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Defects in semiconductors after electron irradiation or in high-temperature thermal equilibrium, as studied by positron annihilation

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Abstract. We report on positron lifetime studies which investigate vacancy-type defects in elemental and compound semiconductors after electron irradiation or in thermal equilibrium concentrations at high temperatures.

In Si the upper limits of positron lifetimes in monovacancies (272 ps) and divacancies (285 ps) as well as the lifetime in phosphorus–vacancy complexes (~255 ps) are determined after low-temperature electron irradiation and annealing. In addition, the influence of doping on positron trapping and defect annealing is studied.

In electron-irradiated GaAs the annealing between 200 K and 350 K, which is not observed after low-energy irradiation, is ascribed to divacancies or Ga vacancies present in defect complexes. In the annealing processes above 450 K As vacancies disappear. The detection of radiation-induced vacancies is substantially influenced by doping and by the temperature at which measurements are made.

In as-grown GaSb a positron lifetime of 253 ps is found, which increases by about 12 ps on slow-temperature electron irradiation. The annealing occurs in stages at 200 K and 350–500 K.

In Si and Ge the temperature variation of the mean positron lifetime between ambient temperature and the melting points does not exceed a few picoseconds at most. This is in contrast to results in Si recently reported by Dannefaer and co-workers. The present high-temperature results on Si and Ge may be interpreted in terms of a thermal vacancy concentration too low to be detected by positrons. However, an insufficient interaction between positrons and high-temperature vacancies cannot be excluded.

1. Introduction

Positron annihilation studies of atomic defects in elemental and compound semiconductors have developed into a broad field of investigation during the last few years (for recent reviews on specific topics see Dlubek and Krause (1987), Dannefaer (1987)). In the investigation of intrinsic and radiation-induced defects at ambient and low temperatures the positron annihilation technique can provide valuable information due to its sensitivity to vacancy-type defects. This information is useful in addition to that

derived from the 'classical' detection techniques in semiconductors, i.e. electrical conductivity, Hall resistance, electron paramagnetic resonance (EPR), infrared (IR) absorption, and deep level transient spectroscopy (DLTS). Furthermore, in contrast to the 'classical' techniques, positron annihilation is in principle well suited to the study of thermal vacancies at high temperatures, it being successfully applied to the study of metals (Schaefer 1987).

In the present paper we report on recent positron lifetime studies of defects in semiconductors after low-temperature electron irradiation (Si, Ge, GaAs, GaSb) and at high temperatures in thermal equilibrium (Si, Ge).

Studies of compound semiconductors after low-temperature irradiation with electrons of energies below and above the threshold for multiple displacements may provide specific information on vacancy-type defects in the two crystal sublattices (Bourgoin *et al* 1987). Hence, they may also elucidate the structure of intrinsic point defects, like the EL2 in GaAs (Bourgoin *et al* 1988, Meyer *et al* 1986). Based on our previous results on electron-irradiated GaAs (Würschum and Schaefer 1987) the present work aims at a more comprehensive study of irradiation-induced defects in GaAs crystals of different type or doping and after irradiation with various electron energies (§ 3.2). In addition, similar studies have been performed on GaSb, for which the present picture of point defect properties is not nearly as advanced as in GaAs, although GaSb is an important material for opto-electronic devices.

The investigation of vacancy-type atomic defects in the elemental semiconductors Si and Ge has extended over several decades (for an early review see Seeger and Chik (1968)). A general picture of low-temperature vacancy properties in Si was developed by using the results of EPR, IR and DLTS studies (Watkins 1975, 1986, Kimerling 1977; Corbett *et al* 1977; Watkins *et al* 1979). Detailed knowledge about vacancies and their agglomerates is expected from positron lifetime measurements which can provide the specific signatures of these defects (§ 3.1). A reliable determination of the characteristic positron lifetimes of these defects is desirable when analysing the vacancy pattern after heavy-particle irradiation or its development during annealing. Moreover, it appears to be helpful in the investigation of structural elements of disordered semiconductors (Schaefer *et al* 1986; Würschum *et al* 1987).

With regard to high-temperature defects formed in thermal equilibrium concentrations it was concluded from diffusion experiments (Frank *et al* 1984; Frank and Stolwijk 1987) that in Si both thermally formed vacancies and interstitials contribute to the diffusion processes. From the relatively low self-diffusivities in Si and Ge (see Mayer *et al* (1977); Vogel *et al* (1983)) compared to metals it has been suggested two decades ago (Seeger and Chik 1968) that the thermal equilibrium concentrations of intrinsic defects should be rather low.

Experiments to study the thermal equilibrium concentration of, e.g., vacancies, are therefore expected to aid the understanding of high-temperature defect processes. Positron lifetime measurements whose goal was the investigation of high-temperature thermal equilibrium vacancies were recently reported by Dannefaer *et al* (1986). However, the interpretation of the reported data requires extraordinarily high values of the specific positron trapping rate σ and of the formation entropy S^{F}_{1V} of vacancies. This makes the data hard to understand (Schaefer *et al* 1987c). Hence, a careful extension of positron lifetime measurements in Si and Ge up to the corresponding melting temperatures T_M was considered to be desirable. With availability of the MeV positron beam at Stuttgart (Bauer *et al* 1987, 1989) a 'clean' implantation of positrons into the specimen could be combined with the fast $\beta^+\gamma$ coincidence technique (Bauer *et al* 1987). The

data which we obtained on Si and which differ substantially from those published by Dannefaer *et al* (1986) will be discussed together with the results on Ge in § 4.

2. Experimental procedures

The low-temperature electron irradiations ($E_{e^-} = 1.5, 2.5$ MeV; $T_{irr} = 85$–95 K) were performed at the Stuttgart Dynamitron accelerator. The positron lifetime after isochronal annealing was measured with a sandwiched ^{22}NaCl positron source by means of a fast–slow $\gamma\gamma$ spectrometer (time resolution full width at half maximum (FWHM) = 190–200 ps). The experimental details were described recently (Würschum and Schaefer 1987). The present low-temperature irradiation experiments at low electron energies ($E_{e^-} = 520$ keV, see § 3.2) were performed with nitrogen gas cooling in order to minimise the broadening of the electron energy distribution due to electron scattering in the coolant. In addition, thin specimens (thickness 120 μm) were used in order to obtain homogeneous damage.

