Activation Energies for the Formation and Evaporation of Vacancy Clusters in Silicon

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The thermal evolution of vacancy-type defects in Czochralski (Cz-) and epitaxially grown (epi-) silicon has been investigated using variable-energy positron annihilation spectroscopy. Heating at 300–500 °C caused rapid migration of divacancies and clustering of the resulting defects with activation energies of 2.1(2) and 2.7(7) eV in epi- and Cz-Si. Clustering occurred more rapidly in Cz-Si, attributed to the seeding effect of impurities. Heating at 500–640 °C annealed the clusters with activation energies of 3.9(3) and 3.6(3) eV in epi- and Cz-Si, linked to the vacancy-cluster binding energy.

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The migration, agglomeration, and annealing behavior of vacancies in silicon is of fundamental interest but is also relevant to the development of new methods in nanoelectronics. It is well-known that divacancies (V_2) are the dominant vacancy-type defects formed during room temperature ion implantation via the interaction of monovacancies, which are mobile at room temperature. The evolution of ion-implantation–induced defects upon thermal annealing has been the target of several studies using a wide range of defect characterization techniques. The authors studied 2 MeV self-implanted Czochralski-grown (Cz-) Si using variable-energy positron annihilation spectroscopy (VEPAS) [1]. Agglomeration of the implantation-induced defects was observed upon annealing for a few minutes at high temperatures (~600 °C), forming clusters with a positron response consistent with hexavacancies, and then annealing away or breaking up after annealing for longer times at 600 °C or at higher temperatures. Simpson *et al.* found that whereas the VEPAS response to the defects created by the implantation of MeV Si^+ ions into float-zone Si was constant up to ~600 °C, 300 °C was sufficient to remove the 1.8μm infrared absorption (IR) peak associated with V_2 [2]. This discrepancy was attributed to vacancy aggregation at the temperature at which the V_2 become mobile, the resulting clusters being positron detectable but not optically active. A similar discrepancy was reported by Dannefaer *et al.* [3–5], who explained it in terms of V_2 associating loosely with each other without clustering. However, Makhov and Lewis later suggested that vacancy clustering may well not lead to a clear change in PAS parameters, while the IR response is destroyed [6]. In another study of near-surface implantation-induced V_2 in Cz-Si it was found that if the ion dose is below the critical value for amorphization, vacancy clusters form after annealing at 300 °C, which are stable up to 500 °C but anneal out at ~800 °C [7].

Pinning of V_2 by impurities has been invoked to explain the survival of vacancy defects in Cz-Si to temperatures of ~500 °C [3,8].

The binding energy of vacancies to clusters formed upon annealing in Si implanted with MeV Si^+ is believed to be high, but their formation energy is low; i.e., the clusters are formed quickly at low temperatures but survive for long times or to high temperatures. A value of 3.2 ± 0.2 eV has been reported for the binding energy of vacancy clusters in a 1.8μm thick Si top layer of Si-on-insulator structure implanted with 2 MeV Si^+ ions and annealed at temperatures between 800 and 900 °C [9].

The aim of the investigation reported in this Letter was to gain an understanding of the agglomeration and annealing processes of vacancy defects in epi- and Cz-Si and to attribute activation energies to them.

Cz- and epi-Si samples were implanted with 50 keV Si^+ ions at 5×10^{13} cm^{-2} at the University of Surrey Ion Beam Centre. The implantation was performed at room temperature so that the ion dose was below the critical value for amorphization. *In situ* annealing of the samples was carried out over a temperature range from 300 to 640 °C and the positron response was measured at each temperature as a function of annealing time. The Ge gamma ray detector head was cooled by air circulation, and electrons from the filament of the electron-beam sam-

