Influence of defects and temperature on the annihilation of positrons in neutron-irradiated silicon*

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Positron-annihilation lifetime spectra have been obtained from neutron-irradiated silicon. Isochronal annealing shows that positrons trapped in divacancies have a lifetime of 325 ± 20 psec and in quadrivacancies, a lifetime of 435 ± 30 psec. From this a positron lifetime of 270 psec is predicted for monovacancies. Divacancies are found to anneal out according to a second-order process with an activation energy of 0.8 ± 0.1 eV. Breakup of divacancies is found to follow a first-order process with an activation energy of approximately 1.7 eV. The positron trapping cross section for divacancies varied with temperature approximately as $T^{-2.5}$, which is in good agreement with theoretical calculations based on the cascade capture model of the electron capture cross section. At 296°K the positron capture cross section was estimated to be about 4×10^{-16} cm^2.

I. INTRODUCTION

Positron-annihilation studies in silicon[1-3] and germanium[4] have shown that defects created by irradiation act as traps for positrons, as inferred from the observation that the mean lifetime of the positrons increases with radiation dose. Brandt and Cheng[3] found in electron-irradiated silicon that the mean lifetime increased with decreasing temperature which they interpreted, on the basis of the trapping model, as being due to a temperature-dependent detrapping rate. In deformed germanium, Kuramoto *et al.*[6] succeeded in separating the bulk lifetime from a longer lifetime which they attributed to annihilation of positrons trapped at dislocations. The effect of doping with different impurities is not clear since Sen and Sen[7] found a small dependence of the positron lifetime on the doping while Dorikens *et al.*[8] did not observe any such dependence.

In this paper we will report results from positron-lifetime studies of isochronal annealing of neutron-irradiated silicon and also of the temperature dependence of the lifetime spectra. For the first time the defect and bulk lifetimes have been separated, thus providing a more detailed picture of the annihilation characteristics. This is a promising development since the positron technique can then complement the more traditional microscopic techniques such as EPR and optical spectroscopy.[9]

II. EXPERIMENTAL

High-purity dislocation-free single crystals of p-type silicon (1900 Ω cm) with less than 10^{14} oxygen atoms per cm^3 were irradiated simultaneously with 2.2×10^{17} thermal neutrons per cm^2 and 4.0×10^{-15} fast neutrons per cm^2 at about 30 °C. After cutting and polishing, the crystals were etched in a solution of HF and HNO_3. The isochronal anneal was performed in an oil bath regulated to within $\frac{1}{2}$ °C in the temperature range 70–220 °C. A furnace was used for the annealing at higher temperatures, with the same accuracy. The annealing time for each temperature was 20 ± 0.2 min. The positron measurements were made at a temperature of 23 °C on the annealed samples using a ^{22}NaCl positron source of strength 1.5 – μCi deposited on 0.28-mg/cm^2 Al foil. In the lifetime spectra this source gave a background-to-peak ratio of 5×10^{-5}. For the low-temperature measurements a variable-temperature cryostat, with a temperature regulation better than ±$\frac{1}{2}$ °C, was used. A 20-μCi source was used in order to compensate for the increased separation of the detectors. The lifetime spectrometer had a time resolution of 320 psec at full width at half-maximum and each lifetime spectrum contained about 1.3×10^6 counts, accumulated during a time period of 20 h. Further details of the lifetime spectrometer are to be found in Ref. 10.

The lifetime spectra were analyzed using the program POSITRONFIT.[11] A source correction was applied and was determined from measurements on well-annealed Si crystals, by making the reasonable assumption that only one lifetime is present in perfect Si (the so-called bulk lifetime). Any further components in the observed spectrum are defined as source components. The relative intensity of the source corrections amounted to 0.50% and 3.5% for the weak and strong sources, respectively.

