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Search for thermally generated monovacancies in silicon using monoenergetic positrons

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Using a monoenergetic, variable-energy positron beam, measurements of Doppler broadening and positronium fraction for positron-annihilation radiation from high-resistivity silicon have been made up to the melting point. The measurements show no clear evidence of positron trapping into thermally generated monovacancies which Dannefaer, Mascher, and Kerr observed by measuring the lifetimes of positrons emitted by an *in situ* source. A lower limit of about 3.6 eV is placed on the formation enthalpy of a neutral monovacancy, subject to assumptions about positron-trapping rate, binding energy, and monovacancy formation entropy.

The correct value of the formation enthalpy for neutral monovacancies in silicon is a matter of some controversy and importance. Two different recent measurements of positron lifetimes in silicon at high temperatures have produced confusing results.[1,2] Dannefaer, Mascher, and Kerr[1] created a positron source by irradiating high-resistivity (2000 Ω cm) silicon with protons to form *in situ* ^{22}Na. Their observations indicate that effects associated with positron trapping at monovacancies begin to appear at 800 °C, and that all positrons annihilate from trapped states for temperatures above 1150 °C. They derive a neutral monovacancy enthalpy of 3.6 ± 0.2 eV. The data analysis, however, is quite complicated because the ^{22}Na begins to migrate out of the sample in the same temperature regime where the monovacancy effects are observed, creating an increasing source component (i.e., a component not related to the sample) in the lifetime data. In contrast to Dannefaer's results, Würschum *et al.*,[2] using an MeV positron beam for β-γ lifetime measurements,[3] observed no substantive change in the positron lifetime in a high-resistivity, dislocation-free sample up to the melting point of 1414 °C.

In an attempt to resolve these inconsistencies we have made a complementary measurement of the energy spectra of the radiation produced by positrons annihilating in silicon at temperatures up to the melting point. The monoenergetic positron beam used for this experiment is described elsewhere.[4,5] The spectra have been analyzed to yield two quantities that would be expected to show changes if positrons annihilate while localized at monovacancies rather than from a freely diffusing Bloch state. First, the Doppler broadening parameter S has been measured.[6] This is simply defined as the ratio of the area under the central portion of the 511-keV photopeak to the total area under the peak. The peak is broadened by the momentum of the electron in the lab frame. A high-S value indicates annihilation with low momentum valence electrons, while a low-S value indicates annihilation with high-momentum electrons. Thus, positrons annihilating at monovacancies would be expected to yield a higher-S value.

A typical set of S parameter measurements indicating positron trapping into monovacancies would show a small positive slope generally ascribed to lattice expansion effects, with a much steeper increase at the onset of vacancy formation, leveling off when essentially all positrons annihilate from trapped states (saturation trapping).[7] The expected shift in S between the bulk value and the value characteristic of monovacancies could be obtained from a measurement of S caused by saturation trapping produced by radiation-induced monovacancies. These monovacancies are, however, highly mobile, annealing out to form other defect complexes at about 150 K. Fuhs *et al.*[8] observed an increase of approximately 2% in the height of the 511-keV peak after annealing out monovacancies, and a total shift of about 5% after further annealing at higher temperatures. Keinonen *et al.*[9] observed a 3.4% increase in S due to trapping at divacancies. These numbers suggest that the expected shift in S for saturation trapping at monovacancies would be of the order of a few percent. Although this estimate is admittedly crude, we know of no system where a change in positron lifetime has not also been detectable as a change in Doppler broadening.

The second type of measurements presented here reflects positron diffusion characteristics.[10] Positrons which form positronium before annihilating decay via three γ rays rather than two by 3:1, and thus the annihilation γ-ray spectrum can be used to determine what fraction of the positrons decayed from a positronium state in vacuum. Positronium can be formed in silicon only at the surface-vacuum interface. Therefore, measurements of f, the positronium fraction, provide information about diffusion of positrons back to the surface after implantation. If f is measured for varying implantation depths (varying positron beam energies), then positron diffusion properties can be determined without knowing the branching ratio for surface processes other than positronium formation, as long as this branching ratio is not changing during an energy scan.

The quantity determined from these measurements is L_+, the positron diffusion length. Trapping at monovacancies will reduce the diffusion length. In contrast to Doppler-broadening measurements, where vacancy trapping effects saturate at some concentration, L_+ continues to decrease with increasing vacancy concentration. Further information about measurements of S and f can be found in review papers on slow positron beam techniques.[7,11]

The sample was slightly n-type, phosphorous-doped,

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dislocation-free, float-zone silicon with a resistivity of greater than 8000 Ω cm and a recombination lifetime of about 2000 μs.[12] Before insertion in the sample chamber, the sample was cleaned in peroxide solutions and HF to form a clean oxide layer easily removable by heating. A slab of size 14×30 mm^2 was clamped at each of its short edges by a pair of tantalum bars. In order to prevent silicide formation, each bar was slotted at the center along the surface facing the sample. A piece of lower-resistivity silicon wafer of thickness greater than the depth of the slot was then fitted into the slot to prevent direct contact between the tantalum and the sample. The tantalum clamps were fastened somewhat loosely to the binding posts with tantalum foil and wire. Thus, the sample could expand (contract) in length as it was heated (cooled). Tungsten springs allowed the clamps to adjust to changes in sample thickness during temperature changes.