The positron lifetime studies of Si and Ge at high temperatures were performed using the mono-energetic MeV positron beam of the Pelletron accelerator at the Stuttgart Max-Planck-Institut für Metallforschung. A detailed description of the performance of the positron beam (4 MeV in the present experiments) as well as of the set-up of the positron lifetime spectrometer (time resolution FWHM = 175 ps) using the $\beta^+\gamma$ coincidence was given by Bauer *et al* (1987, 1989). For the high-temperature measurements the specimens were heated by an electron beam in a high-purity graphite crucible positioned in a water-cooled high-vacuum quartz chamber (diameter 35 mm). This chamber was equipped with a Au evaporation layer for heat shielding and with a thin quartz window on top (thickness 0.2 mm) for the incident positron beam.

For the various high-temperature runs on Si and Ge cylindrical specimens were cut from monocrystals (Si: float zone, $\rho \geqslant 30000\ \Omega$ cm, p-type; Ge: Czochralski grown, $\rho \geqslant 50\ \Omega$ cm). The specimen dimensions after chemical polishing (CP4) were at least 12 mm (Ge) or 17 mm (Si) in diameter and 12 mm in height in order to stop the positrons (beam diameter 5 mm (Bauer *et al* 1989)). Temperature measurement and control were by means of two W–W/Re(3%)-thermopcouples which were mounted in the graphite crucible and calibrated at the melting points of Si and Ge.

For the numerical analyses the time resolution functions and the contributions from positron annihilation in the source material ($\gamma\gamma$ coincidence) or outside of the specimen ($\beta^+\gamma$ coincidence, see § 4.1) were determined (Kirkegaard *et al* 1981) using spectra obtained from as-grown semiconductor crystals. These contributions were subtracted from the spectra (containing between 10^6 and 3×10^6 coincidences), which were measured after electron irradiation or in high-temperature thermal equilibrium, prior to one- or two-component analyses (Kirkegaard and Eldrup 1974).

3. Defects in semiconductors after electron irradiation

3.1. Results and discussion on electron-irradiated Si

The annealing behaviour of float-zone (FZ) n-type Si ($\rho = 1300\ \Omega$ cm) after electron irradiation is plotted in figure 1. The mean positron lifetime $\bar{\tau} = 249$ ps after irradiation (figure 1(a)) shows a dip-like annealing at about 170 K and subsequently decreases in annealing stages at $T_a = 480$, 600 and 700 K to attain the value of unirradiated Si ($\bar{\tau} =$

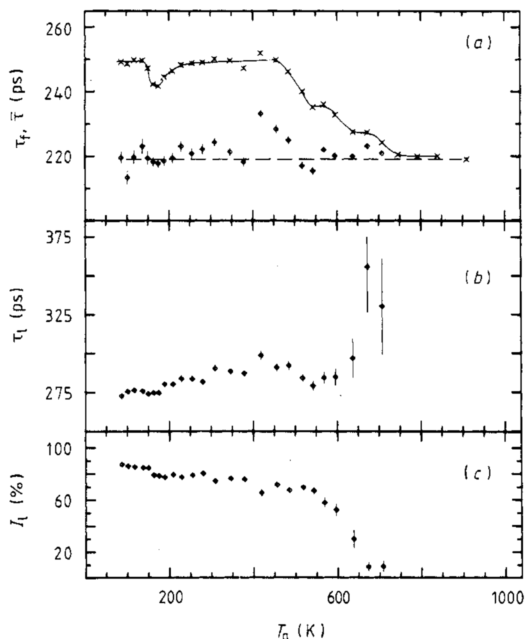

Figure 1. Isochronal annealing of positron lifetimes measured at T_m = 87 K on float-zone, n-type Si (ρ = 1300 Ω cm) after low-temperature electron irradiation E_{e^-} = 1.5 MeV, $\Phi = 6.0 \times 10^{22}$ electrons m^{-2}). Annealing time t_a = 20 min. (*a*) ×××, mean positron lifetime $\bar{\tau}$, and ◇◇◇, free positron lifetime $\tau_f = (I_0/\tau_0 + I_1/\tau_1)^{-1}$ deduced according to the simple two-state trapping model. The broken line indicates the positron bulk lifetime in the non-irradiated state. (*b*) Positron lifetime component τ_1. (*c*) Intensity I_1 of the positron lifetime component τ_1.

219 ps) after annealing at 747 K. From a two-component fit after irradiation, a lifetime τ_1 = 272 ps (figure 1(*b*)) is deduced for positrons trapped in radiation-induced defects. This value increases slightly for T_a = 190–400 K (τ_1 = (285 ± 5) ps) and a value of about τ_1 = 340 ps is observed after annealing above 600 K, where the intensity I_1 decreases (figure 1(*c*)). During annealing the free positron lifetime $\tau_f = (I_0/\tau_0 + I_1/\tau_1)^{-1}$ derived by using the time constants and intensities τ_0, τ_1, I_0, and I_1 of a two-component analysis is rather similar to the bulk lifetime of unirradiated Si specimens (τ_b = 219 ps). This indicates the validity of the simple two-state trapping model (Seeger 1974).

Assuming a production rate $\eta = 2 \times 10^{-28}$ m^2/electron for the vacancy concentration C induced by electron irradiation at T = 85–95 K (Stein and Vook 1967, Kimerling 1977, Watkins 1975), a specific positron trapping rate $\sigma = 5 \times 10^{14}$ s^{-1} may be estimated from $\sigma C = (5.8 \pm 0.4) \times 10^9$ s^{-1} (measurement temperature T = 87 K) which was determined in the as-irradiated state. Similar values may be derived for the trapping rates σ_{e^-} = (5–50) × 10^{14} s^{-1} of electrons in neutral vacancy-type defects (A- and E-centres or divacancies) from the trapping cross sections of electrons of between 10^{-14} and 10^{-15} cm^2 (Brotherton and Bradley 1981, Kimerling 1977, Krynicki *et al* 1979). We would like to point out that the positron trapping rate σ in the small defects that are stable at ambient temperature (mainly divacancies and some larger agglomerates) shows a strong decrease of more than a factor of 10 from 100–200 K (Würschum and Schaefer 1989).

