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At-temperature annealing of near-surface vacancy-type defects observed by positronium formation spectroscopy

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Abstract

The *in situ*, at-temperature, real-time monitoring of open-volume defect formation, migration, coalescence and annealing has long been possible in bulk solids by measuring the Doppler broadening of annihilation radiation arising from the implantation of energetic positrons from a radioactive source. However, equivalent measurements on vacancy-type defects in thin films or within $\sim 10^2$ nm of a solid surface have not been made, principally because of the distorting influence on the data of surface annihilations. This paper describes the first measurements known to the authors of *in situ*, at-temperature annealing studies of near-surface open-volume defects, using as an example a silicon sample implanted with 50 keV Si^+ ions. The technique involves the measurement of the fraction of controllable-energy positrons which diffuse back to the surface and there form positronium. The applicability and limitations of this method are discussed.

1. Introduction

Positron annihilation spectroscopy (PAS) has long been recognized as a valuable tool for studying open-volume defects in solids [1, 2]. *In situ*, at-temperature, real-time monitoring of the growth, evolution and annealing of defect structures has been extensively studied using Doppler broadening spectroscopy of annihilation radiation, which is sensitive to the mean electronic momentum at the annihilation sites. Positrons are efficiently trapped by open-volume defects; there, in the absence of core electrons, they annihilate predominantly lower-momentum electrons, and the extent of the Doppler broadening of the 511 keV annihilation line is reduced. Thus the mean annihilation linewidth is a measure of the fraction of positrons trapped in defects. If the nature of the defects is known, allowing one to assume a value for the specific positron trapping rate, then the trapped positron fraction leads one to the

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open-volume defect concentration. The Doppler broadening technique, described in detail by MacKenzie [3], is particularly suitable for at-temperature, real-time annealing studies [4, 5]; data collection is relatively rapid (typically $\sim 10^2$ s at each temperature), and the HPGe gamma detector is not in contact with the sample chamber.

Nielsen *et al* [6] studied the annealing of defects created in Si by 5 MeV Si ion implantation; because the defects were lying at a mean depth of 0.7 μm, the effects of positron diffusion to the surface were assumed to be negligible and the study was therefore bulklike. To the authors' knowledge, no at-temperature, *in situ* observations of the annealing behaviour of near-surface defects have been made using controllable-energy positron beams. The principal reason for this is the contamination of the signal—for example the Doppler-broadened linewidth—by contributions from annihilation events at the surface; not only does the fraction of positrons reaching the surface change as the temperature changes, but so also may the signal characteristic of surface annihilations. This paper describes a method by which these inherent problems are overcome.

The sample used in the present study/demonstration was n-type, phosphorus-doped (40 Ω cm) FZ Si implanted with 50 keV Si^+ ions at a dose of 5×10^{13} cm^{-2}, with vacancy-type damage at depths of $\sim 10^2$ nm. The implantation process introduces vacancy–interstitial Frenkel pairs into the structure of the material; although many of the interstitials and vacancies anneal out at room temperature, there remains a detectable fraction ($\leqslant$5%) of stable defects such as divacancy–impurity complexes [7, 8]. Open-volume defects may have an important effect on dopant mobility and activation, as well as playing a role in processing procedures such as impurity gettering [9, 10] so that knowledge of their concentration, distribution and evolution with temperature is valuable.

2. *Ex situ* measurements

PAS measurements were first carried out on seven n-type, P-doped (40 Ω cm), FZ-Si(100) samples, all implanted with 5×10^{13} cm^{-2} Si^+ at room temperature and then individually annealed for a total of 30 s at 250, 350, 450, 550, 650, 750 and 850 °C at the University of Surrey Centre for Ion Beam Applications.

Doppler broadening measurements were performed on the computer-controlled, magnetically guided variable-energy positron beam at the University of Bath [11]. The extent of the Doppler broadening of the annihilation line is described by the parameter S; the definition and use of this parameter is described and discussed by van Veen *et al* [12]. The mean S, being a linear combination of values characteristic of positrons annihilated in defects, in the bulk material and at the surface, was measured as a function of positron implantation energy E. All measurements were performed at room temperature.

The experimental results $S(E)$ are presented in figure 1(a). The value of the peak S parameter, corresponding to the maximum positron response to the defects, decreases rapidly between the annealing temperatures of 450 and 550 °C. If one assumes that the defects do not change in size but only concentration then one can deduce by eye that they are annealed out in this temperature range.

