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Temperature dependence of the annihilation of positrons in Si containing divacancies and quadrivacancies

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Positron-lifetime and Doppler-broadening measurements have been performed on Si samples containing divacancies and quadrivacancies in the temperature range 10 to 286 K. The trapping rate is found to increase with decreasing temperature and its behavior is described in terms of a cascade model of positron trapping. The positron lifetime in divacancies decreases from 320 ps at 286 K to 270 ps at temperatures less than 150 K. The lifetime in quadrivacancies is higher (430 ps) at 286 K but attains the same value as in divacancies at low temperatures. Both the lifetime and Doppler-broadening data suggest that the nature of the trapped state varies with temperature and evidence indicating partial dissociation of the divacancies is presented.

I. INTRODUCTION

The positron annihilation technique is very useful for studying defects in semiconductors since the annihilation characteristics of trapped positrons are influenced by the charge of the defects. Various defect charge states exist, dependent on the position of the Fermi level, and have been determined for a number of defect types in other experiments, e.g., electron paramagnetic resonance (EPR) measurements.

In a previous work by Dannefaer *et al.*[1] (henceforth referred to as paper I), we reported on measurements of positron lifetimes in neutron-irradiated Si. This included the study of defect kinetics in isochronal annealing measurements which resulted in the identification of the positron lifetime in divacancies and quadrivacancies, and the prediction of the lifetime in monovacancies. In addition, the temperature dependence of the annihilation parameters was determined in the temperature range 88–296 K. It was found that the positron trapping cross section in divacancies increased significantly with decreasing temperature, in good agreement with theoretical calculations by Lax[2] based on a cascade capture model. The data also indicated that the positron lifetime decreased with decreasing temperature.

More recently, Fuhs *et al.*[3] studied the annihilation of positrons in electron-irradiated pure and boron-doped Si and obtained positron-lifetime values in monovacancies and divacancies, in good agreement with the values in paper I. Their study included isochronal annealing measurements, the results of which were interpreted in terms of different charges of the defect states in pure and doped Si.

In the present work, measurements have been performed on two different samples, one containing primarily divacancies and the other quadrivacancies. The temperature range has been extended down to 10 K to further investigate the applicability of the cascade model of positron trapping, and a combination of lifetime and Doppler-broadening data are used to examine the characteristics of multivacancy conglomerates.

II. EXPERIMENTAL

The Si samples, as described in paper I, were high purity, dislocation-free single crystals and were irradiated with 2.2×10^{17} thermal neutrons per cm^2 and 4×10^{15} fast neutrons per cm^2. After cutting and polishing, the crystals were etched in a solution of HF and HNO_3 and then mounted in a sandwich arrangement with a positron source consisting of 20 μCi of ^{22}NaCl deposited on 0.28 mg/cm^2 Al foil.

Lifetime measurements were performed using a digitally stabilized spectrometer having an operating time resolution of 360 ps full width at half maximum (FWHM). This value was determined by fitting the total lifetime spectrum from perfect Si with a single lifetime component, together with a double Gaussian resolution function (computer program kindly supplied by M. Eldrup, Riso, Denmark). The time stabilization was done on the symmetric lifetime spectrum[4] providing a constant time-zero for the asymmetric spectrum and allowing the use of the RATIO method[5,6] of analysis. This method yields the annihilation parameters through a comparison of the lifetime spectra from defect-free samples and samples containing defects by taking the ratio of the two spectra.

Samples were held in a variable temperature cryostat and lifetime measurements were made over the temperature range 10–286 K on samples in which most of the vacancies were in the divacancy state. The samples were then heated to 437 K for one hour, forming quadrivacancies (see paper I) and measurements were repeated. S-parameter Doppler-broadening measurements were also made on the samples containing quadrivacancies using a hyperpure Ge detector with a resolution function of 1.1 keV FWHM at 514 keV.

III. RESULTS

The results of the analysis of the lifetime spectra are shown in Fig. 1. The top panel shows the fraction, I_2, of the long-lived component associated with trapped positrons as a function of temperature. As seen in paper I, I_2 increases strongly with decreasing temperature. The values of I_2 in the present investigation are less than observed earlier, due to a slow annealing at room temperature over the three-year period between the two sets of measurements. The middle panel shows the temperature dependence of the lifetime, τ_2, of positrons trapped at vacancies. In accordance with paper I, the room-temperature lifetimes characteristic of divacancies and quadrivacancies are approximately 325 and 430 ps, respectively. These values are rather uncertain due to the small values of I_2 at room temperature. The salient feature in this graph is the decrease in τ_2 with decreasing temperature, reaching a common value of ~270 ps for both types of vacancy aggregates. The apparent lifetime, τ_1, of positrons not trapped by defects is shown in the lowest panel of Fig. 1. The horizontal line marked 222 ps signifies the temperature-independent lifetime of positrons annihilating in perfect Si. This value is slightly lower than found in paper I (226 ps), probably because of the better current determination of the resolution function.