Figure 2 shows the results measured on Czochralski-grown, n-type Si (ρ = 29 Ω cm) with an oxygen concentration of 10^{18} cm^{-3} as determined from IR absorption. In the annealing stage at 170 K (see $\bar{\tau}$, figure 2(*a*)) no significant change of the lifetime of trapped positrons (τ_1 = 275 ps) occurs (figure 2(*b*)). The complete 'annealing-out' of the irradiation-induced defects is shifted slightly towards higher temperatures compared with the float-zone specimen.

In the case of highly phosphorus-doped CZ-Si (n-type, ρ = 0.005 Ω cm), the main annealing of $\bar{\tau}$ (figure 3) starts at lower temperatures (~400 K) compared with lower dopant concentrations (figures 1 and 2). Unconstrained two-component analyses, feas-

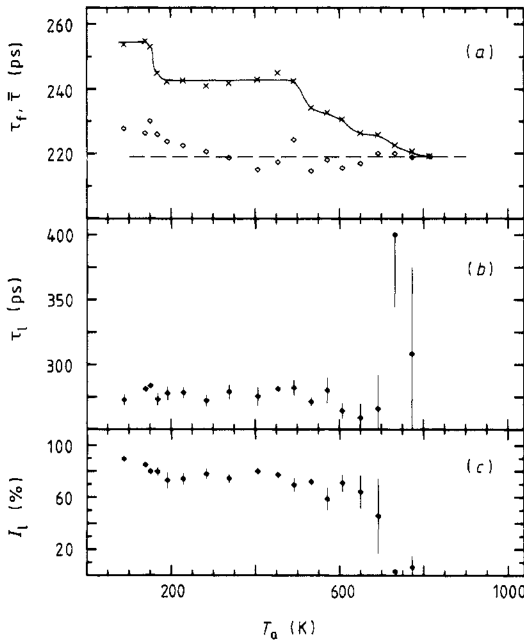

Figure 2. Isochronal annealing of positron lifetimes measured at $T_m = 87$ K on Czochralski-grown, n-type Si ($\rho = 29\ \Omega$ cm) after low-temperature electron irradiation $E_{e^-} = 1.5$ MeV, $\Phi = 5.8 \times 10^{22}$ electrons m^{-2}). Annealing time $t_a = 20$ min. (*a*) ×××, mean positron lifetime $\bar{\tau}$, and ◇◇◇, free positron lifetime $\tau_f = (I_0/\tau_0 + I_1/\tau_1)^{-1}$ deduced according to the simple two-state trapping model. The broken line indicates the positron bulk lifetime in the non-irradiated state. (*b*) Positron lifetime component τ_1. (*c*) Intensity I_1 of the positron lifetime component τ_1.

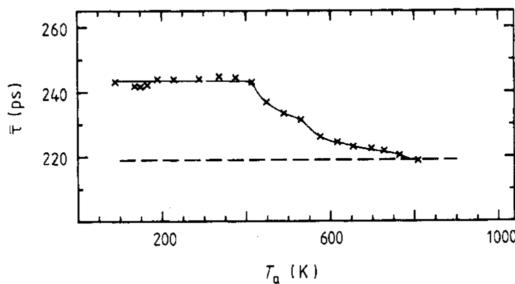

Figure 3. Isochronal annealing of the mean positron lifetime $\bar{\tau}$ measured at $T_m = 87$ K on highly P-doped Si (n-type, $\rho = 0.005\ \Omega$ cm) after low-temperature electron irradiation ($E_{e^-} = 1.5$ MeV, $\Phi = 4.1 \times 10^{22}$ electrons m^{-2}). Annealing time $t_a = 20$ min.

ible for the annealing states between $T_a = 330$ K and 550 K, yield a positron lifetime $\tau_1 \simeq 255$ ps.

It should be pointed out that in highly doped p-type Si ($\rho = 0.005\ \Omega$ cm) positron trapping has been found to be negligible after irradiation ($\Phi = 4.1 \times 10^{22}$ electrons/m^2) as concluded from the unchanged value of $\bar{\tau} = (217 \pm 2)$ ps.

For the *discussion* of the results on electron-irradiated Si we wish to emphasise that the positron lifetime spectra measured in the various annealing states can be well described within numerical uncertainty with a single-lifetime component for the trapped positrons. This indicates the dominance of one type of trap or similar positron lifetimes for coexisting vacancy-type species.

In the *as-irradiated state* divacancies may be present in addition to monovacancies due to the following: secondary displacements (Corbett and Watkins 1965, Krynicki *et al* 1979), thermally activated, charge-state dependent migration of monovacancies (Watkins 1975), or athermal motion of monovacancies (Watkins *et al* 1979, Bourgoin and Corbett 1978) below 90 K during ionising irradiation. Therefore, the lifetime $\tau_1 = 272$ ps observed after irradiation (figure 1) should not be attributed exclusively to

positron annihilation in monovacancies; divacancies may also contribute.

According to the present results positron trapping in radiation-induced defects is negligible in strongly doped p-type Si. This is a manifestation of the sensitivity of the specific trapping rate to the charge state of vacancies. In p-type Si both the monovacancy, with its negative-U properties (Newton *et al* 1983), and the divacancy (Watkins and Corbett 1965, Kimerling 1977) are assumed to exist in positive charge states which are expected to repel positrons.

The *recovery stage centred at 175 K* in FZ-Si (figure 1) coincides with the temperature range in which the annealing of monovacancies in various charge states with activation energies of 0.33 eV or 0.45 eV could be detected by EPR (Watkins 1963) and DLTS (Watkins *et al* 1979). Therefore, the variations of I_1 and τ_1 at about 170 K are attributed to the partial 'annealing-out' of neutral vacancies and their agglomeration to divacancies and small vacancy clusters (Schaefer *et al* 1986, 1987c). Furthermore the migration of negatively charged self-interstitials (I^-) at 170 K (Watkins 1975, Lee *et al* 1976, Frank 1975) may contribute to this annealing stage. A measurable contribution to τ_1 from positron annihilation in monovacancy impurity complexes, e.g., E- or A-centres (see below), may be excluded due to the low carbon and oxygen concentrations and the high specific resistivity of the FZ-Si specimens.