This direct observation is put on more quantitative foundations by fitting the data with the program POSTRAP [13]. The fitting parameters were the defect concentrations and their depths, modelled by a single box of depth 250 ± 50 nm, and were varied until (a) there was a good visual fit to the data, and (b) the calculated defect S parameter (S_D) was $\sim$1.036, a typical value for saturation positron trapping in vacancy-type defects created in Si by ion implantation [14]. The defect concentration (C_D) values for the samples annealed at 750 and 850 °C were indistinguishable from zero. Defect concentration is plotted against annealing temperature in figure 1(b).

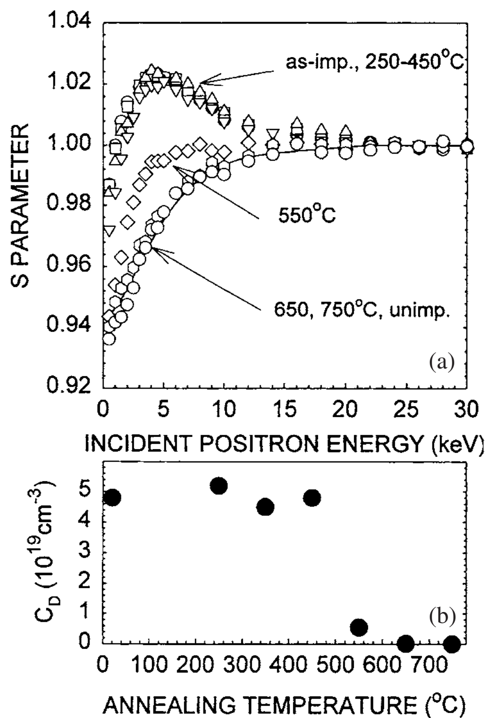

Figure 1. (a) Measured S parameter versus incident positron energy for FZ Si implanted with 5×10^{13} cm^{-2} Si ions: unimplanted, as-implanted and annealed at 250, 350, 450, 550, 650 and 750 °C. (b) Defect concentrations deduced from POSTRAP analyses of the data in (a) versus annealing temperature.

This type of experiment is typical of studies of vacancy annealing carried out using slow positron beams. Note that while the assumption that it is the defect concentration alone that varies, and not defect size, is not necessarily valid, the measurement of the temperature at which all defects detectable by PAS are annealed out is not in question.

3. *In situ* measurements

3.1. Experimental technique

Inspection of figure 1(a) suggests a straightforward method for at-temperature annealing studies; even though measurement of an entire $S(E)$ spectrum at each temperature is impractical (each data set would take several hours to collect), one could select the incident positron energy giving peak response to the defects (in this case, 4 keV) and measure the S parameter as the sample temperature is increased. One would expect to see $S(4)$ decrease as in figure 1(a) during annealing, resulting in a plot similar in nature to that in figure 1(b). A data collection time of about 500 s would be required at each temperature.

This measurement scheme, however, is not practical. As the sample temperature increases in the range applied here (i.e. room temperature to 750 °C), those positrons which are able to diffuse to the sample surface—the number of which is affected by the annealing of defect trapping sites and the change in the positron diffusion length—are able to leave the surface as the positron–electron bound state, positronium (Ps). Because of electron screening effects Ps can only form above the surface of metals and semiconductors ($r_s \approx 6$); furthermore, at elevated temperatures positrons trapped in the surface potential well are desorbed as Ps [15]. Therefore, as the temperature is increased, the fraction of implanted positrons which eventually form Ps also increases. 75% of the Ps formed is in the triplet (*ortho-*) state, *o*-Ps; this predominantly decays with the emission of three gamma photons, a negligible number of which appear in

the 511 keV photopeak recorded by the HPGe detector. Conversely, the 25% of Ps formed in the singlet (*para*-) state, *p*-Ps, decays just above the sample surface with the emission of two 511 keV photons, which do contribute to the photopeak and which cause an increase in the measured value of the S parameter. Uedono *et al* [16], in their report of equilibrium at-temperature measurements of undefected Si, show this increase in surface S parameter with temperature up to 1200 °C, above which they report a decrease, which they attribute to surface melting.

In summary, the increase in S as the sample temperature rises, caused by increasing Ps formation, more than compensates for the decrease expected from figure 1(a) as the defects are annealed. Therefore, without careful correction of the data by independent measurement of the fraction of positrons forming Ps at each temperature, measurement of S as a function of temperature yields no direct information on defect annealing.

