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The effect of the annealing ramp rate on the formation of voids in silicon

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Abstract

We show the strong dependence on annealing ramp rate of residual open-volume defects in silicon following helium ion implantation and annealing. Helium was implanted at 60 keV energy, 1×10^{16} cm^{-2} fluence into silicon and subsequently annealed to 800 °C for 30 min, with ramp rates ranging from 1 to 100 °C s^{-1}. The residual defect distribution was probed by means of positron annihilation spectroscopy and ion channeling, with results demonstrating a strong dependence on the ramp rate. For these conditions, open-volume defects to which the positron technique is sensitive are present in significant concentrations only for annealing ramp rates greater than 5 °C s^{-1}.

There has been considerable interest in recent years in the formation of nanovoids in silicon formed by ion implantation and subsequent annealing. The choice of ion species, energy and fluence, and of annealing time and temperature have been investigated [1]. Co implantation with H and He has been shown to require smaller threshold implant fluences for void formation [2, 3], and a giant isotope effect has been reported when comparing H versus D implantation [4].

Annealing of the implanted samples often takes place using a rapid thermal process [5]. This is particularly important in processes such as impurity gettering [6–8], defect engineering [9, 10], blistering and pop-out [11, 12], and wafer splitting [13]. It is somewhat surprising then that comparatively little attention has been paid to the effect of the temperature ramp rate, to such an extent that this parameter is often not included in published reports. The importance of this parameter has however been reported for exfoliation of InP [14], and for

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bubble formation in He-implanted Si [15]. Simpson and Mitchell [15] used measurements of He retention following implantation and annealing, along with cross-sectional scanning electron microscopy, and showed that retained He varies by more than an order of magnitude as a function of annealing ramp rate. The purpose of the study described here is to further investigate the role of temperature ramp rate on void formation in silicon, using positron annihilation spectroscopy and Rutherford backscattering/channeling to study the post-anneal residual defect distribution.

'Hyper-pure' 150 mm, 8.5 μm epi-Si(100) wafers background doped with boron to a resistivity of 12–16 Ω cm were implanted with 60 keV He ions to a fluence of 1×10^{16} cm^{-2}. 12×12 mm^2 samples were cleaved from the wafer for annealing. Rapid thermal annealing (RTA) was performed in an 'AET Thermal RX' rapid thermal processor in a flowing N_2 ambient immediately following surface oxide stripping by a 3 stage solvent clean and etch in buffered hydrofluoric acid (48% HF:H_2O 1:10). Each anneal consisted of a 5 min purge at room temperature, followed by a ramp up to 800 °C and a dwell for 30 min at this temperature, before cooling to room temperature. The ramp rates up to 800 °C were varied from 1 to 100 °C s^{-1}, with a separate sample used for each anneal.

Residual open-volume defects following RTA were measured by positron annihilation spectroscopy (PAS) using the University of Western Ontario's positron beam. Details of the technique can be found elsewhere [16, 17]. Positrons are implanted into the sample to a controllable depth, and may be trapped by open-volume defects ranging in size from single vacancies to vacancy clusters or voids. The technique can provide estimated vacancy concentrations to a lower limit of a few times 10^{15} cm^{-3}. Interpretation can be ambiguous however—relevant to this study is the difficulty in distinguishing data due to a large concentration of vacancies versus a small concentration of larger open-volume defects such as vacancy clusters.

Samples were also examined using channeling Rutherford backscattering spectrometry (RBS-c) to probe displaced atoms. A beam of 1.5 MeV He^+ ions was channeled normal to the sample surface with the backscattered particles detected by a surface barrier detector positioned at an angle of 170° to the incident beam.