III. RESULTS

The results of the isochronal annealing experiments are shown in Figs. 1 and 2. The bulk lifetime was determined from a preirradiated crystal

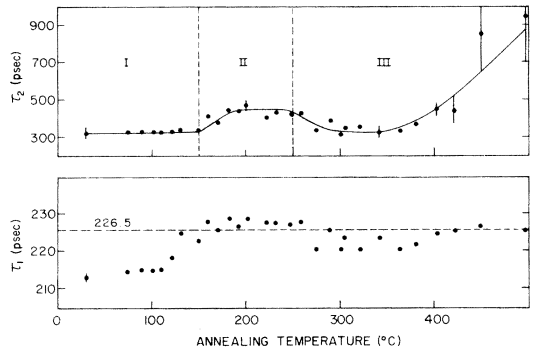

FIG. 1. Lifetimes τ_1 and τ_2 measured after 20-min isochronal anneals. The measuring temperature was 23 °C. The vertical dotted lines in the panel for τ_2 separate the annealing stages I, II, and III (see text). The bulk lifetime is indicated by the broken line.

as well as from four different sets of irradiated crystals annealed for 1 h at temperatures of 500, 750, 1000, and 1250 °C. A mean value of 226.5 ± 1.0 psec was determined, and is indicated in Fig. 1 by the broken line in the panel for τ_1.

On the basis of the behavior of both the lifetime τ_2 (Fig. 1) and the intensity of this component I_2 (Fig. 2), we divide the annealing range into three stages, designated arbitrarily as I, II, and III. Stage I (30–150 °C) is characterized by a nearly constant value of $\tau_2 \simeq 325$ psec and a large decrease of I_2 from 24% to 7%. Stage II (150–250 °C) is characterized by τ_2 having a new, approximately constant level at ≃435 psec. Stage III (250–420 °C) is characterized by a decrease in τ_2 and at about 340 °C the same value is again obtained as in stage I. I_2 increases and reaches a maximum at about 340 °C. In Fig. 2 is also shown the intensity I_3 of a third component with a lifetime τ_3, of approximately 4 nsec (not shown). The intensity of this component is very small (<0.2%) and was only found in the temperature range 90–300 °C.

The temperature dependence of the lifetime parameters for an unannealed irradiated sample

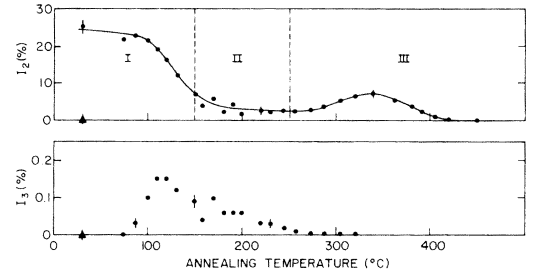

FIG. 2. Isochronal anneal (20 min) of the two intensities I_2 and I_3 of the lifetimes τ_2 and τ_3. The triangles show a measurement on a post-irradiated sample.

is shown in Fig. 3, as investigated in the temperature range 88–296 °K. With increasing temperature a slight increase in the lifetime τ_2 is observed, while its intensity I_2 decreases significantly. The curve shown in the panel for τ_1 is calculated on the basis of the simple trapping model (see Sec. IV A) by use of the values of I_2 and τ_2. In these measurements no long-lived component of the order of nanoseconds was found. For well-annealed samples the bulk lifetime showed no temperature dependence.

IV. DISCUSSION

Before discussing the results, we will first consider the defect structure in neutron-irradiated silicon. Later, the discussion will be divided into part A, dealing with the annealing experiments, and part B, dealing with the temperature dependence.

The radiation damage suffered by silicon depends on the neutron energy. Fast neutrons are known to create displacement spikes with high concentrations of defects,[12] of the order 10^{20} cm^{-3}, which can be surrounded with an extended dipole[13,14] region exceeding 1000 Å. The number of displacement spikes can be estimated to be about 6×10^{14} cm^{-3}, using a mean elastic scattering cross section[15] of 3 b and by assuming that only one spike is formed per scattered fast neutron, which probably is an underestimate. The number of defects in each spike is estimated[12] to be 200, yielding a total defect concentration of approximately 1.2×10^{17} cm^{-3}.