Further consideration of the problems associated with S parameter measurement caused by Ps formation, however, leads one to a solution based on the measurement of the fraction of implanted positrons which are able to diffuse back to the sample surface; this is possible via measurement of the Ps fraction as a function of temperature for the sample being studied and an undefected, but otherwise identical, sample. This method was applied in principle by Mäkinen *et al* 15 years ago to study the defects (and their *ex situ* annealing) near the surface of Al(110) created by keV Ar^+ ion bombardment [17].

In general, for a sample with subsurface defects, the fraction $F_{Ps}(T)$ of implanted positrons forming Ps at a temperature T is given by

$$F_{Ps}(T) = F_S(T)\eta_{Ps}(T) \tag{1}$$

where $F_S(T)$ is the fraction of positrons which diffuse back to the sample surface, and $\eta(T)$ is the temperature-dependent Ps formation branching ratio. Now for an identical but undefected sample of Si we have

$$F_{Ps0}(T) = F_{S0}(T)\eta_{Ps}(T) \tag{2}$$

where the additional subscripts 0 refer to the unimplanted ('perfect') sample, and $\eta_{Ps}(T)$ is assumed to be the same in both cases. $F_{S0}(T)$ can be computed using

$$F_{S0}(T) = \int_0^\infty P(z, E)\exp(-z/L_+(T))\,dz \tag{3}$$

where $P(z, E)$ is the positron implantation profile for the chosen incident energy E, z is depth beneath the surface and $L_+(T)$ is the positron diffusion length at temperature T (L_+ varies as $T^{-1/4}$ [18]). $L_+(300)$ is deduced, from fitting $S(E)$ curves for unimplanted Si such as that shown in figure 1, to be 250 nm. $P(z, E)$ is assumed to have the Gaussian derivative form, widely used in positron implantation studies [19].

Therefore, if the Ps fraction $F_{Ps0}(T)$ is measured for unimplanted Si at any chosen incident energy—here 4 keV—and $F_{S0}(T)$ is derived from equations (2) and (3), the Ps branching ratio $\eta_{Ps}(T)$ is determined. Substituting $\eta_{Ps}(T)$ into equation (1) and measuring $F_{Ps}(T)$ yields the surface fraction $F_S(T)$ for the defected sample being studied.

Although a plot of the surface fraction $F_S(T)$ versus sample temperature in itself provides an indication of defect annealing, it is desirable to convert $F_S(T)$ to $C_D(T)$, the mean subsurface vacancy-type defect concentration. This is achieved by first computing the effective positron diffusion length L_{+eff} in the defected sample at temperature T for a range of values of $C_D(T)$, using the expression

$$L_{+eff}(T) = L_+(T)\sqrt{\lambda/(\lambda + \nu(T)C_D(T))} \tag{4}$$

where λ is the bulk positron lifetime in Si (4.55×10^9 s^{-1}) and $\nu(T)$ the specific trapping rate, assumed to be 10^{15} s^{-1} at room temperature and to have a $T^{-1/2}$ temperature dependence [20].

Measured values of the latter temperature dependence have varied greatly, and depend on defect size, but such variations have only a small, second-order effect on the present analysis. Thus at a given temperature T each value of C_D corresponds to a value of $L_{+\mathrm{eff}}$ and, using equation (3), a value of $F_S(T)$. By comparing with the value of $F_S(T)$ determined by the experimental method described above, a value of C_D is thus selected.

The technique of Ps formation spectroscopy was widely used in the early days of defect profiling with positrons [21]. It was supplanted by Doppler broadening spectroscopy, a technique which has the potential to give more information on the type and depth profile of subsurface vacancy-type defects and which is less sensitive to changes in surface conditions. However, the advantages of Ps formation as a technique for studying the annealing of defects are (a) the absence of problems discussed above associated with Doppler broadening measurements, (b) the speed of measurement—good statistics at one incident positron energy are obtained in $\sim 10^2$ s, and auxiliary measurements are performed separately, and (c) it is insensitive to small changes in gamma detector resolution caused by heating of the detector head.

Fortuitously, positrons are insensitive to any thermally created vacancies in silicon [22], and so only the annealing of the defects in the implanted Si causes the Ps and surface fractions to change. Also, the use of FZ Si and Si ions greatly reduces the possibility of complications associated with the formation of microvoid–oxygen complexes in the sample, which may be stable to very high temperatures. The measurements are also aided by the absence of positron re-emission from the surface of Si, which has a positive positron work function; therefore, no potential had to be applied to the Si sample in order to return any re-emitted positrons to the surface.