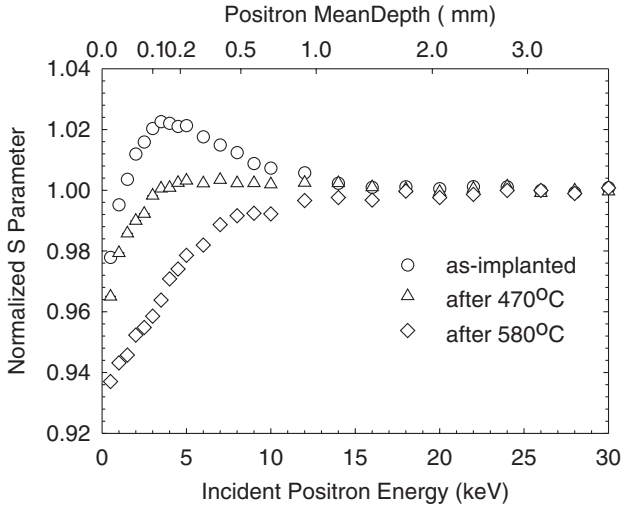

FIG. 1. $S(E)$ for an epi-Si sample, as-implanted and after annealing at 470 and 580 °C.

ple heater assembly (held at −625 V) were prevented from escaping and being accelerated back into the positron source by a potential of −800 V applied to a high-transmission mesh mounted in the beam line [8].

The positron response to vacancy-type damage in the implanted Si is expressed in terms of the conventional line shape parameter S, which characterizes the Doppler broadening of the 511 keV line due to the annihilation gamma photons. S is defined as the ratio of counts in a central region of the annihilation line to that in the whole line and is higher for positrons trapped in vacancies in Si than for those annihilated while freely diffusing in bulk Si, because the average momentum of annihilated electrons is lower and the Doppler broadening consequently smaller [10].

The peak of the VEPAS response to vacancy-type damage caused by 50 keV Si^+ in Si is at incident energy $E \sim 3.5$ keV (see Fig. 1). The mean depth probed by 3.5 keV is 120 nm, in reasonable agreement with the predictions of the simulation code TRIM [11] for the peak in vacancy damage. Therefore, to monitor the evolution of defects with annealing time, the S parameter at $E = 3.5$ keV incident energy was measured at regular intervals (usually 600 s, but shorter for temperatures above 600 °C). S at 1 and 24 keV were also measured frequently, to monitor any possible real or systematic changes in the near-surface and the bulk VEPAS responses during annealing.

After each at-temperature measurement, samples were cooled and $S(E)$ curves measured at room temperature for E from 0.5 to 30 keV, for comparison with data for the as-implanted sample or at different stages of its annealing history. An example of $S(E)$ for an as-implanted sample is shown in Fig. 1. V_2 in the first 100 nm below the surface give rise to the broad peak in $S(E)$. S_b, the measured S for the bulk material, is normalized here to unity.

Representative examples of raw data taken for epi-Si samples are presented in Figs. 2 and 3. Figure 2 shows $S(t)$ for implanted epi-Si (a) at 470 °C and (b) after leaving at room temperature for five weeks and then annealing at 580 °C, and Fig. 3 shows similar curves for a sample that has been annealed at 350 °C and then 600 °C. In both figures two stages of evolution at the two annealing temperatures can be readily distinguished. In Fig. 2(a), S starts from the value measured in the as-implanted case and reaches equilibrium after ~20 h at 470 °C. The second stage starts from approximately where the first one ends and falls to its final asymptotic value of ~0.98 after ~30 h at 580 °C.

Figure 1 shows $S(E)$ curves for the sample featured in Fig. 2, measured at room temperature after annealing at 470 and 580 °C as well as for the as-implanted sample. The incompleteness of the first annealing stage can clearly be seen and is thought to be associated with the formation of vacancy clusters via the migration of smaller clusters formed almost instantaneously by the migration and agglomeration of V_2, together with the loss of some small clusters—most probably to the nearby surface sink. The loss of some of the small clusters is the reason why S(3.5 keV) decreases as the clustering process proceeds. The second stage (seen here at 580 °C) is enough to remove all the remaining defects.

