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Temperature dependence of positron lifetime in GaAs crystals with defects

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Abstract. Positron lifetime has been measured as a function of temperature in Si-doped GaAs single crystals subjected to various heat treatments. Defects produced by these heat treatments trap positrons. In all the GaAs samples containing defects positron lifetime was found to decrease with temperature in the range from 375 K to 16 K. The decrease is explained as due to the decrease in the trapping rate. The trapping rate is mainly controlled by the diffusion of the positron to the trap. The diffusion constant is determined mainly by the scattering from charged Si impurities.

Keywords. Positron annihilation; lifetime; low temperature; gallium arsenide; defects; trapping model; diffusion.

1. Introduction

Positron annihilation technique can be used for the determination of formation energies of vacancies in metals (Seeger 1973, Siegel 1978). This is based on the following: (i) vacancy-type defects trap positrons, (ii) the trapping rate is dependent on the concentration of defects, and (iii) the annihilation characteristics of trapped positrons are different from those of positrons in the bulk metal. Positrons are also trapped by radiation-induced defects and by dislocations introduced by plastic deformation. The temperature dependence of positron trapping in metals has been investigated for monovacancies (Bergersen and Pajanne 1974), dislocations (Rice-Evans *et al* 1976) and voids (Mantl *et al* 1978, Nieminen *et al* 1979). Positron annihilation studies of defects in semiconductors are not as extensive as in metals. Positron trapping has been observed in radiation-induced defects in Si (Cheng *et al* 1973), Ge (Yeh *et al* 1975) and GaAs (Fabri *et al* 1966), in plastically deformed Ge (Kuramoto *et al* 1974) and GaAs (Kuramoto *et al* 1973), and in heat treated GaAs (Gopinathan *et al* 1977, Bharathi *et al* 1979). The effect of doping on positron annihilation spectra in GaAs has been reported earlier (Gopinathan *et al* 1977, Takai *et al* 1979). Positron annihilation measurements of defects in thermal equilibrium upto very high temperatures in Ge (Tanigawa *et al* 1979) and in GaSb and InSb (Bernardin *et al* 1976) show no change in the annihilation characteristics. Study of the temperature dependence of positron lifetime in defects is of interest in determining the mechanism of trapping.

The present paper reports positron lifetime measurements in Si-doped GaAs single crystals containing defects. Defects are produced in the crystals by various heat treatments. Lifetime measurements were also carried out at various temperatures from 16 K to 375 K in order to study the positron trapping characteristics in these defects.

2. Experimental

Single crystals of Si-doped GaAs of commercial origin, similar to those used by Swaminathan and Copley (1976) were used in the present measurements. The concentration of Si in the crystals was 5×10^{19} atoms/cc. The crystals were sealed in evacuated quartz ampoules for heat treatments. A pair of samples were annealed at 1100°C for 15 min and cooled to room temperature. These were considered to be defect-free and taken as reference samples. All other samples were initially annealed at 1100°C for 15 min and then quenched in water. Following this treatment different pairs of samples were aged at 400° and 700°C for 50 hr. These heat treatments were chosen because the defect structure resulting from these is known (Swaminathan and Copley 1976; Kung and Spitzer 1973, 1974). After heat treatments the crystals were mechanically polished with 1μ diamond paste and then chemically polished in a solution of 50 $H_2SO_4 + 1H_2O_2 + 1H_2O$ at 50°C.

The positron source was prepared from a solution of carrier-free ^{22}Na on a 1·25μ thick nickel foil. The strength of the source was approximately 10 μCi. It was sandwiched between two identically treated crystals. The assembly was mounted on the copper cold-finger of a variable temperature cryostat as shown in figure 1. The temperature of the sample could be varied by passing a suitable current through a heater coil wound around the tip of the cold finger. The temperature was monitored continuously using a platinum resistance thermometer and a thermocouple and was constant to ± 1K during each measurement. The lifetime spectrometer used for the measurements consisted of two detectors of 2·5 cm diameter × 2·5 cm thick NE 111 plastic scintillators mounted on RCA 8575 photomultipliers, two constant fraction discriminators, a time-to-pulse height converter, and a gated multichannel pulseheight analyser. The gating signal for the multichannel analyser was provided by the slow-coincidence between the pulse-height selected outputs from the two detectors.