A positron incident energy of 4 keV was chosen for the Ps formation measurements, being the energy at which the response to subsurface defects was a maximum in the *ex situ* annealing measurements (figure 1). However, any energy in this region could have been chosen, as long as the fractions of positrons which can return to the surface are large enough. The same energy positrons are used in measurements on the implanted and unimplanted samples, so that the system geometry is unchanged, and effects due for example to backscattering are identical in the two sets of measurements.

The temperature of the sample was increased by electron beam heating. Two problems with the heater had to be overcome. First, the Ge detector, mounted inside a re-entrant flange-mounted can with a foil endcap 20 mm from the sample, was pulled back and cooled by circulating air. Second, a relatively high flux of electrons escaping from the heater assembly were guided towards the slow-positron source; on reaching the positron accelerating potential the electrons were accelerated back towards the source, resulting in a long-term reduction of the incident positron signal rate to close to zero. The effect was greater for higher accelerating potentials and higher temperatures (i.e. higher electron energies/currents). This latter effect, attributed to a reduction in the source potential by the passage of current, and/or charging effects in the vicinity of the source, was eliminated by (a) surrounding the sample and heater assembly with Mo foil to reduce electron leakage, and (b) mounting a 92% transmission tungsten mesh in the beam line, 0.3 m from the sample and held at -800 V. As the maximum energy of electrons from the heater filament was 600 eV, this potential effectively prevented any electrons from reaching the source end of the system.

3.2. Positronium fraction measurements

The production and detection of Ps has been described in detail elsewhere [15]. The fractions of positrons incident on a surface that leave as Ps, F_{Ps} and F_{Ps0}, are determined by recording gamma ray energy spectra. Such spectra exhibit two main features: a broad distribution of energies dumped in the Ge detector crystal by the gamma rays via Compton scattering, and a sharp peak at 511 keV corresponding to gamma rays giving up all their energy in the detector

via the photoelectric effect. Between the two regions is a valley. When more Ps is formed, annihilation events in the photopeak are reduced and those in the valley are increased because of the increase in the three-photon annihilation of o-Ps. R, defined as the ratio of counts in the valley region between about 300 and 505 keV (V) to counts in the photopeak (P), therefore reflects the amount of Ps formed. By determining this ratio, R_0, when no Ps is formed (with sample at room temperature, $E = 30$ keV to prevent any measurable diffusion to the surface) and R_1 when all the positrons are annihilated as Ps (sample at high temperature to desorb all trapped positrons as Ps, E low to ensure that all implanted positrons can reach the surface), intermediate values for F_{Ps} can be determined from the expression [23]

$$F_{Ps} = \left[1 + \frac{(R_1 - R)}{(R - R_0)} \cdot \frac{P_1}{P_0}\right]^{-1}. \tag{5}$$

Before any ratios R were determined, the mono-energetic positron beam was prevented from reaching the sample and a background gamma energy spectrum was measured. Background counts were subtracted from V and P prior to the evaluation of R.

Measurement of the zero Ps fraction parameter R_0 is straightforward. However, R_1 is more problematical. If a direct measurement of R is made at very low incident positron energy E (i.e. for $E < 1$ keV) the resulting value can be corrupted by the effects of epithermal, or non-thermalized, positrons. These can both leave the surface as free positrons [24] or pick up an electron and form positronium [25]. Consequently, R_1 was measured for $E = 1, 2, 3$ and 4 keV for an unimplanted sample at 800 °C and the value at $E = 0$ found by extrapolation. For the purposes of this study R_1 was assumed to correspond to $F_{Ps} = 1$; Mills [26] found for clean Si(100) that at 800 °C the absolute Ps fraction was close to 1.0.

3.3. Experimental results

Figure 2(a) shows the fractions of positrons returning to the surface and forming Ps, $F_{Ps0}(T)$ and $F_{Ps}(T)$ for unimplanted and implanted FZ Si samples. The temperature was ramped in steps and left at temperature during measurement for 100 s. (Ramping between temperatures took ~100 s.) Figure 2(b) shows the corresponding fractions reaching the surface, evaluated from the data in (a) following the procedure described earlier.

The average subsurface defect concentrations $C_D(T)$ obtained from the surface fractions in figure 2(b) are plotted in figure 3, together with the results from *ex situ* measurements (in which rapid thermal annealing was performed in each case).

4. Discussion and conclusions

Comparison with *ex situ* S-parameter measurements (figure 3) suggests that the procedure described here has been successfully tested. It can be seen from figure 2(b) that computation of mean defect concentrations is desirable but not essential for determining annealing temperatures (i.e., surface fractions can give equivalent information).