Figure 1 shows the 'shape' or S parameter versus mean depth obtained from positron annihilation spectroscopy. The data for high-ramp-rate samples are typical of those obtained from silicon containing voids formed by high-dose inert ion implantation and annealing [3, 18, 19] or by low-temperature epitaxy [20]. The most striking feature of these data is the very strong dependence on annealing ramp rate with the peak S parameter increasing with annealing ramp rate. Some details can be extracted by a more careful examination. S values are normalized to $S = 1.0$ for defect-free bulk silicon, and any increase in S above this value is indicative of open-volume defects. The measured S parameter depends on both the concentration of defects and the defect-specific value S_d characteristic of the particular defect species. Approximate assignments can be made [21] of S_d values to vacancy clusters by size: V2 yields $S = 1.045$ and so on up to V5, $S = 1.08$. The interpretation of results can be hampered by the non-uniqueness of data resulting from a large concentration of small defects versus a small concentration of large defects.

Positron data in figure 1 were modeled using POSTRAP5 [22], which calculates the positron implantation profile, and subsequent positron diffusion and trapping by defects, for a user-supplied model. To accurately model the data in this study would introduce a very large number of free parameters since each sample may contain several species of defect, each with its own depth distribution. It is thus necessary to make simplifying assumptions, and so we have used a model which gives each sample a single 'average' defect species (and associated 'average' S parameter) with a depth distribution that mimics the SRIM [23] profile

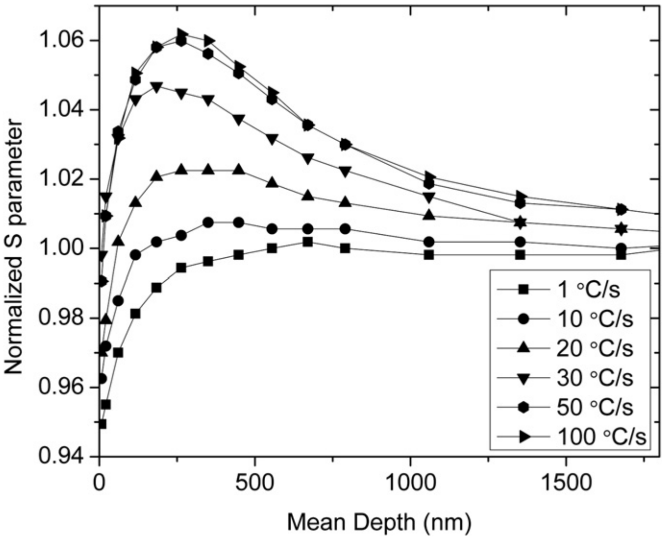

Figure 1. Positron annihilation lineshape (S) parameter versus mean positron implantation depth, from the He-implanted samples following annealing at 800 °C with ramp rates from 1 to 100 °C s^{-1}. The peak S parameters for the samples with the highest ramp rates (at ~250 nm depth) are characteristic of voids. Spectra for the 2 and 5 °C s^{-1} samples are omitted for clarity—the data are similar to those obtained from the 1 °C s^{-1} sample.

Table 1. Parameters obtained from modeling the positron data using POSTRAP5 with the model described in the text.

Annealing ramp rate (°C s^{-1})	Normalized defect S parameter, S_d	Areal defect density (cm^{-2})	Peak defect concentration (cm^{-3})
100	1.065	7.0×10^{14}	2.0×10^{19}
50	1.065	6.0×10^{14}	1.8×10^{19}
30	1.050	7.0×10^{14}	2.0×10^{19}
20	1.027	4.0×10^{14}	1.3×10^{19}
10	1.010	2.0×10^{14}	5.0×10^{18}
5	1.003	2.0×10^{14}	5.0×10^{18}
2	1.001	1.0×10^{14}	3.0×10^{18}
1	1.002	1.0×10^{14}	3.0×10^{18}

of vacancy production. The defect concentration and S parameter are then adjusted for each sample to obtain the best fit to the data, with results as shown in table 1. The modeling results summarized in table 1 are not unique—other combinations of parameters can also model these data, particularly since the defect S parameter Sd and the defect concentration C are somewhat coupled. The data for ramp rates of 50 and 100 °C s^{-1} are very similar; this may be due to saturated positron trapping rather than indicating that the samples are identical.