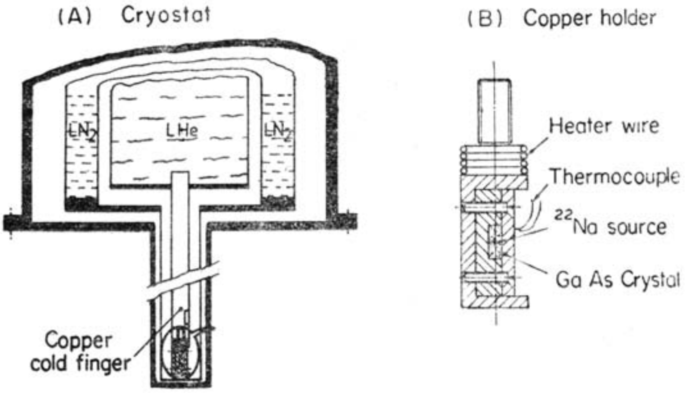

Figure 1. Schematic diagram of the cryostat and sample assembly. For measurements above 77 K the liquid helium in the inner cylinder was replaced by liquid nitrogen.

The prompt time resolution of the spectrometer for the settings used for the present measurements was, full width at half maximum=280 psec and slope=40 psec.

Each spectrum was accumulated over a period of ~12 hrs to give a peak count of ~10^4 or more. A typical lifetime spectrum is shown in figure 2. The data corrected for random coincidences (which were <0·05% at the peak) were analysed by fitting a single exponential function convoluted with a gaussian resolution function (Powell and Macdonald 1972) and the mean lifetime was evaluated. No evidence was found for any long lifetime component due to possible annihilation from positronium-like states (Arefiev *et al* 1976; Dekhtyar *et al* 1978). The upper limit for the intensity of any long lifetime component in the present work is <1%. This was not considered in the analysis given below. Errors due to electronic and temperature drifts were evaluated (Gopinathan *et al* 1979) to be <3 psec and were taken into account.

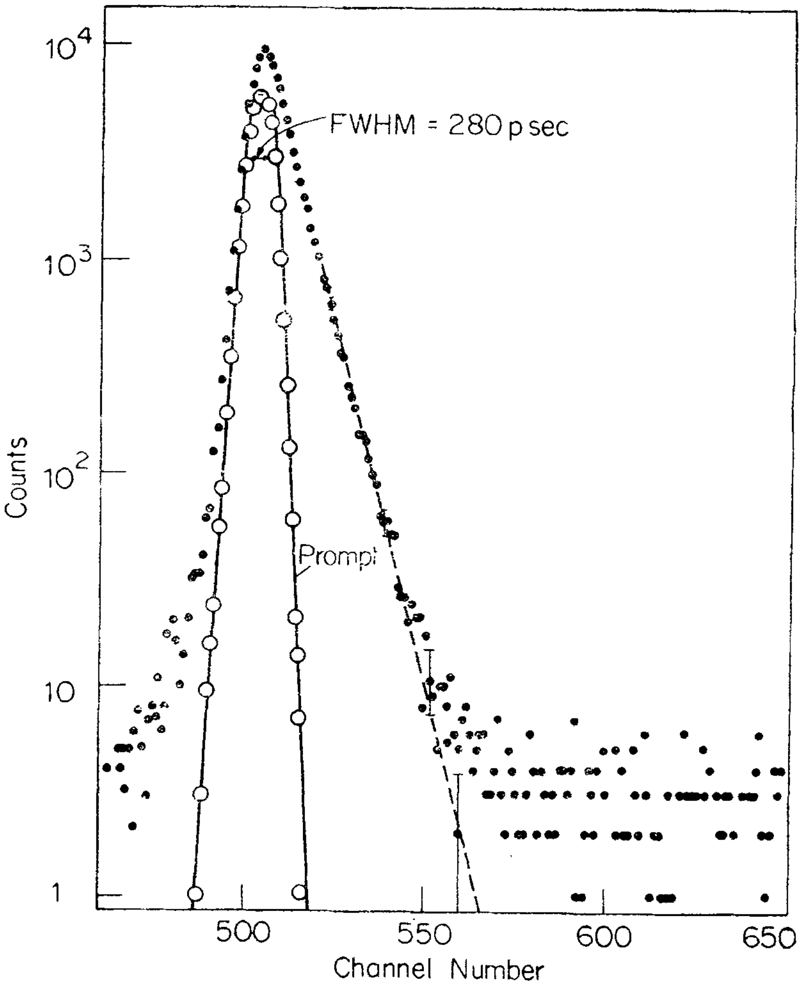

Figure 2. A typical lifetime spectrum of Si-doped GaAs at room temperature. The prompt time distribution using a ^{60}Co source is also shown.