To avoid carbon contamination from a hot filament and to achieve a more uniform temperature, heating was achieved by passing a dc current of up to about 25 A through the sample. Enclosing the sample and mount in a furnace consisting of seven concentric outgassed layers of 0.25-mm tungsten also improved thermal uniformity. A 1.2-cm-diam aperture allowed entry of the positron beam.

Temperature measurements were made by an infrared pyrometer[13] viewing the sample reflected in a tantalum mirror, which had been coated with silicon by evaporation from previous samples. Previous pyrometer measurements on a low-resistivity sample, viewed directly, showed a temperature gradient of less than 30 °C across the beam aperture for temperatures up to about 1300 °C. Unfortunately, changes in the optical properties of the mirror create oscillations up to 100 °C in the pyrometer reading for temperatures above ≈ 1300 °C. These fluctuations are not real temperature fluctuations as they are not observed in samples that can be viewed directly. An independent temperature measurement was provided by a (W 5% Re)-(W 26% Re) thermocouple bonded to the back of the sample by a thin layer of Ultratemp 516,[14] a zirconia-based high-temperature adhesive. Because the sample was acting as its own heat source and the glue provided imperfect thermal contact, the thermocouple readings can be considered as lower bounds to the true temperature. The maximum pyrometer reading at the melting point was used to calibrate the emissivity of the sample-mirror system. The uncertainty in the calibration of the temperature measurements is < 100 °C.

Measurements taken at 100 °C indicated that S had reached its bulk value for positron implantation energies of 20 keV. The energy was increased to 45 keV (average penetration depth about 8 μm) to ensure bulk behavior, and measurements of S were performed as a function of temperature. The positronium fraction f was also measured and used to determine L_+. The branching ratio for positronium formation was initially extremely low due to the presence of an oxide layer. After the oxide had been removed by heating, the temperature was decreased so that more accurate determinations of L_+ could be made. Each measurement of S takes about 10 min, while each measurement of f takes about 1 h.

Figure 1 shows the S parameter as a function of temperature. Each point represents an average of three 10-min measurements. First of all, it should be noted that all of the S parameter data falls within a range of less then 0.75%. Certainly, no increase of the order of 1% has occurred at any temperature, and no change of any kind is evident in the temperature range where Dannefaer *et al.*[1] saw changes in the positron lifetime, which they ascribed to positron trapping at thermally generated monovacancies. The small positive slope indicating a fractional change in S of about 3.7×10^{-6} K^{-1} is comparable in magnitude to the volume thermal expansion of about 1.2×10^{-5} K^{-1}.[15]

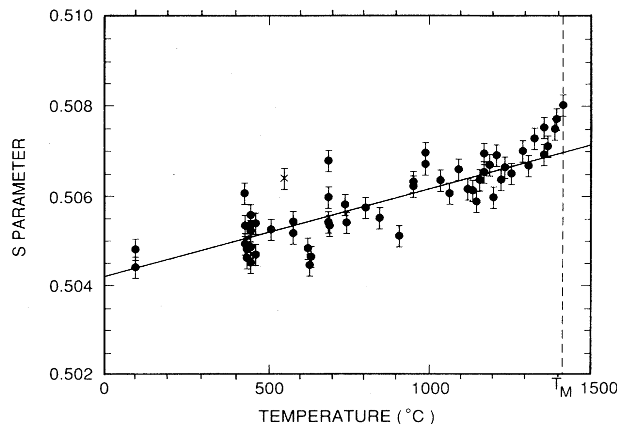

FIG. 1. Doppler-broadening parameter S as a function of temperature. The dashed line marks the melting point of silicon. The solid line is a least-squares fit to the data for temperatures below 1300 °C. The data point marked as an x was measured after the sample had been heated to 1390 °C and then cooled.

The statistical estimate of the standard deviation in each data point is 0.0002. Some of the data shows more variation than what would be statistically expected. The detection system is sensitive to environmental conditions. For this reason, if a change is observed in S, part of the temperature range is retraced to check consistency. Therefore, the data is not taken in order of monotonically increasing temperatures.