While it is outside the scope of this paper to discuss the physics of the annealing results in the example system chosen for this study, it is clear that there appears to be one major annealing step at 550 ± 50 °C. This temperature is higher than that accepted for bare vacancies and divacancies, and it is therefore assumed that the residual divacancy-type defects left after ion implantation are pinned in the lattice by complexing with impurity atoms. This has been seen in Si implanted with other ions (e.g. O, F) and in Cz Si [27]. However, because Si ions and FZ Si were used here, the agglomeration of open-volume defects and their persistence to very high temperatures (i.e. above 1000 °C) is not seen.

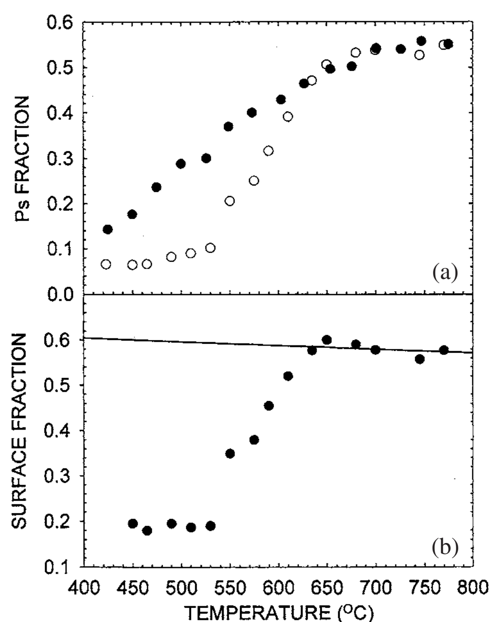

Figure 2. (a) Ps formation fractions measured at temperature for unimplanted FZ Si (solid circles) and FZ Si implanted with 5×10^{13} cm^{-2} Si ions (open circles). 100 s ramp times, 100 s at each temperature. (b) Fractions of positrons implanted with 4 keV returning to the sample surface for the implanted and control Si samples. Solid line: calculated surface fraction for 4 keV positrons in undefected Si.

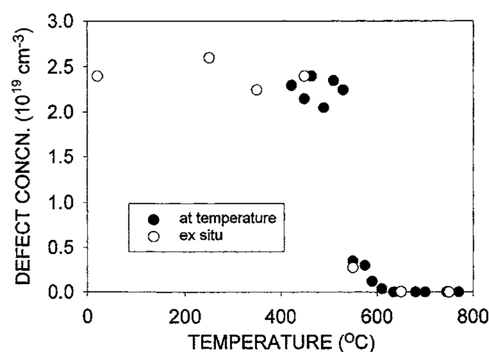

Figure 3. Mean defect concentrations versus annealing temperature from at-temperature *in situ* Ps formation measurements (solid circles) and from *ex situ* S-parameter measurements (open circles).

The method suggested here for at-temperature annealing studies, which revisits the pioneering days of near-surface defect profiling with positrons, is rapid (requiring $\leqslant 10^2$ s per datum) and is robust against temperature-dependent effects in the gamma-ray detector system. It assumes that the surface conditions, and thus the Ps formation branching ratio at any temperature T, is the same for the implanted sample and for a similar unimplanted, undefected sample of the same type; for example, if the native oxide structure or thickness changes as T is increased, it is assumed that the same changes are seen in the implanted and reference samples. The test system studied here appears to confirm that this assumption is reasonable.

If an electron beam heater is used to elevate the sample temperature, steps may need to be taken to prevent a relatively high current of electrons from being accelerated to the source end of the positron beam apparatus and potentially reducing to zero the positron beam intensity. In this study this was achieved by placing a fine mesh, held at –800 V, in front of the sample. If the technique is used to study defects in solids which have a negative positron work function, and hence re-emit thermalized positrons into the vacuum, a small negative potential should be applied to the sample throughout the measurements to pull back any such positrons to the surface so that they eventually can form Ps there.

The technique described is only suitable if the Ps formation probability F_{Ps} is sizeable. F_{Ps} may or may not be temperature dependent in the range where annealing occurs. An annealing range above 200 °C would appear particularly amenable to this technique; annealing below room temperature, where F_{Ps} is low, would be more difficult. However, there are many systems for which defects may anneal at several hundred °C, and Ps formation spectroscopy should find wide application in at-temperature defect annealing studies. In addition to the extension of the measurements described herein to the study of the annealing characteristics of defects formed in semiconductors by implanted ions of different masses and doses, and the formation and annealing of vacancy–impurity complexes, the technique may also be applied to defect formation and annealing in thin films and the near-surface regions of metals for which the surface Ps formation probability is readily measurable in the temperature range of interest.

Acknowledgments

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