In oxygen-doped Si the decrease of $\bar{\tau}$ and I_1 in the annealing stage at 175 K again indicate the disappearance of radiation-induced vacancies (figure 2). The lifetime τ_1 = 275 ps is unchanged in this stage. Above T_a = 190 K this value of τ_1 is considered as a positron lifetime averaged over oxygen–vacancy complexes (A-centres) formed in the CZ crystal and coexisting small vacancy clusters (divacancies etc). Therefore we conclude that the A-centre, which either exists after irradiation at $T \leqslant 90$ K (Watkins 1975) or which is formed during annealing, may act as a positron trap. This appears to be reasonable due to its off-centre configuration (DeLeo *et al* 1984) and its vacancy-like electronic structure (van Kemp *et al* 1986). The positron lifetime may be similar to or slightly reduced in comparison with that in an 'undecorated' vacancy. Evidence for positron trapping in A-centres has also been reported in the literature, however, with controversial values for the positron lifetime in the trap, i.e., 270 ps (Dannefaer 1987) or (τ_f + 7) ps = 226 ps (Dannefaer *et al* 1989).

Only minor changes of $\bar{\tau}$ were observed in highly P-doped irradiated Si below 420 K (figure 3). This may be explained by the formation of vacancy–phosphorus complexes (E-centres) during irradiation due to migration of negatively charged vacancies (Watkins 1975). These complexes appear to be stable up to 420 K as reported earlier (Kimerling *et al* 1975). The positron lifetime of 255 ps in these complexes (a similar value of 248 ps was measured recently by Moser *et al* (1989)) appears to be substantially smaller than in undecorated vacancies. A contribution to this component from positron annihilation in A-centres or vacancy-agglomerates is assumed to be negligible due to the high concentration ($\geqslant 10^{19}$ cm^{-3}) of phosphorus atoms and their high efficiency of vacancy capture (Stein 1971).

The *annealing of positron traps above 450 K* (see $\bar{\tau}$, figure 1) can be first interpreted in terms of the recombination of mobile interstitials (Frank 1975) or interstitial complexes (Lee *et al* 1972, 1976) with vacancy-type defects. The further agglomeration of vacancy-type defects as indicated by the increase of τ_1 ($T_a \geqslant 570$ K, see figure 1) is due to the migration of divacancies (Watkins and Corbett 1965, Cheng *et al* 1966) and of smaller agglomerates. In the case of O-doping (figure 2) and annealing temperatures above 570 K, multivacancy–oxygen complexes are formed (Lee and Corbett 1976, Corbett *et al* 1977). Their decay above 700 K gives rise to the delayed formation of

Table 1. Specifications, doping and irradiation dose of the GaAs crystals investigated after irradiation with electrons of energy $E_e^- = 1.5$ MeV at 85–95 K (specimen 8: $E_e^- = 520$ keV, $T_{irr} \leq 120$ K). The abbreviations for the growth methods stand for Liquid Phase Epitaxy (LPE), Liquid Encapsulation Czochralski (LEC), and Horizontal Bridgeman (HB), where in the case of the LPE-layers (thickness d) LEC-type GaAs was used as substrate material.

Specimen	Method of growth	Dopant	Carrier concentration (cm^{-3})		Irradiation dose Φ (10^{22} electrons m^{-2})
1	LPE ($d \geq 60$ μm)	—	$\leq 10^{15}$	(n-type)	4.1
2	LEC	—	semi-insulating		5.8
3[a]	LEC	—	semi-insulating		6.0
4	HB	—	$\leq 10^{16}$	(n-type)	8.4
5	LEC	Zn	10^{18}	(p-type)	8.4
6	LPE ($d \simeq 85$ μm)	Sn	$1–4 \times 10^{18}$	(n-type)	4.1
7	HB	Si	$1–4 \times 10^{18}$	(n-type)	5.8
8	HB	Si	$1–4 \times 10^{18}$	(n-type)	7.7 ($E_e^- = 520$ keV)

[a] Würschum and Schaefer 1987.

vacancy clusters as shown by the increase of τ_1 in figure 2(b).

A few comments should be made on the positron lifetimes in electron-irradiated high-purity Si and on how they should be correlated with vacancies and vacancy clusters. The positron lifetime of 272 ps observed in the present experiments and a similar value of 266 ps observed in an earlier study (Fuhs *et al* 1978) is to be ascribed to monovacancies with some contribution from divacancies (see above). After annealing above 190 K, where monovacancies are mobile, a value of $\tau_1 = 285$ ps is observed (see also Fuhs *et al* (1980); Motoko-Kwete *et al* (1989)) which is attributed to positron trapping mainly in divacancies. The higher value of 318 ps reported for this annealing state earlier (Fuhs *et al* 1978) is questionable since the numerical results of the lifetime analysis lead to values of $\bar{\tau} (= \Sigma\, \tau_i I_i)$ and τ_f ($\leq$205 ps) significantly less than the free lifetime (219 ps) of positrons in the defect-free crystal. Above $T_a = 570$ K, where long-range migration of divacancies occurs (Watkins and Corbett 1965), tetravacancies or pentavacancies (Lee and Corbett 1974) are formed with positron lifetimes of about 320 to 350 ps. Therefore, positron traps with $\tau_1 \geq 400$ ps observed, e.g., in amorphous Si (Schaefer *et al* 1986) have to be ascribed to microvoids definitely exceeding the size of tetra- or pentavacancies (Dannefaer *et al* 1976, Dannefaer 1987). The experimental positron lifetimes given here for vacancies and vacancy clusters are in general agreement with theoretical results (Puska 1987, Puska and Corbel 1988).

3.2. Results and discussion on electron-irradiated GaAs and GaSb

In GaAs the annealing of the mean positron lifetime $\bar{\tau}$ was used in a detailed study of defects in specimens of different type and also after low-temperature irradiation with electrons of various energies (see table 1). The results obtained on undoped and doped crystals are shown in figure 4(a) and 4(b), respectively. After annealing treatments at sufficiently high temperatures, measurements at ambient temperature ($T_m = 296$ K) were performed in addition to the low-temperature measurements ($T_m = 87$ K). These measurements show a strong reversible increase of $\bar{\tau}$ with T_m (see Würschum and Schaefer 1987), which is opposite to the trend observed in Si (see § 3.1). This increase with temperature may be caused by de-trapping of positrons from shallow traps (Saarinen