The behavior of the epi-Si sample shown in Fig. 3 for annealing at 350 and 600 °C is similar to that shown in Fig. 2. The low starting value of the S parameter when annealing at 600 °C could indicate that some agglomeration and/or annealing occurs in this case within the first ten minutes (i.e., during measurement of the first data point).

To investigate whether the change observed in S at 3.5 keV could result partly or totally from changes in surface condition—the measured S value is a combination

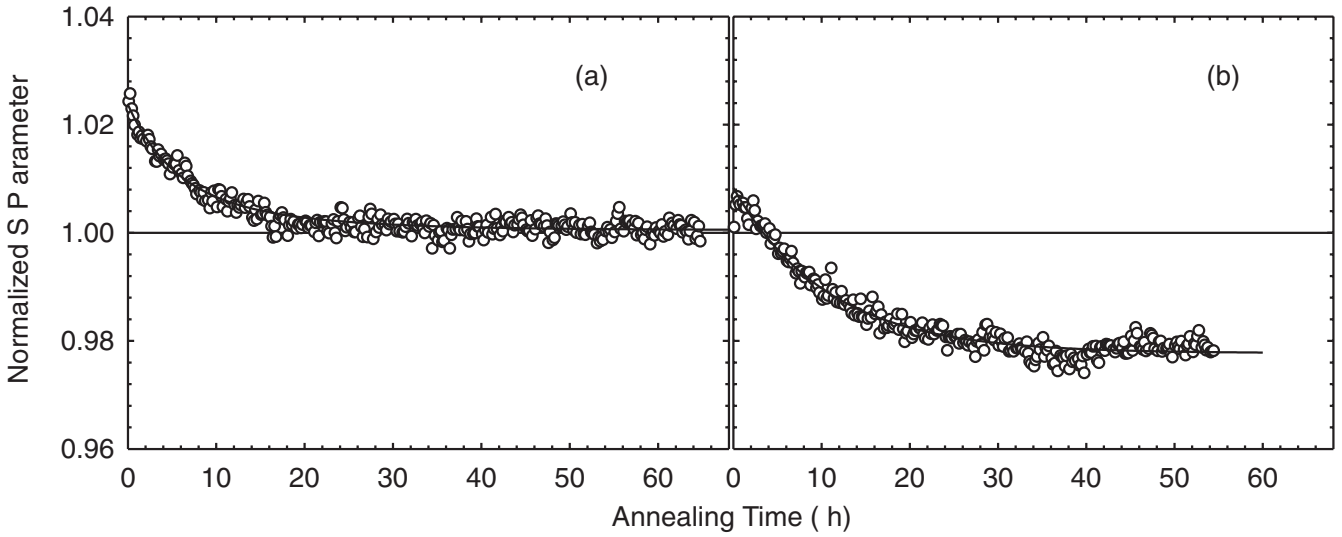

FIG. 2. S(3.5 keV) vs annealing time for implanted epi-Si at (a) 470 °C and (b) 580 °C. The solid lines through the points are exponential fits. The horizontal solid line indicates the bulk level measured with 24 keV positrons.