3. Results and discussion

The measured values of positron lifetimes at room temperature and liquid nitrogen temperature in samples subjected to various heat treatments are shown in table 1. Annealing studies in similarly treated Si-doped GaAs crystals have been made earlier by carrier concentration measurements (Kung and Spitzer 1973), local mode vibration studies (Kung and Spitzer 1974), transmission electron microscope observations (Narayanan and Kachare 1974) and yield stress measurements (Swaminathan and Copley 1976). The defect structure of the samples has been determined from a model based on the results of the above studies and the rate equations for the formation of each type of defect (Swaminathan and Copley 1976). The possible positron traps are given in table 1.

3.1 *Defects produced by heat treatment*

Point defects in thermal equilibrium in Si-doped GaAs are vacancy at Ga site, V_{Ga}; vacancy at As site, V_{As}; substitutional Si at Ga site, Si_{Ga}; and substitutional Si at As site, Si_{As}. All these defects are present both in the neutral and charged (ionised) states. There is also evidence for the existence of the $(Si_{Ga}Si_{As})$ defect complex. These defects are retained when the sample is quenched after the anneal at 1100°C for 15 min. Further aging at 400°C for 50 hrs leads to the formation of the $(Si_{Ga}\,V_{Ga})$ complex as shown from local mode vibration measurements (Kung and Spitzer 1974). Microstructure studies on samples aged at 700°C indicated the formation of dislocation loops in the {110} planes, apart from the existence of $(Si_{Ga}V_{Ga})$ complex (Narayanan and Kachare 1974).

One of the samples aged at 700°C in the present work was examined with a transmission electron microscope. Figure 3 shows the micrograph of the sample. The dislocation loops could be clearly identified.

Table 1. Results of positron lifetime measurements in Si-doped GaAs crystals at room temperature and liquid nitrogen temperature.

Heat treatment	Positron trapping defects	Lifetime (psec)	
		Room temp.	Liquid nitrogen temp.
(1) As grown (no treatment)	Prismatic dislocation loops in the {110} planes	243 ± 3	234 ± 3
(2) Annealed at 1100°C for 15 min and cooled	—	232 ± 3	230 ± 3
(3) Annealed at 1100°C for 15 min and quenched in water	V_{Ga}	269 ± 3	252 ± 3
(4) Same as in (3); further aged at 400°C for 50 hrs.	V_{Ga}, $(Si_{Ga}\,V_{Ga})$	261 ± 3	237 ± 3
(5) Same as in (3); further aged at 700°C for 50 hrs.	V_{Ga}, $(Si_{Ga}\,V_{Ga})$, dislocation loops in the {110} planes	263 ± 3	244 ± 3