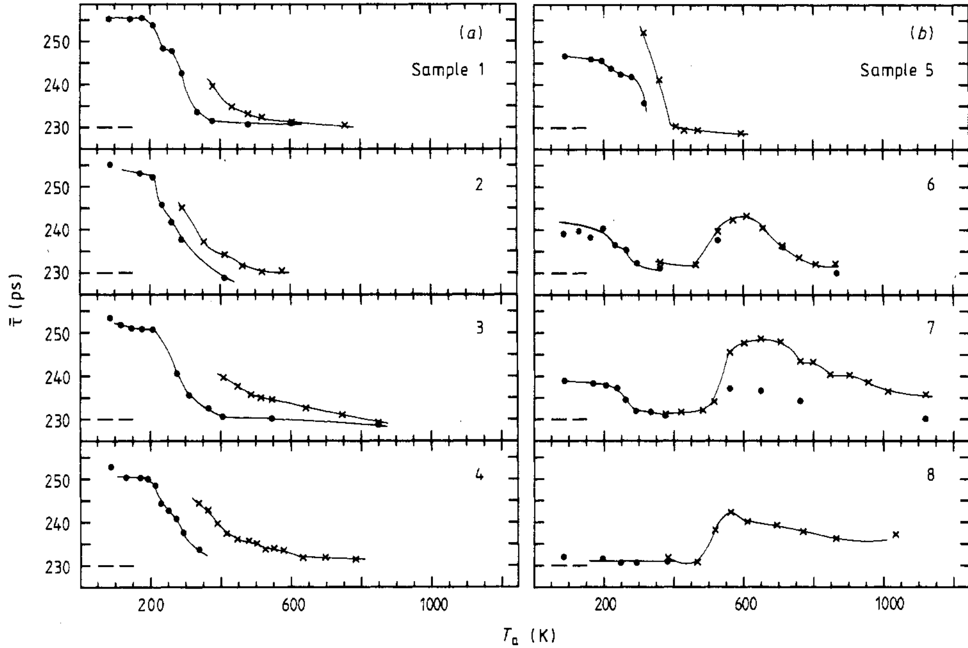

Figure 4. Isochronal annealing of the mean positron lifetime $\bar{\tau}$ measured on (*a*) undoped, and (*b*) doped GaAs-crystals, at T_m = 87 K (● ● ●) and at T_m = 296 K (× × ×) after low-temperature electron irradiation (specimens 1–7: E_{e^-} = 1.5 MeV, specimen 8: E_{e^-} = 520 keV; see table 1 for specimen specification). Annealing time t_a = 20 min. The broken lines refer to the free lifetime τ_f = 230 ps. The numerical uncertainty limits of $\bar{\tau}$ are less than 1 ps.

et al 1989, Krause *et al* 1989, Corbel *et al* 1988) with short positron lifetimes and subsequent trapping in vacancy-type defects which act as strong traps with longer positron lifetimes.

With about the same irradiation conditions, the increase of $\bar{\tau}$ with respect to the free positron lifetime of 230 ps in the as-grown crystal is observed to be higher in undoped GaAs (figure 4(*a*), specimens 1–4) than in doped specimens (figure 4(*b*), specimens 5–7). A main annealing stage occurs between 210 and 350 K for all specimens irradiated with E_{e^-} = 1.5 MeV (specimens 1–7). Two substages are resolved at about 225 K (stage I) and 280 K (stage II) in some of the annealing curves (specimens 1, 4, 5, 6).

The further annealing studied at T_m = 296 K depends strongly on the doping of the crystal. In n-type specimens (figure 4(*b*); specimens 6 and 7) an increase in $\bar{\tau}$ at about 500 K is observed with a subsequent decrease at higher annealing temperatures. In the case of undoped GaAs specimens prepared by different techniques (see table 1) a decrease in $\bar{\tau}$ (T_m = 296 K, figure 4(*a*)) occurs during annealing with substages at 350 K to 450 K (specimens 1–4) and above 550 K (specimens 3 and 4).

For p-type GaAs (figure 4(*b*), specimen 5) the recovery of $\bar{\tau}$ is complete at $T_a \simeq$ 410 K. In a specimen of the same material, no radiation-induced change in $\bar{\tau}$ could be observed at all after irradiation with a lower dose ($\Phi = 2.4 \times 10^{22}$ electrons/m^2 (not included in figure 4)).

After low-energy irradiation (E_{e^-} = 520 keV) of n-GaAs, where a maximum energy $\leqslant$25 eV is transferred to a Ga or an As atom, no recovery in the temperature range of stages I, II is observed; only the typical increase of $\bar{\tau}$ above 500 K (figure 4(*b*); specimen 8) occurs.

In p-type and n-type *GaSb* a mean positron lifetime of (253 ± 1) ps in the unirradiated specimens and a radiation-induced increase of 9 to 12 ps (figure 5) were found. This increase starts to anneal out at approximately 200 K. The annealing continues in a main stage between 350 and 500 K.

The *discussion of the results on GaAs* will follow the lines developed earlier in our investigations on semi-insulating GaAs (Würschum and Schaefer 1987).

The partially resolved substages at 225 K (I) and 280 K (II) coincide with those observed in electrical resistivity and Hall coefficient measurements (Thommen 1970). Furthermore, it can be shown that the annealing behaviour of $\bar{\tau}$ up to $T_a \simeq 300$ K (specimens 1 and 4) may be well described by the activation energies 0.72 eV (stage I) and 0.83 eV (stage II) as well as first order kinetics as reported by Thommen (1970). As concluded from the low-energy irradiation experiment where no annealing below 400 K was detected (figure 4(*b*), specimen 8) the defects annealing-out up to 300 K appear to require a higher displacement threshold energy ($E_{th} \geqslant 20$ eV) compared to the defects annealing-out above $T_a = 500$ K ($E_{th} \simeq 10$ eV (Pons and Bourgoin 1981)). The higher displacement energy of the low-temperature defect (see figure 4(*b*), specimens 7 and 8) suggests that in stages I and II annealing processes occur which either involve divacancies or other complex defects formed by multiple displacement. Pons and Bourgoin (1985) have proposed that in stages I and II defect complexes containing a Ga vacancy (e.g. V_{Ga}–Ga_{As}) transform into vacancy-type defects on the As sublattice which anneal out at higher temperatures. This would be consistent with the observation that the concentration of defects stable up to 500 K increases after the annealing in stages I and II (Rezazadeh and Palmer 1985, Guillot *et al* 1981). The decrease of the radiation-induced change in $\bar{\tau}$ with doping (see figures 4(*a*), (*b*)) may indicate an increased contribution from positron annihilation in the surrounding of dopant atoms, which may act as shallow traps with a positron lifetime near τ_f.