There is some evidence of an increase in the slope of S for some of the highest-measurement temperatures. The change in the data is small, and the temperature scale may be distorted in this temperature range (> 1300 °C). Also, the positron diffusion length calculated from the positronium fraction measurements showed a decrease of about 60% over the temperature range from 1210 to 1380 °C. The sample temperature was decreased to 550 °C, and additional measurements of S and f were made. The change in the diffusion length was irreversible. Although the S values were also higher than previous measurements (see the x at 550 °C in Fig. 1), they are no more out of line than some of the other measurements. Therefore, no conclusions can be drawn about the reversibility of the change in S. The sample was returned to high temperatures, and data was taken at increasing currents until the sample partially melted.

The upturn in S could arise either from the diffusion of

an impurity into the sample or from the onset of monovacancy formation, depending on whether or not it is irreversible. The clear irreversibility of the diffusion length indicates that impurities are the source of this effect. The most likely source of an impurity would be the zirconia based adhesive used to affix the thermocouple to the sample. In any case, the changes in S and f do not agree with the observation of Dannefaer *et al.* of saturation trapping in thermally generated monovacancies by 1150 °C since the temperature is much higher (>1200 °C at onset).

The absence of any clear evidence of thermal monovacancy formation is our S and f measurements indicates that either monovacancies are not forming in detectable numbers in our sample or they are not trapping positrons. It is possible that the binding energy of positrons at vacancies is too small for trapping to occur at these temperatures or that detrapping is significant. A theoretical value of 0.42 eV for the positron binding energy at a neutral monovacancy, which should be considered to be a crude estimate, leaves this open to question.[16] In any case, a low binding energy would not resolve the conflict with the finding of Dannefaer *et al.* of saturation trapping in vacancies. It is also possible that vacancies form complexes with impurities present in the sample, and that these complexes do not trap positrons. Mascher, Kerr, and Dannefaer evidence of such a process occurring in silicon heavily doped with phosphorous.[17] Many impurities diffuse rapidly into silicon at high temperatures, and our data shows some evidence of an impurity entering the sample for $T>1300$ °C. Therefore, this possibility cannot be ruled out. However, it should be noted that Dannefaer's sample was apparently of lower purity than ours; therefore, the effect of impurities on their data is also subject to question. A very low estimated value for the diffusion constant of vacancies in silicon[18] would not have prevented us from observing positron trapping into vacancies on the time scale of our experiment.

The possibility that the equilibrium number of monovacancies is below the threshold for detection will now be discussed using the two-state trapping model.[19] We should be able to detect a change of a few tenths of a percent in S, while the expected change in S for 100% trapping at monovacancies is expected to be a few percent. Therefore, a change should be detectable if about 10% of positrons annihilate from trapped states. If detrapping is neglected, this corresponds to a trapping rate of about $5\times10^{8}\ \mathrm{s}^{-1}$. The trapping rate κ is given by

$$\kappa=\nu_0 C_v=\nu_0 e^{S_F/k} e^{-H_f/kT} ,$$

where ν_0 is the specific trapping rate, C_v is the monovacancy concentration, and S_f and H_f are the formation entropy and enthalpy for the monovacancy. If, as in metals, $\nu_0\approx10^{15}\ \mathrm{s}^{-1}$, then we can conclude that the monovacancy concentration for temperatures below the melting point is less than about 5×10^{-7}. The formation entropy of a monovacancy in silicon is a matter of some debate.[20-22] If we use the lower limit of $S_F=6.5$ k given by Lannoo and Allan,[22] which is within the range of values consistent with the data of Dannefaer *et al.*, then we find that $H_f>3.6$ eV for the neutral vacancy. The correction factors given by Dannefaer *et al.* to reflect the fact that trapping is actually more likely to occur at charged vacancies have been included in deriving this value. Divacancy effects have not been considered.[23]

It should be noted that the typical specific trapping rate used above may not be appropriate in this case. The data of Dannefaer *et al.* suggested a specific trapping rate of the order of $10^{17}\ \mathrm{s}^{-1}$ or greater. A rate of this magnitude is explained by a cascade process through a succession of bound states with energy carried away by phonon emission.[24] If this large specific trapping rate were used in the calculation, the lower limit of H_f would be increased.

Similar S measurements on doped samples (p-type 1–10 Ω cm and n-type 0.005–0.020 Ω cm) were performed with a less-stable detection system. The data showed that S was constant to within 0.75% in the temperature range where Dannefaer *et al.* saw a change in lifetime ascribed to monovacancy formation.

In conclusion, in agreement with the lifetime measurements of Würschum *et al.*,[2] we see no evidence of positron trapping at thermally generated monovacancies in Doppler-broadening and diffusion-length measurements performed on high-resistivity silicon for temperatures up to the melting point. This is in disagreement with Dannefaer's observation of saturation trapping.[1] Lower-resistivity samples also exhibit no evidence of trapping at monovacancies. A lower limit of approximately 3.6 eV can be placed on the formation enthalpy for neutral monovacancies, subject to assumptions about the formation entropy of the vacancies and about positron trapping in the vacancies.

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