Slow neutrons, on the other hand, can be captured by the silicon nuclei which leads to γ-ray emission from the excited nuclei, imparting an

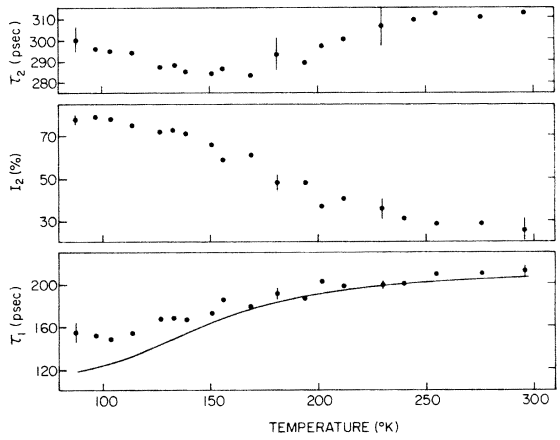

FIG. 3. Temperature dependence of τ_2, I_2, and τ_1; the curve in the panel for τ_1 is calculated from the trapping model.

average recoil energy of 800 eV to the silicon atom.[16] Since this energy is large enough to create displacements, the thermal neutrons will cause radiation damage which is homogeneous (approximately 26 displacements could be created, but only about two remain at room temperature). The dose of 2.2×10^{17} slow neutrons per cm^2 also gives rise to the formation of roughly 3×10^{13} ^{31}P atoms per cm^3 (from ^{30}Si) and the total number of recoiling Si atoms (^{28}Si and ^{29}Si) is about 7.5×10^{14} per cm^3, thus creating $\sim1.5\times10^{15}$ defects per cm^3.

The monovacancy is the primary vacancy-type defect created by radiation, but since it migrates at -200 or $-100\,^\circ C$ (depending on its charge[17]) it cannot be stable at room temperature. The divacancy, however, migrates at $\sim170\,^\circ C$ and is stable to $\sim350\,^\circ C$, so one would expect that the divacancy is the dominant secondary defect type at room temperature. The fact that the migration energy of divacancies is higher than for monovacancies (in contrast to the case for metals) is owing to the crystal structure of silicon. Higher aggregates of vacancies are of course possible, but the probability of their formation decreases rapidly with increasing cluster size, since, in a migration process involving only monovacancies of concentration c_v, this probability varies as c_v^n, n being the number of monovacancies in the cluster. Although monovacancies are highly mobile at room temperature, they can be stabilized at temperatures well above by trapping at impurities, e.g., phosphorous or oxygen.

A. Isochronal annealing

We attribute the τ_2 component to annihilation of positrons trapped in radiation produced defects, since this component is removed by annealing beyond $440\,^\circ C$. At present no attempt to correlate the very-long-lived τ_3 component to a physical process will be made, but, as its intensity is very low, we will disregard it in the following. Adopting the simple trapping model,[5] the trapping rate from the bulk to the defect is given by

$$\kappa=[I_2/(1-I_2)](\lambda_0-\lambda_2)\,, \tag{1}$$

where λ_2 ($\equiv1/\tau_2$) is the annihilation rate in the defect and λ_0 is the bulk annihilation rate. We have $\lambda_0=1/0.2265$ nsec^{-1}. Furthermore,

$$\lambda_1=\kappa+\lambda_0\,, \tag{2}$$

where λ_1 ($\equiv1/\tau_1$) is the observed annihilation rate of the shortest component. In order to check the applicability of this version of the trapping model we use (2) in the form

$$\lambda_0^m=\lambda_1-\kappa\,. \tag{3}$$

If the model is correct the "model value" λ_0^m of the bulk annihilation rate will equal the observed bulk rate, but otherwise a discrepancy will be found. In Fig. 4 the calculated bulk lifetime $1/\lambda_0^m$ using (1) and (3) is shown. The broken line shows again the observed bulk lifetime, and it is clear, that in the temperature range 30–270 °C, a systematic deviation is present, while for higher temperatures good agreement is observed. On this basis, and also because τ_1 exceeds the bulk lifetime in the temperature range 160–260 °C (see Fig. 1), it is suggested that another component with a somewhat longer lifetime than the bulk lifetime is mixed into the bulk lifetime. This component could arise from positrons trapped in monovacancies which have been stabilized by impurities. The precise nature of the defect cannot be determined with certainty, but it seems that the phosphorous vacancy complex can be ruled out because it is stable[18] only below $150\,^\circ C$. The present experiments do not provide a direct determination of the lifetime in monovacancies (an indirect determination will be presented later), which means that it is not possible to modify the trapping model and obtain quantitative results. It is believed, however, that since the discrepancy between the calculated and observed bulk lifetime only amounts to about (2–3)%, the trapping rate calculated from (1) is sufficiently accurate.