A reasonable alternative approach to modeling these data would be to use two regions: a near-surface region, and a region for the end-of-range of the ions. However, this would double the number of free parameters, and so was avoided. Independent of the approach taken to modeling the data, there are some features here which are unambiguous. It was not possible to model the data for high-ramp-rate samples (50 and 100 °C s^{-1}) without including open-volume defects in both the near-surface and end-of-range regions of the sample.

For the samples with the lower ramp rates (30 °C s^{-1} and below), it was essential to reduce the value of S used for the near-surface region in order to model the data. This indicates that the size of the voids/vacancy clusters is smaller for the lower ramp rates. For the samples annealed with ramp rates below 10 °C s^{-1}, the defect S parameter is only slightly higher than that from defect-free silicon.

The value of $S_d = 1.065$ ascribed to the high-ramp-rate samples corresponds to a defect of size V4 according to [21]. We emphasize however, that this is better interpreted as a lower limit, since it is also possible to fit the data with a somewhat larger value of S_d, corresponding to larger vacancy clusters/voids. However, this value of S_d appears inconsistent with annihilation in voids with diameters of several nanometers which would have the equivalent open volume of many more than V4. We suggest that positrons may be insensitive to the large ($>$10 nm) [25] voids expected to be formed in these samples, due to competitive trapping by smaller but more numerous vacancy clusters. It is also possible that a sufficiently large void behaves much like a clean silicon surface and thus has an S parameter of 1.0, and so is not detected.

It is of interest to consider the nature of the defects in the low-ramp-rate samples, and in the near-surface region of the high-rate samples. The low S parameter values obtained for the low-rate samples imply that these defects are not a small concentration of voids. For the near-surface region of the high-rate samples, voids are unlikely since this region did not receive a significant concentration of He sufficient to facilitate void formation. Divacancies are unlikely since they break up at temperatures well below our 800 °C anneal. The high purity of the starting substrate material makes vacancy–oxygen complexes unlikely. A possible candidate would appear to be boron–vacancy complexes. The low S parameter value observed is consistent with other impurity–vacancy complexes, however the defect concentrations measured (a few times 10^{18} cm^{-3}) exceed the doping concentration (about 10^{15} cm^{-3}). This suggests that the high defect concentrations required to model the data in the near-surface region may be an artifact of a near-surface electric field in the samples resulting in an apparent short positron diffusion length.

Figure 2 shows RBS-c data acquired using 1.5 MeV He ions. Features to note include (i) a much higher dechanneling signal for the near-surface region in the 100 °C s^{-1} sample compared with the other samples, (ii) a rapid increase in dechanneling at a depth of $\sim$400 nm for most of the samples (the spectra obtained from the samples annealed with ramp rates below 10 °C s^{-1} are indistinguishable from the virgin spectrum and are not shown), the magnitude of which increases monotonically with increasing anneal ramp rate. It is not possible to be certain whether this is due to dislocations, or to voids. It has been suggested by Cerofolini [24] that dechanneling can be caused by the distortion of the lattice surrounding a cavity. Either way, the channeling data indicate a distinct and fairly abrupt change in the samples at the transition between the near-surface region and the end-of-range region. This tends to support our assumption that some degree of void formation takes place in most samples (with ramp rates greater than 5 °C s^{-1}) in this study. The increase in dechanneling with annealing ramp rate is consistent with the positron data. The increased yield in the near-surface region of the 100 °C s^{-1} sample over the virgin silicon sample and those annealed with lower ramp rates certainly indicates the presence of defects after annealing. It does not mean, however, that the other samples which have a virgin-like spectrum in the near-surface are defect-free in this region but that the concentration of defects is below the threshold for detection by RBS (approximately a tenth of a monolayer which equates to a concentration of $\sim 10^{19}$ cm^{-3} over this 400 nm surface region).