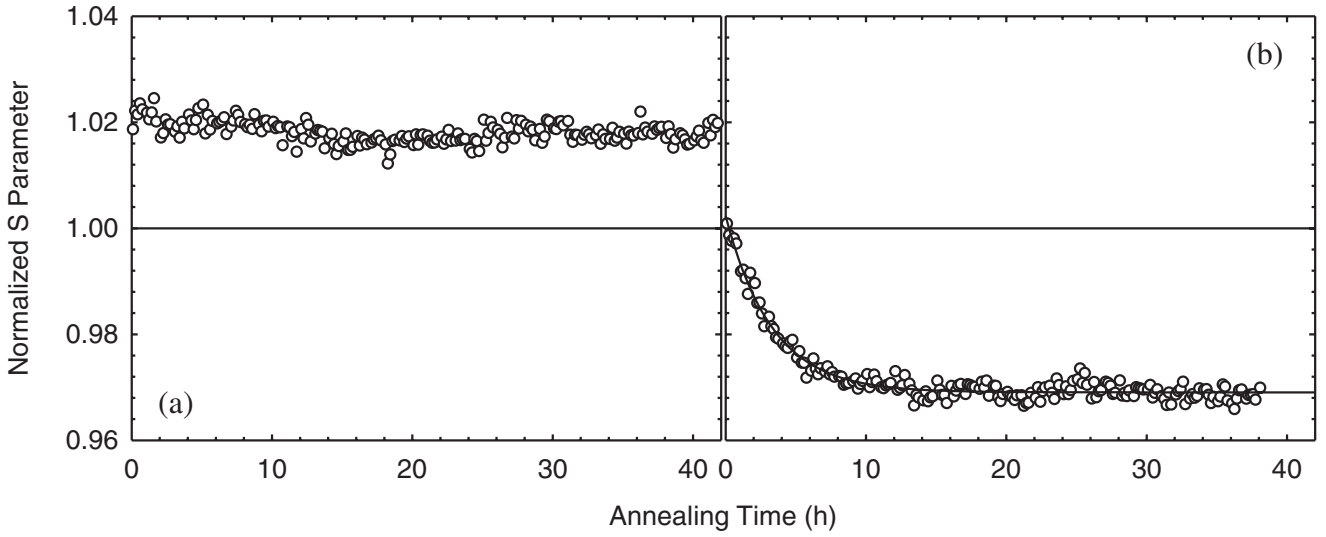

FIG. 3. S(3.5 keV) vs annealing time for implanted epi-Si at (a) 350 °C and (b) 600 °C. The solid line through the points in (b) is an exponential fit. The horizontal solid line indicates the bulk level measured with 24 keV positrons.

of contributions from surface, defect, and bulk—$S(E)$ curves were constructed using the VEPFIT program [12] with different fixed values of the surface S value. It was found that the resulting change in S at 3.5 keV is negligible compared with those observed during annealing. Positronium formation and annihilation at the surface of silicon at elevated temperatures was also monitored throughout the experiment and was found not to influence the $S(t)$ results presented here.

S(3.5 keV) measured at room temperature for all samples after annealing at temperatures between 300–500 °C was always found to be ~1, and ~0.97 after annealing at higher temperatures, as shown in the example in Fig. 1. This behavior is consistent with earlier observations on the stability of vacancy clusters up to ~500 °C and their annealing at higher temperatures [2,5,7].

The $S(t)$ data for all temperatures T have been fitted to the approximate form $S(t) = S(\infty) + A\exp(-\lambda t)$; λ here represents the rate of any change in the physical state of the system. As expected, λ becomes shorter with increasing T, implying that annealing (at high temperatures) or clustering (at lower temperatures) proceeds more quickly as the temperature is increased. To obtain an activation energy (E_a) for each process, $\lambda(T)$ was fitted to the Arrhenius relation $\lambda(T) = \lambda_0 \exp(-E_a/k_B T)$, where k_B is Boltzmann's constant and λ_0 is a constant.

The Arrhenius plots and fits for Cz- and epi-Si are shown in Fig. 4. The plots suggest that there are two thermal processes happening in the two temperature ranges. It is proposed that in the low temperature range vacancy clustering is occurring with $E_a = 2.1 \pm 0.2$ and 2.7 ± 0.7 eV associated with cluster agglomeration in epi- and Cz-Si, respectively, whereas $E_a = 3.9 \pm 0.3$ and 3.6 ± 0.3 eV are associated with the annealing of those clusters at higher temperatures (> 500 °C) in epi- and Cz-Si.