The annealing of I_2 (Fig. 2) in stage I takes place at about the same temperature as that of the 1.8-μm optical-absorption band[12] arising from divacancies, and we therefore assume that in this stage the positrons annihilate, at least mainly, in divacancies with a lifetime of 325 ± 20 psec. This value is close to the saturation level of the mean lifetime determined by Cheng *et al.*[1] It is noted that, since τ_2 is approximately constant in stage I, this indicates that the divacancies are not forming aggregates.

The annealing rate of vacancies can be described by the expression

$$\frac{dc_v}{dt}=-Ac_v^n e^{-E^M/kT}\,,$$

where c_v is the vacancy concentration, A is a constant, n is an integer and E^M is a migration

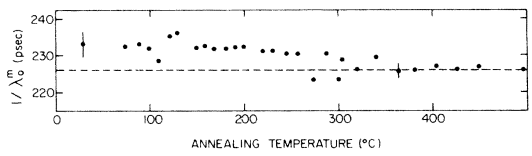

FIG. 4. "Bulk" lifetime $1/\lambda_0^m$ calculated from the trapping model using the isochronal annealing data shown in Figs. 1 and 2. The broken line indicates the experimentally determined value (226.5 psec).

energy. The isochronal annealing measurements yield E^M according to

$$Y^{(1)} \equiv \ln[\ln(c_v^{(i)}/c_v^{(i+1)})] = B - E^M/kT^{(i+1)} \quad (n=1), \tag{4}$$

$$Y^{(2)} \equiv \ln[1/c_v^{(i+1)} - 1/c_v^{(i)}] = B - E^M/kT^{(i+1)} \quad (n=2), \tag{5}$$

where $c_v^{(j)}$ is the vacancy concentration at the end of the jth annealing step at temperature $T^{(j)}$, and B is a constant; $n=1$ corresponds to a first-order process and $n=2$ to a second-order process. E^M can be found from (4) and (5) by making the usual assumption that the trapping rate is proportional to the vacancy concentration. Assuming first that the annealing in stage I follows a first-order process, this gave a poor fit to a straight line, and further, a value of E^M of only 0.3 eV, which is too low for a process taking place at room temperature. A second-order process, on the other hand, gave a good fit to the data (see curve $Y^{(2)}$ in Fig. 5) yielding a migration energy of $E^M = 0.8 \pm 0.1$ eV, which is somewhat lower than the migration energy of 1.2 eV for divacancies.[21] This indicates that the divacancy is not the moving species, and we therefore suggest, in agreement with Seeger,[19] that it is the interstitial which is the migrating species. This interpretation is supported by the fact that the lifetime τ_2 in stage I is constant. Furthermore, Lee and Corbett[20] found from EPR measurements that the migration energy of interstitials is 0.6 ± 0.2 eV, in good agreement with our determination.

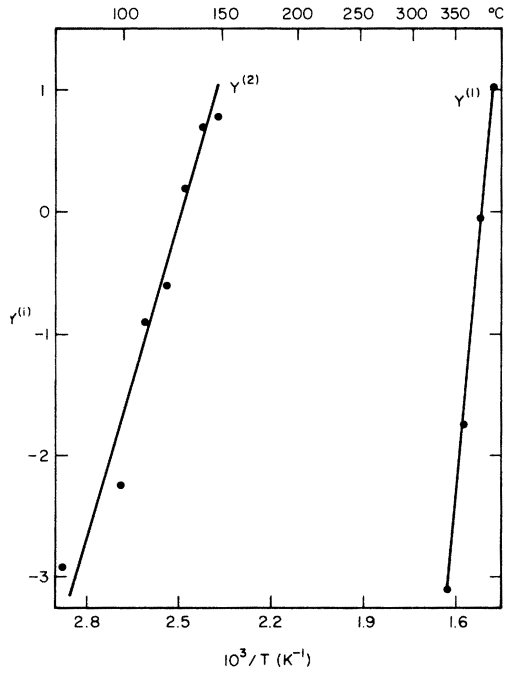

FIG. 5. Arrhenius plot of the parameter $Y^{(i)}$ calculated according to Eqs. (4) and (5) (see text) and using the isochronal annealing data in Figs. 1 and 2. $Y^{(1)}$ and $Y^{(2)}$ refer to a first- and second-order process, respectively.