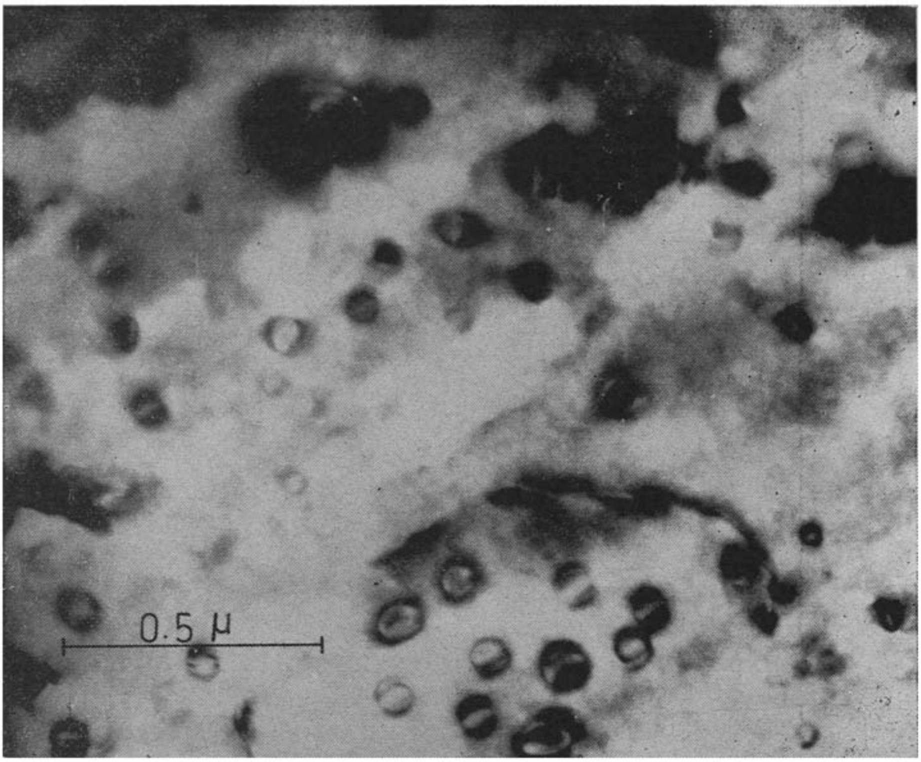

Figure 3. The transmission electron micrograph of the sample aged at 700°C. The dislocation loops are clearly seen in the picture.

3.2 *Positron trapping by defects*

It is known that heavily Si-doped GaAs crystals having [Si] $\gtrsim 4\times 10^{19}$/cc when grown will have prismatic dislocation loops in the {110} planes and extrinsic stacking faults in the {111} planes due to excess Si. These disappear after annealing at 1100°C (Narayanan and Kachare 1974). The disappearance of these structural defects accounts for the decrease in lifetime from 242 psec to 232 psec on annealing. When the sample is quenched after annealing at 1100°C the vacancies at the gallium and arsenic sites, V_{Ga} and V_{As} are retained. Positron trapping at V_{Ga} accounts for the increase in lifetime to 269 psec in the quenched sample. This is corroborated by the recent work of Cheng *et al* (1979) who established positron trapping at V_{Ga} through electron irradiation and annealing studies. Further aging at 400°C and 700°C leads to the rearrangement of a fraction of the point defects to form (Si_{Ga} V_{Ga}) and vacancy type dislocation loops (Swaminathan and Copley 1976). The lifetime in these samples (263 psec) is close to the value in quenched samples. The observed lifetime values at room temperature as given in table 1 are thus qualitatively explainable.

3.3 *Temperature dependence of lifetime*

As can be seen from table 1 all samples containing positron-trapping defects show a decrease in lifetime as the temperature is lowered. The lifetimes measured as a function of temperature in samples aged at 400°C and 700°C are shown in table 2. These are plotted in figure 4 along with the values for an annealed sample. The decrease in lifetime in an annealed defect-free sample is consistent with that due to lattice contraction on cooling (figure 4A). On the other hand the observed decrease in lifetime is much greater than this in samples containing positron-trapping defects (figures 4B and C). This is in contrast with the behaviour in irradiated Si (Brandt and Cheng 1975; Dannefaer *et al* 1976). To explain this temperature variation of lifetime a two-state trapping model (Seeger 1973, 1974; Brandt 1974) is invoked. The mean lifetime, $\bar{\tau}$ is given by

$$\bar{\tau} = \tau_f \frac{[1+\kappa(T)\,\tau_d]}{[1+\kappa(T)\,\tau_f]}, \tag{1}$$

Table 2. Mean positron lifetimes in Si-doped GaAs at various temperatures.

Sample aged at 400°C		Sample aged at 700°C	
Temp. (K)	Lifetime (psec)	Temp. (K)	Lifetime (psec)
375	261 ± 3	300	263 ± 3
359	261 ± 3	269	257 ± 3
330	261 ± 3	225	256 ± 3
300	261 ± 3	181	253 ± 3
211	253 ± 3	136	248 ± 3
181	250 ± 3	116	246 ± 3
135	244 ± 3	81	244 ± 3
86	237 ± 3	69	241 ± 3
		16	236 ± 4

where τ_f and τ_d are the positron lifetime in a perfect crystal and the saturation value of lifetime in a crystal with defects; $\kappa(T)=\sigma_t\, c_t$ is the trapping rate at temperature T; σ_t is the trapping rate per unit concentration of defects and c_t is the defect concentration.

At room temperature a certain fraction of positrons annihilate at defect sites. The decrease in lifetime as the temperature is lowered suggests that the fraction of positrons annihilating at the defect site decreases. This in turn is due to the decrease in the trapping rate, $\kappa(T)$. It now remains to find the trapping mechanism that accounts for this decrease in the trapping rate.