The increase of $\bar{\tau}$ in n-GaAs above 500 K (figure 4(*b*), specimens 6–8), which was earlier observed by Stucky *et al* (1986) after low-dose electron irradiation, can be well understood in terms of a partial recombination of As Frenkel pairs, V_{As}–I_{As} (Pons and Bourgoin 1985). This raises the Fermi level so that the residual As vacancies attain a charge state attractive for positrons (Stucky *et al* 1986). The observation that no annealing can be detected below 450 K after low-energy electron irradiation (figure 4(*b*), specimen 8) supports the idea that the positron traps being annealed above this temperature have to be considered as simple defects (V_{As}). These As vacancies subsequently anneal out at above 500 K (see Würschum and Schaefer 1987).

Annealing in the temperature range 300–400 K was observed in the present lifetime studies in undoped and p-type GaAs, but not in n-type material. This has also been detected in p-GaAs by measurements of the Hall coefficient, of the electrical conductivity (Aukerman and Graft 1962) and by DLTS (Kamada and Ando 1988; Guillot *et al* 1981). The defects and small complexes annealing in this temperature range may be partly formed during annealing at lower temperatures (Guillot *et al* 1981) or may be generated due to an athermal, doping-dependent mobility of As interstitials (I_{As}) during irradiation (Stievenard *et al* 1986). Furthermore, as known from DLTS these defects exhibit rather different annealing kinetics (Kamado and Ando 1988, Stievenard *et al* 1986), which strongly depend on their charge states (Kamada and Ando 1988). Yet a detailed defect identification is still lacking. The present positron lifetime measurements, however, give evidence that vacancy-type defects are involved in these recovery processes.

No annealing can be detected by positrons in p-GaAs after high-dose electron irradiation and annealing above 400 K (figure 4(*b*), specimen 5) or after low-dose

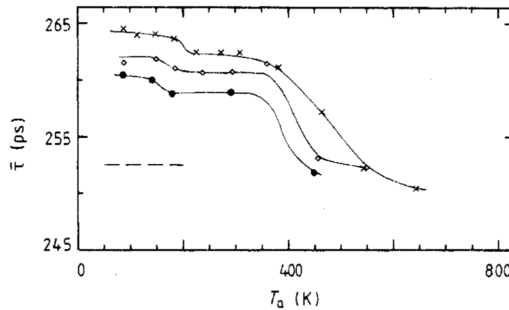

Figure 5. Isochronal annealing of the mean positron lifetime $\bar{\tau}$ measured on GaSb at T_m = 87 K after low-temperature electron irradiation. Annealing time t_a = 20 min. Undoped GaSb (p-type, 1×10^{17} cm^{-3}): ×××, E_e^- = 2.5 MeV, $\Phi = 4.9 \times 10^{22}$ electrons m^{-2}; ●●●, E_e^- = 1.5 MeV, $\Phi = 5.8 \times 10^{22}$ electrons m^{-2}. Te-doped GaSb (n-type, 3×10^{17} cm^{-3}): ◇◇◇, E_e^- = 1.5 MeV, $\Phi = 5.8 \times 10^{22}$ electrons m^{-2}. The broken lines refer to the non-irradiated state. The numerical uncertainty limits of $\bar{\tau}$ are less than 1 ps.

irradiation. In these cases all defects are in positive charge states with the Fermi level positioned in the vicinity of the valence band edge.

The *annealing of* $\bar{\tau}$ *in electron-irradiated GaSb* observed at 200 K and predominantly above 350 K (figure 5) may be identified with the recovery stages II, III (T_a = 163, 203 K) and IV ($T_a \geqslant 350$ K), respectively, as were reported earlier in studies of the Hall coefficient (Thommen 1967). In addition, irradiation-induced defects in GaSb that are stable up to ambient temperature have been observed more recently by DLTS (Murawala *et al* 1986). A large width of the main recovery ($T_a \geqslant 350$ K, see figure 5 and Thommen (1967)) and a displacement threshold energy of the corresponding defects that is higher than for the defects annealing-out at lower temperatures was observed (Thommen 1968). We therefore conclude that various complex vacancy-type defects anneal out above 350 K.

In Hall coefficient measurements on GaSb (Thommen 1967) after electron irradiation, an annealing stage at 122 K (stage I) was observed. This stage was tentatively attributed to the recombination of Sb Frenkel pairs due to the first-order annealing kinetics (Thommen 1967) and the variation with the crystallographic direction of the electron irradiation (Thommen 1968). The present observation that no significant change of the mean positron lifetime occurs in stage I may again indicate the role of the charge state of defects on the positron trapping process, as in the cases of GaAs (see above) and Si (§ 3.1).

4. High-temperature thermal equilibrium studies on Si and Ge

4.1. Experimental results

In an initial run, the experimental set-up and the positron lifetime measurements at the MeV positron beam (Bauer *et al* 1989) were tested by performing positron lifetime measurements on Al at various temperatures in the same geometrical set-up as for the elemental semiconductors. A positron lifetime component τ_1 = (166 ± 2) ps with I_1 = 72% at T_m = 296 K, τ_1 = (249 ± 3) ps with I_1 = 84% at T_m = 873 K, as well as an increase of τ_1 by 11 ps upon melting (τ_1 = (260 ± 2) ps, I_1 = 86% at T_m = 1173 K) was derived

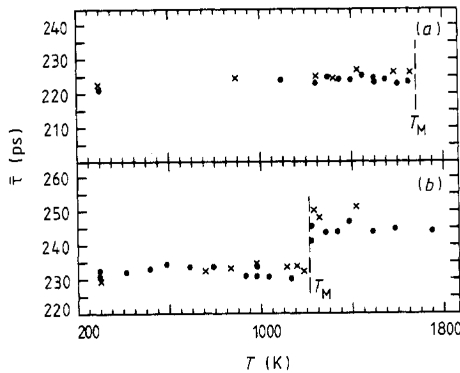

Figure 6. Temperature variation of the mean positron lifetime $\bar{\tau}$ measured on Si and Ge in two independent measuring runs after subtracting positron annihilation events occurring outside of the specimens (see text). (*a*) Si, and (*b*) Ge; ● ● ●, run 1; × × ×, run 2.

from three-component analyses. This is in good agreement with the positron lifetimes in Al obtained by the $\gamma\gamma$ technique (Schaefer *et al* 1987b, Eckert and Schaefer 1989). The two long-lived components ($I_2 + I_3 \simeq 16\%$; $\tau_2 \simeq 580$ ps, $\tau_3 \simeq 1660$ ps) which appeared in the spectra in addition to the τ_1-component can be well separated due to the low background (Bauer *et al* 1989). They mainly originate from positrons annihilated in the surroundings of the specimen, e.g., due to scattering into the quartz chamber.