Comparing the Arrhenius plots for epi- and Cz-Si samples in Fig. 4, one sees that vacancy clustering in Cz-Si samples proceeds more quickly than in epi-Si at the same temperatures. It can be concluded that fewer steps are needed to reach the equilibrium state in Cz-Si than in epi-Si, possibly because of the impurity atoms acting as seeds.

In the high temperature range, the difference between the behavior of Cz- and epi-Si samples is not large enough to make unambiguous conclusions. If the small differences in rates of change and in activation energies are real, then these may be associated again with the impurities in Cz-Si. A value of 3.2 ± 0.2 eV has been reported for the binding energy of vacancies to vacancy clusters [9]; the closeness of this value to those measured here for the high-

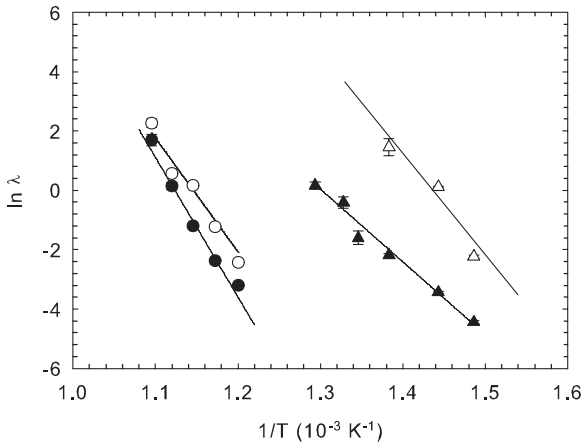

FIG. 4. Arrhenius plots for epi- and Cz-Si samples. The slopes of the fitted lines give activation energies for vacancy clustering (lower temperatures, triangles) and cluster breakup and annealing (higher temperatures, circles). Solid symbols, epi-Si; open symbols, Cz-Si.

temperature process in both Cz- and epi-Si suggests therefore that the complete annealing of the vacancy clusters is preceded by dissociation of the clusters into smaller ones, and we interpret E_a here as being associated with such dissociation.

Theoretical research on the stability of vacancy clusters in silicon [6,13–15] suggests that the clusters formed and eventually annealed in the present work are most likely to be hexavacancies, or possible decavacancies, which are both stable configurations, although Makhov and Lewis [6] find that V_3, V_4, and V_5 are also stable. Further evidence for the formation of V_6 prior to annealing was presented by the authors in Ref. [1]. Hastings *et al.* [13] calculate that it takes 3.76 eV for the process $V_6 \rightarrow V_5 + V_1$, which would be the first stage in evaporation of hexavacancy clusters, and this value is close to the mean of the high-temperature activation energies measured in the present work. Other authors have presented energies for this process between 3.0 and 3.5 eV ([6,9,15] and references therein).

In summary, we have reported observations of vacancy-defect migration, clustering, and annealing in Si, both Cz- and epigrown. At-temperature measurements of the Doppler-broadened annihilation peak have been performed to follow the evolution of the defects upon annealing at temperatures between 300 and 640 °C. At low temperatures (300–500 °C) clustering of the implantation-induced defects occurs; we assume that as divacancies are mobile at ~300 °C, rapid agglomeration into V_{2n} is followed by the observed slower formation of larger clusters until equilibrium is reached. This picture is consistent with the measured activation energies (of ~2.5 eV) being higher than that accepted for V_2 migration (1.3 eV [16]). At higher temperatures (500–640 °C) we see similar annealing of the clusters in both Cz- and epi-Si, with a mean activation energy of 3.7 ± 0.2 eV. This figure is similar to a previously reported figure (of 3.2 ± 0.2 eV [9]) for the binding energy of vacancies to clusters, and even closer to a calculated value for V-V_5 binding [13], and suggests that the annealing proceeds by evaporation of the clusters into very mobile smaller defects. Differences between clustering behavior in Cz- and epi-Si are attributed to the influence of impurity atoms in Cz-Si; no significant difference is seen between E_a for cluster evaporation in Cz- and epi-Si, suggesting that impurities play a negligible role in this process.

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