The trapping rate is dependent on the diffusion of the positron to the trap and its transition to the trapped state by overcoming the barrier (Frank and Seeger 1974).

$$\kappa(T)=\frac{4\pi r_0 c_t}{\Omega_A}\left(\frac{1}{D_+}+\frac{1}{k_0 r_0 \Delta r_0}\right)^{-1} \tag{2}$$

where D_+ is the positron diffusion coefficient, k_0 is the rate constant for the capture by the trap, r_0 is the radius of the potential well, Δr_0 is the width of the potential barrier and Ω_A is the atomic volume. From the form of (2) it is clear that the slower of the two processes, *viz.* the diffusion of the positron to the trap and its transition over the potential barrier, determines the trapping rate. The two limiting cases of the trapping process are (i) transition-limited trapping and (ii) diffusion-limited trapping.

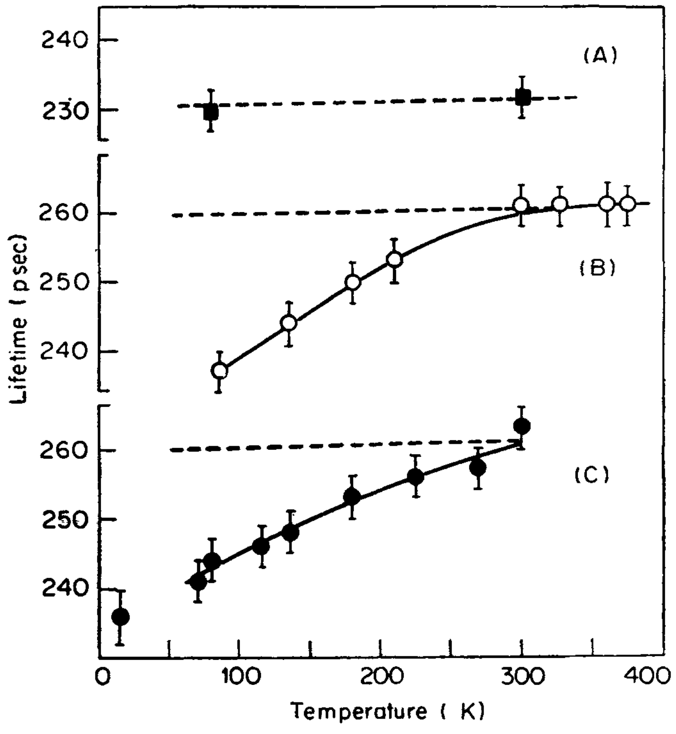

Figure 4. Positron lifetime in Si-doped GaAs as a function of temperature. A sample annealed at 1100°C, B. aged at 400°C and C. aged at 700°C. The dashed lines represent the expected variation based on thermal expansion ($[\alpha]=5\cdot7\times10^{-6}/^\circ\mathrm{C}$). The full lines are the least-squares fit to equation (8).

3.4 *Transition-limited trapping*

For the case of a classical transition-limited trapping process, the rate is

$$\begin{aligned}\kappa(T) &= k_0 \frac{4\pi c_t r_0^2 \Delta r_0}{\Omega_A}, \\ &= \nu_0 \exp\{-\Delta E/(k_B T)\} \frac{4\pi c_t r_0^2 \Delta r_0}{\Omega_A}.\end{aligned} \tag{3}$$

Here ΔE is the barrier height, and ν_0 is the attempt frequency of the positron to overcome this barrier. Combining (1) and (3), the mean lifetime $\bar{\tau}$ is given by

$$\bar{\tau} = \tau_f \frac{[1+C\,\tau_d \exp\{-\Delta E/(k_B T)\}]}{[1+C\,\tau_f \exp\{-\Delta E/(k_B T)\}]}, \tag{4}$$

where $C=(c_t/\Omega_A)\, 4\pi r_0^2 \Delta r_0 \nu_0$. It was found that (4) does not give a good fit to the observed variation of $\bar{\tau}$ with temperature (figure 4), but indicated the value of ΔE to be $\sim$ 0·03 eV.

