga vacancies are probably annealed out during deformation.

The effects of temperature on the positron lifetime spectrum are studied in figure 1, which shows the lifetime components and intensities in deformed Si-doped GaAs (sample 3). At all temperatures, the lifetimes corresponding to the monovacancies and voids remained constant at values of 260 ps and 490 ps, respectively. To decrease the statistical scattering in τ_1 and τ_2, the data below 250 K were analysed with fixed τ_3 = 490 ps. The second component τ_2 was no longer detectable at temperatures below 175 K.

Although the defect lifetimes 260 ps and 490 ps remain constant over the complete range 85–600 K, large temperature effects are seen in the intensities of the components. The average lifetime changes are about 80 ps from 258 ps to about 340 ps in the temperature interval 85–600 K. In figure 1 this can be seen as a large decrease in the void intensity I_3 from 40% to about 10%. The dominant component at temperatures lower than 150 K is τ_1, which increases and saturates at 230 ps with an intensity of almost 90%.

The increase of τ_1 below 200 K is similar to that observed earlier in as-grown GaAs (Saarinen *et al* 1989). The saturation of τ_1 at low temperatures close to the bulk lifetime 230 ps has been shown to be due to positron localisation at Rydberg states around negative ions. The detrapping from the Rydberg states occurs at higher temperatures; in n-type as-grown GaAs it typically occurs between 100 and 200 K (Saarinen *et al* 1989). In deformed GaAs we see (figure 1) that the detrapping from the negative ions begins at about 130 K, when the lowest component τ_1 starts to decrease from the saturation value 230 ps. The fact that the onset temperatures are the same in both the as-grown and deformed material indicates that the binding energy of the positron and the negative ions is about the same in the two cases, and consequently the origin of the shallow positron traps is probably also the same.

Below 125 K, the annihilations from the bulk state are completely suppressed, and all the positrons annihilate by becoming trapped, to a negative ion, vacancy or void. At this saturation, the intensity ratios of the different lifetime components are directly proportional to the positron trapping rate ratios at the corresponding defect (West 1979). In order to get a good estimate of the trapping rates, the lifetime data were reanalysed with fixed lifetimes of 230 ps, 260 ps and 490 ps. The intensities of the components then became $I_1 = 66 \pm 2\%$, $I_2 = 25 \pm 2\%$ and $I_3 = 8.3 \pm 0.2\%$. By extrapolating κ_{vac} at 100 K from the high temperature (250–600 K) data we obtain from the intensity ratios an estimate for the rate of trapping to the negative ions: $\kappa_{st} = (I_1/I_2)\,\kappa_{vac} = 30\ \mathrm{ns}^{-1}$ at 100 K. This value is two times higher than κ_{st} in the reference sample. Hence we can get an indication that the concentration of the negative ions is also increased in the deformation by a factor of two.

In as-grown GaAs the negative ions acting as shallow positron traps consist of residual acceptors and intrinsic point defects (Saarinen *et al* 1989). Because the impurity concentration of the material is not changed during the deformation, the negative ions formed must be intrinsic point defects. Recently, electron irradiation of semi-insulating GaAs has been shown to create negative ions, which are probably Ga_{As} antisites (Corbel *et al* 1989). We attribute the negative ions in deformed GaAs also to Ga antisites, because As antisites as well as both As and Ga interstitials are usually believed to exist only in positive or neutral charge states (Bourgoin *et al* 1988, Baraff and Schlüter 1985).

In conclusion, we have shown by positron lifetime experiments that voids are formed in the deformation of n-type GaAs. In addition, the concentration of monovacancies is increased from the native population by a factor of three to six, depending on the degree of deformation, temperature and subsequent annealing. The strong temperature dependence of the positron lifetime spectrum also indicates that the concentration of negative ions in deformed GaAs is about twice that in the as-grown material. We attribute this to the formation of Ga_{As} antisite defects during the deformation.

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