In the beginning of stage II, τ_2 increases at the temperature where reorientation (and hence migration) of divacancies is known to take place,[21] and we therefore interpret this increase in τ_2 as being due to aggregation of divacancies. From a statistical point of view an aggregate of two divacancies (a quadrivacancy) is the most probable. This is further substantiated if the assumption is made that the increase of the positron lifetime over the bulk value is proportional to the number of vacancies in the cluster. The increase in stage II is 210 psec, which is approximately twice the increase for the divacancy (99 psec), thus suggesting the quadrivacancy formation. As a corollary of this hypothesis one can determine, from a plot of annihilation rate versus number of vacancies (zero, two, and four), that the lifetime in monovacancies is roughly 270 psec. The decrease of τ_2 beyond 260 °C in stage III is interpreted as being a result of a break up of the quadrivacancy complex, resulting in an increase in I_2. The temperature of 260 °C is somewhat lower than found from EPR measurements[22] where the quadrivacancy complex is found to break up at 300–350 °C. At 340 °C, τ_2 is again close to 325 psec, indicating that most of the vacancies are again in divacancy form. The trapping rate at this temperature is 0.10 nsec^{-1}, which is close to the rate at 150 °C (0.11 nsec^{-1}), thus indicating that only a minor loss in divacancy concentration has taken place. This suggests that essentially all interstitials have disappeared at 150 °C or have formed clusters stable to at least 340 °C. The decrease of I_2 beyond 340 °C was found to be approximately of first order (see curve $Y^{(1)}$ in Fig. 5) with an activation energy of ~1.7 eV, which agrees well with the binding energy of divacancies.[19]

B. Temperature effect

The temperature dependence of positron trapping has previously been investigated principally in metals, where experiments and theoretical calculations indicate a T^n dependence where $n \geq 0$ (see, e.g., Ref. 23). If only a mean lifetime is determined experimentally, this dependency will result in a constant or increasing mean lifetime. In contrast to this situation in metals, Brandt and Cheng[3] observed, in silicon, a decrease of the mean lifetime with increasing temperature, which they interpreted as being a result of an increase in detrapping rate from shallow traps. We point out that their result may also be interpreted in

terms of a trapping rate which increases with decreasing temperature, i.e., the opposite of the situation in metals. In order to decide between these two interpretations, we include detrapping in the trapping model[23] and obtain for the detrapping rate, δ, valid for all values of δ:

$$\delta = (\lambda_2 - \lambda_t)(\lambda_1 - \lambda_t)/(\lambda_0 - \lambda_t) .$$

Here $\lambda_2 (\equiv 1/\tau_2)$ is the observed annihilation rate in the trap while detrapping is occurring, and λ_t is the annihilation rate in the trap if no detrapping occurs. λ_1 is the observed annihilation rate of the shortest component, and λ_0 is the bulk annihilation rate. We argue, from a physical point of view, and in accordance with Brandt and Cheng,[3] that the detrapping rate should increase with temperature, and, since $\delta \geq 0$, λ_2 must increase. Our results given in Fig. 3 show, however, that λ_2 actually decreases (as does λ_1), which suggests that the concept of detrapping is not applicable here. We therefore consider our results in the framework of a temperature-dependent trapping rate, and in order to explain the results, we will make use of Lax's[24] calculations of the trapping of electrons (or holes) by defects. He finds, by adopting the concept of cascade capture,[25] that for charged defects the trapping cross section varies as $T^{-1.5}$ if only acoustic phonons are important in the trapping process, whereas optical phonons yield a T^{-n} dependence with n varying from 1 at low temperatures to 4 at high temperatures. For neutral defects, n varies from 1 to 0, i.e., quite differently from the case of charged defects. Furthermore, Lax[24] concluded that the trapping process was not diffusion limited since this gave trapping cross sections four orders of magnitude too large. Experimentally, Bemski[26] observed a $T^{-2.5}$ dependence for electron capture in Au^+ centers (charged defects) in the temperature range 200–500 °K, which shows that scattering with optical phonons is the dominant process.