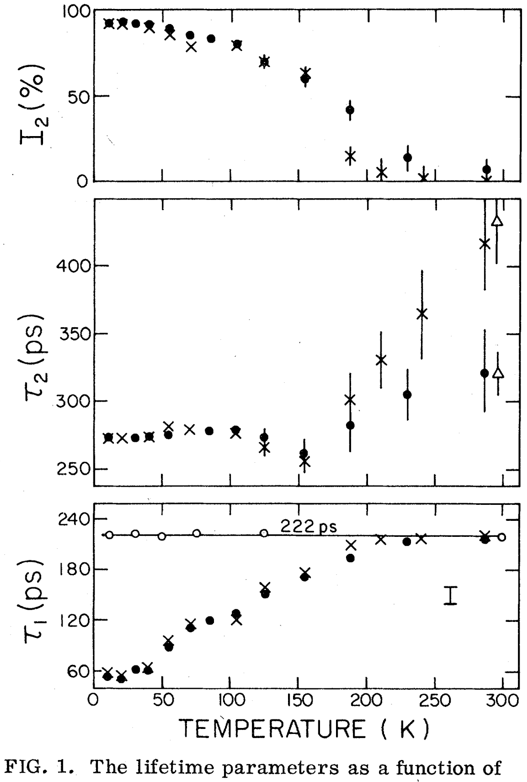

FIG. 1. The lifetime parameters as a function of temperature. The solid circles and crosses refer to divacancies and quadrivacancies, respectively. The triangles in the panel for τ_2 show the room-temperature lifetimes determined in paper I. The error bar in the bottom panel indicates the typical uncertainty in τ_1. The open circles and horizontal line marked 222 ps in the bottom panel show the temperature-independent bulk lifetime in perfect Si. The uncertainties in these measurements are approximately ±4 ps.

According to the simple trapping model[7] (one bulk state and one trapped state with no detrapping), the behavior of τ_1 may be described by

$$1/\tau_1 = \lambda_B + \kappa\,, \tag{1}$$

where λ_B is the bulk annihilation rate (4.50 nsec^{-1}) and κ is the trapping rate which may be expressed in terms of the observable parameters as

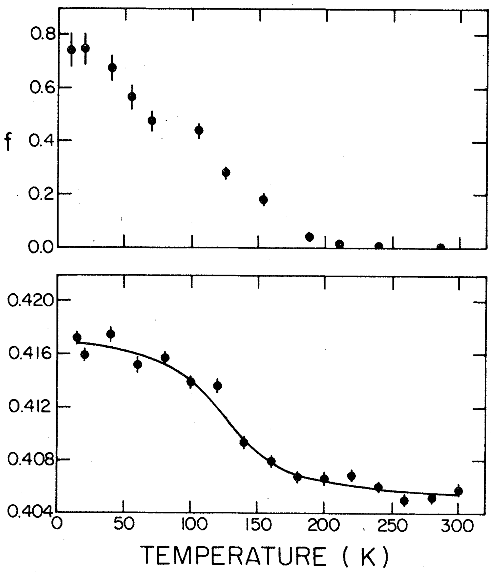

FIG. 2. Top panel: Variation of the trapped fraction, f, with temperature. Bottom panel: Doppler-broadening S parameter as a function of temperature. Since the lifetime and Doppler data were not obtained at the same temperatures, the solid curve was drawn by eye and used for interpolation in obtaining the results shown in Figs. 4 and 5.

$$\kappa = (\lambda_B - 1/\tau_2) I_2/(1 - I_2) . \qquad (2)$$

Since the computer analysis of the ratio spectrum provides the values τ_1, τ_2, and I_2, τ_1 may be calculated from (1) and (2) and compared with the experimentally determined τ_1 values. This may be viewed as an internal consistency check of the fitting procedure or, granting its validity, a check on the applicability of the simple trapping model. Good agreement (within 10 ps) is observed over the whole range of κ values from 12 ns^{-1} at 10 K to 0.1 ns^{-1} at room temperature. Referring again to the simple trapping model, the fraction of trapped positrons is

$$f = \kappa/(\kappa + \lambda_B) . \qquad (3)$$

This trapped fraction and the Doppler-broadening data are shown in Fig. 2 and, as expected, the S parameter reflects generally the behavior of f.