Raineri *et al* [25] reviewed the formation of voids formed by He implantation in Si following post-implant annealing. The formation of bubbles and the subsequent evolution to voids during annealing are dependent on the interaction of the He with point defects

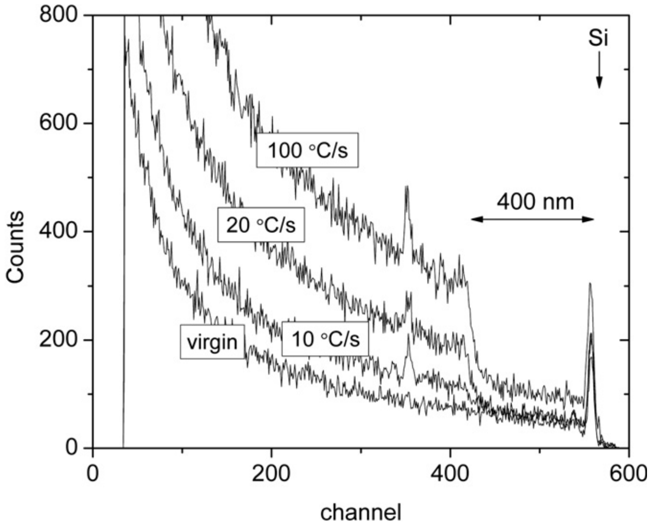

Figure 2. Channeling RBS spectra from the He-implanted samples following annealing at 800 °C with ramp rates from 10 to 100 °C s^{-1}. The spectra from the samples with lower ramp rates are indistinguishable from that of a virgin silicon sample and are therefore not shown. Spectra were collected using 1.5 MeV He^+ ions channeled normal to the sample surface with backscattered particles detected at 170° to the beam. A sharp increase in dechanneling occurs at a depth of ~400 nm.

introduced in the Si lattice during implantation. This, in turn, is dependent on the post-implant annealing schedule (temperature and time) and, as shown here, the ramp rate to the final anneal temperature.

It is believed that the He gas bubbles observed following He implantation evolve from He–divacancy ($He–V_2$) and He–vacancy ($He_m–V_n$) clusters [25, 26]. The He has a stabilizing effect on the vacancy complexes during annealing while Si interstitials diffuse into the Si bulk or annihilate at the Si surface. This results in a vacancy supersaturation which evolves into void-type defects after He has desorbed from the Si. Helium can permeate from the $He_m–V_n$ bubbles and out-diffuse from the silicon sample during annealing, and at temperatures above 800 °C this happens in very short time. Griffioen *et al* [27] described the He release rate from the bubble layer to the surface.

It has also been shown experimentally that appreciable amounts of He can desorb from the silicon during slow ramp ups to 700 °C [15]. Comparing our data with data from [15] for a similar range of ramp rates, we note that Simpson and Mitchell observed a 'transitional' behavior (i.e. from low to high He retention as a function of ramp rate) only for samples with a lower ion dose than ours (5×10^{15} versus 1×10^{16} cm^{-2}). Desorption of He that occurs in the lower temperature range (ramp up) will decrease the number of voids following the full anneal. As the amount of out-diffused He increases, so do the numbers of divacancies and vacancy clusters which can then be annihilated via recombination with silicon interstitials.

In summary the effect of ramp rate on the residual defects in He-implanted silicon has been investigated by positron annihilation spectroscopy and ion channeling. The presence of residual defects to which the positron is sensitive is dependent on not only anneal temperature and time but also the ramp up to the anneal temperature. A slow ramp rate allows He out-diffusion from the silicon at temperatures below 800 °C before interstitial defects have diffused into the bulk or recombined at the surface. Vacancies and vacancy clusters where He has permeated can then be annihilated by silicon interstitials before evolving into voids.

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