In the high-temperature measurements on Si and Ge, the spectra were analysed by three-component fits yielding a short-lived component τ_1 and long-lived components τ_2 and τ_3. The main component τ_1 has to be attributed to the mean lifetime $\bar{\tau}$ (see figure 6) in the measuring specimen. This was confirmed by measurements on a large Si specimen outside the vacuum chamber at room temperature where the same value of $\bar{\tau}$ as in figure 6 was derived from a spectrum containing only minor long-lived contributions ($I_2 < 5\%$). The additional contributions in the high-temperature spectra originating from positrons annihilated outside of the specimen ($I_2 + I_3 \simeq 15\%$; $\tau_2 \simeq 370$ ps, $\tau_3 \simeq 1520$ ps) could be separated accurately and were subtracted from the spectra measured in the various runs prior to numerical analysis (see § 2).

The temperature variation of the mean positron lifetime in both Si and Ge is shown in figure 6. Each high-temperature run includes at least one heating and one cooling cycle. In Si the mean positron lifetime appears to increase between ambient temperature and the highest measuring temperature by 2–4 ps at most.

In the case of Ge a similar situation prevails as in Si with respect to the measurements in the solid state. Only a slight increase of the mean positron lifetime could be observed between ambient temperature and T_M on two specimens (figure 6). At the solid–liquid transition (T_M), a reversible increase of $\bar{\tau}$ by about 12 ps occurs. No significant temperature variation of $\bar{\tau}$ was observed in molten Ge up to the highest measuring temperature ($T_{max} = 1723$ K, see figure 6).

For an assessment of positron lifetimes in lattice vacancies in Ge, additional measurements were performed after low-temperature electron irradiation (see § 2, $E_{e^-} = 2.5$ MeV, $\Phi = 4.9 \times 10^{22}$ electrons/m^2) on the same type of material as used for the high-temperature studies. Before irradiation, a positron lifetime $\bar{\tau} = 231$ ps characteristic of annihilation in the free state in Ge was observed. After irradiation a single lifetime component $\bar{\tau} = 279$ ps was detected at $T_m = 87$ K which can be attributed to saturation trapping of positrons in irradiation-induced vacancies.

4.2. Discussion

The reliability of the positron lifetime data presented here is convincingly demonstrated by quantitatively reproducing the high-temperature increases of $\bar{\tau}$ measured earlier by the $\gamma\gamma$ technique in solid Al (Schaefer *et al* 1987a), in solid In (Weiler and Schaefer 1985) and the increase of $\bar{\tau}$ upon melting of Al (Eckert and Schaefer 1989).

The rather small variation of $\bar{\tau}$ in *Si* between $T_m = 296$ K and the highest measuring temperature $T_m = 1658$ K is in obvious contrast to the data of Dannefaer *et al* (1986) who reported an increase of $\bar{\tau}$ by about 40 ps between 1370 K and 1470 K. Although the positron lifetime measurements in the present study were extended to even higher temperatures than in the work of Dannefaer *et al* (1986), no indication of positron trapping at thermally formed vacancies could be detected (see figure 6).

If we ascribe our present results in Si to a linear temperature increase of the free positron lifetime $\tau_f = \tau_{f0}(1 + \alpha T)$ we obtain a temperature coefficient $\alpha \simeq 10^{-5}\,K^{-1}$ which is considerably lower than in metals (Stott and West 1978, Schaefer *et al* 1987b). This may be correlated with the much smaller thermal expansion of Si (Okada and Tokumaru 1984) compared with that of metals.

Various interpretations may be considered for the observation that no positron trapping due to high-temperature thermal formation of vacancies can be detected in Si.

(i) The high-temperature thermal equilibrium concentration of vacancies lies below the limit of detection by positrons. Considerable evidence indicates that self-diffusion in Si is controlled by vacancies as well as by self-interstitials with the latter being the dominant self-diffusion vehicle above 1270 K (for reviews see Frank *et al* (1984), Frank and Stolwijk (1987)). It is therefore difficult to deduce quantitative information on vacancy properties from tracer self-diffusion studies in Si. However, from diffusion studies of Au in Si, an uncorrelated self-diffusivity due to monovacancies

$$D_V^{SD} = D_V C_V \simeq 0.57 \times 10^{-4} \exp(-4.03\,eV/kT)\,m^2\,s^{-1} \tag{1}$$

may be estimated (Frank *et al* 1984). Here D_V and C_V denote the diffusivity and atomic concentration of monovacancies in thermal equilibrium, respectively, and k is the Boltzmann constant.

If we assume that the low-temperature value of the vacancy migration enthalpy $H_{1V}^M \leqslant 0.5$ eV (Watkins *et al* 1979) is valid at high temperatures, an upper limit of $C_V(T_M) < 10^{-8}$ may be given if the vacancy formation entropy S_{1V}^F does not exceed a value of $6k$. With a specific trapping rate σ of positrons in vacancies of the order of 10^{15} s^{-1}, which is typical for metals (Schaefer *et al* 1987) and which has been estimated for radiation-induced vacancies in Si at low temperatures (§ 3.1), this maximum concentration of vacancies would definitely lie below the detection limit of the positron annihilation technique. A reliable detection of thermal vacancies by positrons is expected for $C_V(T_M) \geqslant 10^{-6}$ and the above value of σ. Together with $S_{1V} = 6k$ and equation (1) this would require a rather high vacancy migration enthalpy $H_{1V}^F \geqslant 1.2$ eV at high temperatures and an even higher value for smaller values of S_{1V}^F.