IV. DISCUSSION

In discussing the results, the variation of I_2 with temperature will be considered first and we compare (as was done in paper I) with Lax's[2] theory of cascade trapping. The trapping rate κ is expressed as

$$\kappa = v\sigma_+(T) C_v , \qquad (4)$$

where $v = (2kT/m_+)^{1/2}$ is the velocity of the positron, $\sigma_+(T)$ is the temperature-dependent trapping cross section, and C_v is the concentration of divacancies. Following paper I, we assume $\sigma_+(T)$ varies as T^{-n} and, using values of κ obtained from (2), a plot of $\ln(\kappa T^{-1/2})$ vs. $\ln T$ yields the value n. These results are shown in Fig. 3. At temperatures below 40 K, the slope of the curve n is -1, while at high temperatures the slope is -4, values which, according to Lax, are indicative of a trapping process involving the emission of optical phonons. Lax's expression for the trapping cross section depends on the dimensionless parameter $\hbar\omega/kT$, where $\hbar\omega$ is the energy of the optical phonons. As seen in Fig. 3, a good fit to the divacancy data can be obtained for $\hbar\omega = 0.025$ eV, a value which is significantly less than the experimental value of 0.06 eV determined by Brockhouse.[8] This discrepancy, which was not apparent in the results of paper I due to the limited temperature range, seems rather large but it should be noted that the phonon-dispersion relation near a defect may be changed, reducing the optical phonon energy from the bulk value. This view is supported by theoretical calculations[9,10] which indicate significant mode softening in the Si lattice in the vicinity of vacancies. It is also apparent from Fig. 3 that the behavior of the trapping rate in quadrivacancies is essentially the same as in divacancies.

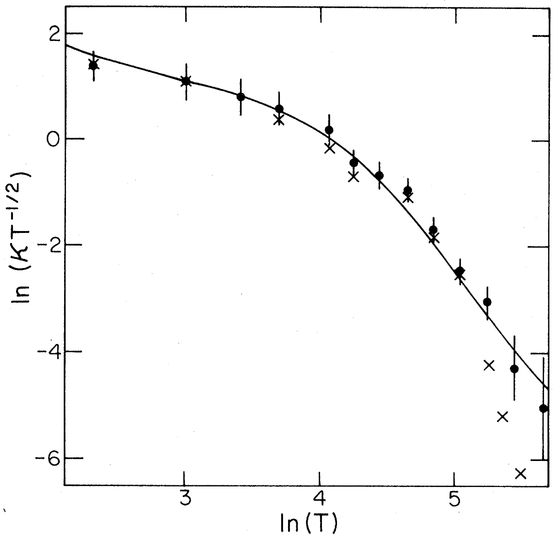

FIG. 3. $\ln(\kappa T^{-1/2})$ vs $\ln T$ for divacancies (●) and quadrivacancies (×). The solid curve is the best fit to the divacancy data using Lax's theory with $\hbar\omega = 0.025$ eV.

The trapping radius $r_t[\pi r_t^2 = \sigma_+(T)]$, may be estimated from (4). In paper I, the concentration of divacancies was estimated to be 10^{17} cm^{-3}, but is reduced in the present investigation by a factor of three as seen from the lower value of I_2 at room temperature. Setting m_+ equal to the mass of the free electron yields, at 10 K where r_t is maximum, $r_t = 10$ Å, a value consistent with the size of divacancies.

We now turn to the variation of τ_2 with temperature. To our knowledge, this is the first time a temperature-dependent lifetime of trapped positrons has been established in Si, although a small temperature dependence of τ_2 has been observed in Pb (Ref. 11). In Si, the lifetime observed in the temperature range 10–160 K for both vacancy aggregate types, is nearly constant (258 ps $< \tau_2 <$ 280 ps), albeit with some definite structure, and is close to the monovacancy value of 266 ± 10 ps determined by Fuhs *et al.*[3] Our value of τ_2 for divacancies then increases to about 320 ps at room temperature. This is initially puzzling since Fuhs *et al.* find an essentially constant value of 318 ± 15 ps for divacancies over the same temperature range. These apparently conflicting observations may be explained in terms of defects with different charge states. The divacancy is in its V_2^{2-}, V_2^-, V_2^0, and V_2^+ states when the Fermi level is above $E_c - 0.4$ eV, $E_c - 0.5$, $E_v + 0.25$, and E_v, respectively, where E_c and E_v denote the conduction- and valence-band edges.[12] In their determination of the lifetime in divacancies, Fuhs *et al.* used undoped Si (10^5 Ωcm); the Fermi level must have been very close to the midgap position with the result that the

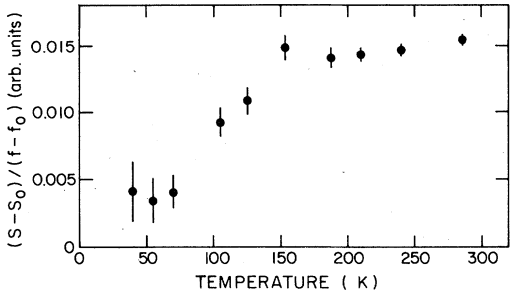

FIG. 4. Plot of $(S-S_0)/(f-f_0)$ as a function of temperature [see (6) in text].