3.5 *Diffusion-limited trapping*

In this case the trapping rate is given by

$$\kappa(T) = D_+ \frac{4\pi c_t r_0}{\Omega_A}. \tag{5}$$

The decrease of the trapping rate at lower temperatures is due to the decrease of the positron diffusion constant D_+. Positron diffusion in semiconductors is, in analogy with the diffusion of electrons and holes, determined by its scattering from phonons and crystal imperfections (Haug 1972). Positron scattering from acoustic phonons decreases as the temperature is lowered. The analysis based on deformation potential theory leads to a $T^{-1/2}$ dependence for the diffusion constant due to phonon scattering (Bergersen and McMullen 1971). Hence positron scattering from acoustic phonons does not explain the decrease in trapping rate at low temperatures. Scattering from optic phonons is also not important at low temperatures.

It is known that Coulomb scattering from ionised impurities is an important mechanism limiting the low temperature mobility of electrons and holes in semiconductors (Haug 1972). In Si-doped GaAs, the donor level due to Si at Ga site is only 5.8 meV below the conduction band (Brebrick 1975). This implies that these impurities are almost completely ionised at temperatures above 70 K. The diffusion constant due to scattering from these impurity centres is given by the Brooks-Herring formula (see Haug 1972)

$$D_+ = \frac{\beta\,(k_B T)^{5/2}}{e\,N_{\mathrm{ch}}}, \tag{6}$$

where $$\beta = \frac{2^{7/2}\,\epsilon^2}{\pi^{3/2}\,e^3\,(m^*)^{1/2}} \left\{ \ln(1+\xi_0) - \frac{\xi_0}{1+\xi_0} \right\}^{-1},$$

and $$\xi_0 = \frac{6m^*\,\epsilon\,k_B^2\,T^2}{\pi\,\hbar^2\,e^2\,n}.$$

m^* is the effective mass of the positron, ϵ is the dielectric constant ($\epsilon = 11{\cdot}1$ for GaAs), N_{ch} is the density of charged impurities ([Si] $= 5 \times 10^{19}$/cc), and n is the conduction electron density. Combining (5) and (6), the trapping rate can be written in the form

$$\kappa(T) = a(T/300)^{5/2}, \tag{7}$$

where

$$a = c_t \frac{4\pi r_0}{\Omega_A} \frac{\beta}{e\,N_{\mathrm{ch}}} (300\,k_B)^{5/2}$$

is essentially a constant as β varies only very slowly with temperature. In order to examine the validity of this form for $\kappa(T)$, the experimental values of the mean lifetime at various temperatures were least-squares fitted to the equation

$$\bar{\tau} = \tau_f \frac{1 + p(T/300)^q\,\tau_d}{1 + p(T/300)^q\,\tau_f}. \tag{8}$$

The results of the fit are shown in table 3. The fitted functions are plotted in figure 4. The exponent q evaluated from the fit is consistent with the prediction of (7). The parameter p can be identified as a in (7). For the sample aged at 400°C the conduction electron concentration can be taken to be $\sim 10^{18}$/cc (Swaminathan and Copley 1976). Assuming $r_0 \approx 5{\cdot}6$ Å (the lattice constant) and using the value of $p = 0{\cdot}03$ (psec)$^{-1}$ from the least-squares fit, the concentration of traps was estimated to be $c_t = 2{\cdot}5 \times 10^{-5}$. This is of the same order of magnitude as the value given by Swaminathan and Copley (1976). A similar estimate holds good for the sample aged at 700°C also. These results therefore favour diffusion-limited trapping of positrons. The diffusion constant is determined predominantly by scattering from charged impurities.

Table 3. Results of the least-squares fit of the temperature variation of the lifetime to the diffusion limited trapping process (equation 8, § 3.5)

Parameter	Sample aged at 400°C	Sample aged at 700°C
τ_f	235 ± 2 psec	240 ± 5 psec
τ_d	262·9 ± 0·1 psec	267 ± 2 psec
p	0·03 ± 0·01 (psec)$^{-1}$	0·01 ± 0·01 (psec)$^{-1}$
q	3·6 ± 1·0	2·4 ± 1·5
χ^2	0·9	3·2

4. Conclusions

Positron lifetime in Si-doped GaAs crystals subjected to various heat-treatments can be understood in terms of the known defect structure of these samples. The observed decrease of the mean lifetime at low temperatures is explained in terms of the decrease in the trapping rate of positrons. The trapping rate appears to be governed by the diffusion of positrons to the trap. Scattering from charged Si impurities is the main process determining the diffusion constant of positrons.

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