(ii) Is the equilibration process too slow? Tan and Gösele (1985) suggested a vacancy diffusivity

$$D_V = 0.1 \times 10^{-4} \exp(-2\,eV/kT)\,m^2\,s^{-1} \tag{2}$$

and a vacancy formation enthalpy $H_{1V}^F \simeq 2$ eV. This would lead to an extremely slow equilibrium process, i.e., a slow filling-up of the dislocation-free specimen with vacancies generated at the surface, which would hamper the experimental detection of thermal

vacancies. Another argument may, however, contradict this. If we assume that the thermal concentration of vacancies may be attained at high temperatures during the production process of the silicon crystals, these vacancies with a small diffusivity would agglomerate into clusters during cooling. These clusters in their turn may act as vacancy sources during repeated heating. Hence the equilibrium vacancy concentration can, indeed, be attained within reasonable times.

Nevertheless, high-temperature lifetime measurements on specimens with a high density of vacancy sources (dislocations and surfaces) may help to clarify whether a slow equilibration process is the reason for there being no detection of positron trapping in Si at high temperatures.

(iii) Do positrons interact efficiently with vacancies at high temperatures? Thermally activated de-trapping of positrons from vacancies may occur at high temperatures if the positron–vacancy binding energy does not suffice for a tight binding of positrons during the positron lifetime. Experimental evidence for thermal de-trapping was deduced from measurements on Cu (Schaefer *et al* 1987b). Assuming a positron vacancy binding energy lower than 1.7 eV as theoretically predicted for various charge states of vacancies in Si (Puska 1987), the corresponding positron de-trapping rates are expected to exceed the positron trapping rate σC at high temperatures. This would be the case even for a low value of $H^{\mathrm{F}}_{\mathrm{1V}}$ as suggested by Tan and Gösele ((1985), see above). In this case or if the positron lifetime is reduced due to a configurational relaxation of the vacancy at high temperatures (Seeger and Chik 1968), we cannot exclude the possibility that high-temperature vacancies are not detected even if they are formed in substantial concentrations. A decrease of the positron–vacancy interaction at high temperatures due to a decrease of σ to a value far below that in metals is unreasonable due to the high density of conduction electrons in Si at high temperatures.

In solid *Ge*, as in the case of Si, no high-temperature increase of the positron lifetime due to positron trapping at thermally formed vacancies has been observed. This is in agreement with earlier angular correlation studies of the annihilation radiation in Ge up to T_{M} (Tanigawa *et al* 1979) and with the very slight increase of the mean positron lifetime between 295 K and 1050 K as reported by Schultz and MacKenzie (1982). Moreover, no indication of vacancy formation could be deduced from the temperature variation of the positron diffusivity D^+ at high temperatures (Jorch *et al* 1981).

In the discussion of our results we should mention that the self-diffusion in Ge is governed by a vacancy mechanism (Frank and Stolwijk 1987). From diffusion experiments (Vogel *et al* 1983) the tracer diffusivity

$$D^{\mathrm{T}}_{\mathrm{V}}(T) = 2 \times 10^{-3} \exp(-3.14\ \mathrm{eV}/kT)\ \mathrm{m}^2\ \mathrm{s}^{-1} \tag{3}$$

was derived. From Cu precipitation experiments in Ge after quenching, Hiraki (1966) estimated the thermal equilibrium vacancy concentration to be

$$C_{\mathrm{V}}(T) = 4.2 \exp(-1.9\ \mathrm{eV}/kT). \tag{4}$$

This has to be considered as an upper limit. Equation (4) yields a value $C_{\mathrm{V}}(T_{\mathrm{M}}) = 5 \times 10^{-8}$ which again is expected to lie below the detection limit of the positron annihilation technique. It should be pointed out that equations (3) and (4) imply a rather high vacancy migration enthalpy in Ge of about 1.2 eV. If this is lower, then an even smaller thermal equilibrium concentration would result from equation (3).

However, in the discussion of the temperature behaviour of $\bar{\tau}$ in Ge, a small and therefore insufficient high-temperature interaction between a positron and a vacancy

cannot be excluded, as in the case of Si. In this case thermal vacancies could not be detected even if they were formed in higher concentrations.

At the solid–liquid transition in Ge, an increase of $\bar{\tau}$ by about 12 ps is observed although the specific volume decreases. This increase is ascribed to positron annihilation in free volumes of the size of one or a few missing atoms. The free volume of this size may be stabilised over the positron lifetime by the repulsive interaction between the positron and the positive ion cores. No larger free volumes could be detected in the present positron lifetime measurements, presumably because they are not stable during the positron lifetime due to fast atomic fluctuations. A more detailed discussion, together with the results of positron lifetime measurements in metallic melts (Eckert and Schaefer 1989), will be given elsewhere (Schaefer *et al* 1989).

5. Conclusions

The results from positron lifetime studies at 87 K in elemental and compound semiconductors after electron irradiation or in high-temperature thermal equilibrium can be summarised as follows:

(i) Positron lifetimes of 272 ps (after irradiation) and 285 ps (after annealing at 190 K) are observed in FZ-Si. They are attributed mainly to monovacancies and divacancies, respectively, presumably with contributions from small vacancy clusters. The specific trapping rate of positrons at monovacancies is estimated to be $\sigma = 5 \times 10^{14}\ s^{-1}$ at 87 K. The trapping rate of divacancies appears to decrease with increasing measurement temperature. The positron lifetime in phosphorus–vacancy complexes (E-centres) is determined to be about 255 ps. In oxygen-doped electron-irradiated Si, the formation of larger vacancy clusters is delayed until higher annealing temperatures (750 K) than in high-purity Si due to oxygen–vacancy interactions.

(ii) In electron-irradiated GaAs the annealing of positron traps between 200 and 350 K is ascribed to Ga vacancies in a defect complex or to divacancies. The generation of these defects, which is shown to be suppressed at low irradiation energies, requires a higher displacement threshold energy than the positron traps which anneal out above $T_a = 500$ K. The annealing above 500 K is attributed to the disappearance of As vacancies. Positron trapping in radiation-induced defects can be suppressed by p-type doping.

After electron-irradiation of GaSb, annealing stages of vacancy-type defects are observed at 200 K and at 350–500 K.

(iii) A nearly constant temperature behaviour of the mean positron lifetime is measured in both Si and Ge between ambient temperature and the melting temperatures. The observation that no high-temperature vacancy formation was detected may be due to a rather low thermal vacancy concentration near the melting temperatures. However, a weak interaction which is insufficient for the detection of vacancies by positrons at high temperatures cannot be excluded.

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