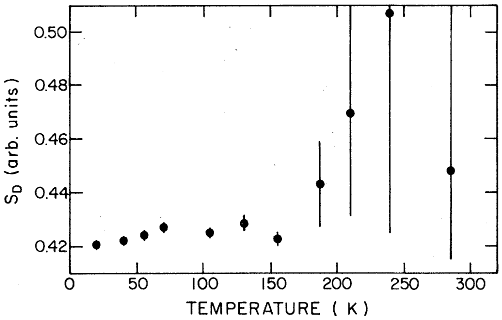

FIG. 5. Defect-shape parameter S_D as a function of temperature.

charge state of the divacancy would have been either V_2^0 or V_2^-. In contrast, our samples were phosphorous-doped due to the neutron irradiation. After complete thermal annealing, the samples had a resistivity of 200 Ωcm. This would place the Fermi level close to the phosphorus donor level which is 0.044 eV below the conduction band. A simple calculation places the Fermi level 0.03 eV below this donor level. Our samples were not completely annealed which would tend to lower the Fermi level, but the reduction would likely be small judging from the very small fraction of trapped positrons (and hence defect concentration) at room temperature. Therefore, the divacancies in our samples were probably in the V_2^{2-} state due to the higher position of the Fermi level.

It has been speculated that the difference in the charge state of the divacancy could have a profound influence on its structure.[13] In contrast to the other charge states, the V_2^{2-} divacancy may be partially dissociated due to the strong repulsion between the two electrons in antibonding orbitals. This would lead ideally to a structure with two vacancies separated by a Si ion, a configuration corresponding to the saddle-point configuration for divacancy migration. The main reason for the speculative nature of this structure is that the V_2^{2-} state has no unpaired electron spin, with the result that EPR measurements cannot be made. Positron measurements, however, lend themselves to the determination of such a structure change, and the present results taken together with those of Fuhs *et al.*, indicate that the dissociated vacancy model for the V_2^{2-} state is indeed correct. We interpret our decrease in τ_2 with temperature as being due to a localization of the positron in only one of the vacancies in the divacancy (or quadrivacancy) complex, thus yielding a monovacancylike lifetime at low temperatures. Since Fuhs *et al.* investigated the undissociated divacancy in the V_2^0 or V_2^- state, it would be expected that they would observe the divacancy lifetime of ~320 ps even at low temperatures.

We consider finally the Doppler-broadening data shown in Fig. 2. The shape parameter S of a Doppler-broadened curve may be expressed as[7]

$$S=(1-f)S_B+fS_D\,, \tag{5}$$

where S_B and S_D are the shape parameters corresponding to the bulk material and the defects, respectively, and f is the fraction of trapped positrons given by (3) and plotted in Fig. 2. Since the defect distribution should be narrower (larger S_D) than the bulk distribution, S is expected to increase with f as is indeed the case. It is convenient to choose some reference temperature, T_0, and to develop from (5) the expression

$$\frac{S-S_0}{f-f_0}=S_{D0}-S_B-\frac{f}{f_0-f}(S_D-S_{D0})\,, \tag{6}$$

where S_0, S_{D0}, and f_0 refer to the values of S, S_D, and f at $T=T_0$. Allowance has been made for a temperature dependence of S_D but, on the basis of the constancy of the bulk lifetime it is reasonable to assume that S_B is not significantly temperature dependent. An examination of the right side of (6) shows that if S_D were temperature independent, a constant value should result. The left side of (6), determined experimentally from the Doppler and lifetime data, is plotted in Fig. 4 with $T_0=20$ K and it is clear from this result that S_D is temperature dependent. The behavior of S_D alone cannot be determined from Fig. 4 since Fig. 4 shows the combined influence of f and S_D. In fact, depending on the relative rates of change of S_D and f, either a positive or negative temperature dependence could account for the observed behavior of $(S-S_0)/(f-f_0)$. An attempt was made to obtain S_D directly from (5) by choosing $S_B=S$ at $T=300$ K (no trapping) and the result is shown in Fig. 5. The uncertainties in the higher-temperature values of S_D are very large but there is at least an indication of a positive temperature dependence. Qualitatively, this result is consistent with the interpretation of the behavior of τ_2, i.e., at low temperatures where the positron is restricted to one of the vacancies in the quadrivacancy complex, the distribution should be relatively wide while at higher temperature the distribution should become narrower as the positron samples the entire quadrivacancy.

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