Considering now the trapping of positrons, we assume, in the light of the above, that the process is not diffusion limited and can then write the trapping rate as

$$\kappa = v\sigma_+(T)c_v , \qquad (6)$$

where $v = (2kT/m_+)^{1/2}$ is the thermal velocity of the positron, $\sigma_+(T)$ is the (temperature-dependent) positron trapping cross section, and c_v is the defect concentration. In view of the above, we assume $\sigma_+(T)$ varies as T^{-n} and a plot of $\ln(\kappa T^{-1/2})$ vs $\ln T$ will then yield the value of n according to (6). In Fig. 6 our experimental values are plotted along with Lax's[24] calculated curve for trapping in a charged defect (taken from his Fig. 9, and adjusted only by a constant), and we conclude from the good agreement that, with respect to trapping, positrons behave similarly to electrons (or holes). Over the main part of the temperature range, n is approximately 2.5. It follows that the positron is trapped in a defect having a negative charge since a neutral defect would result in a much smaller temperature dependence, as mentioned above.

In Sec. IV A it was shown that the dominant defect after irradiation was the divacancy. The charge of this defect is negative when the Fermi level is between $E_v + 0.55$ and $E_v + 0.80$,[17] where E_v is the energy of the top of the valence band (in electron volts). Since the Fermi level in irradiated Si is close to the midgap level $(E_v + 0.6)$,[27] it is suggested that the divacancy can account for the temperature dependence of the trapping rate. The possibility that the phosphorous or oxygen vacancy complex could account for the temperature dependence can be ruled out, because these centers are neutral when the Fermi level is at the midgap position.

The magnitude of the positron trapping cross section at 296 °K can be calculated from (6) using the vacancy concentration estimated in the beginning of the discussion (1.2×10^{17} cm^{-3}). Using the simplifying assumption that all vacancies are in the form of divacancies one gets $\sigma_+(300\ ^\circ\mathrm{K}) \simeq 4 \times 10^{-16}$ cm^2, which is one order of magnitude less than Bemski's[26] result for electrons trapped in Au^+ centers. Several reasons for this difference can be visualized, one arising from the fact that the majority of divacancies are confined to a vol-

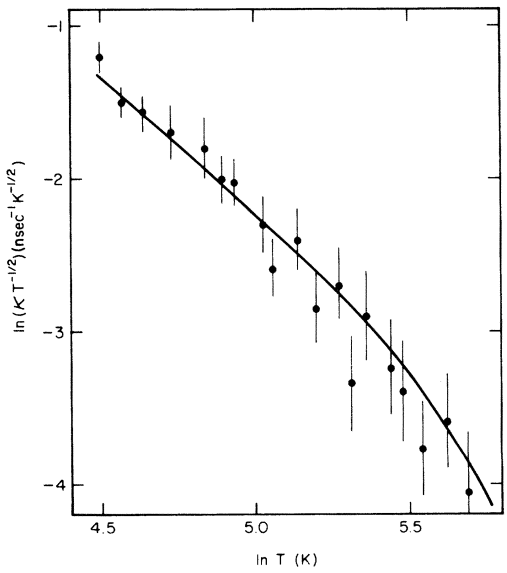

FIG. 6. Temperature dependence of trapping cross section (proportional to $\kappa T^{-1/2}$, κ being the trapping rate). The curve shows the theoretical results based on Lax's calculations (Ref. 24).

ume with very high defect density, which could have the effect of reducing the effective number of vacancies. From an experimental point of view, the large increase in trapping cross section with decreasing temperature is of benefit, since very low densities of defects can be detected.

The reason for the small temperature dependence of τ_2 shown in Fig. 3 is not clear at present. It seems unlikely, however, that the effect could be understood in terms of the thermal expansion of the lattice, since a nonlinear behavior of τ_2 is observed. A possibility is that the positron, depending on the sample temperature, can occupy different energy levels in the vacancy potential as a result of the cascade capture process.

ACKNOWLEDGMENT

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