Mechanism of swelling in low-energy ion-irradiated silicon

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The phenomenon of swelling (surface expansion) in low-energy self-ion implanted silicon has been investigated using atomic force microscopy and transmission electron microscopy, for a wide range of fluence and postimplant annealing conditions. The swelling height in excess to that contributed by implanted ions shows approximately a cube root dependence on the Si^+-ion fluence. Postimplantation annealing exhibits a marked reduction in the swelling at 650 °C. Both the fluence dependence and the annealing characteristics of the excess swelling suggest the involvement of vacancy clusters in the amorphous layer. We propose that the excess swelling in low-energy implanted Si results from the migration and segregation of the displaced Si atoms from the bulk to the surface leaving behind corresponding vacancies in the lattice. We assume that during irradiation, the interstitials are mobile even in the damaged layer. From the measured swelling, we estimate a density reduction of ~3.1% for the amorphous phase with respect to the crystalline phase.

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Ion implantation at high fluences is an established technique to form buried conducting and insulating layers in semiconductors for device applications. Ion-implant-induced stresses can lead to problems such as substrate bending, delamination, and cracking and anomalous diffusion of dopants. During high-fluence implantation, the accumulated damage can give rise to amorphous structures in the host lattice. Despite several decades of studies on irradiation-induced amorphization of silicon, a detailed atomic scale modeling of the structure of pure amorphous silicon (a-Si) produced by ion implantation has not emerged.[1,2] In recent times, it has been reported that the implantation induced amorphization is accompanied by a change in the volume or density of the host material and a swelling of the implanted region.[3,4] While swelling studies on amorphized regions of Ge (Ref. 5) and GaSb (Ref. 6) clearly show the formation of nanopores or voids as responsible for the volume expansion in the implanted region, studies on Si do not reveal any voids or pore structures.[7] Therefore, the mechanism of swelling in silicon is poorly understood. Swelling in silicon has been conventionally studied using surface profilometry. However, no systematic studies have been attempted on its annealing characteristics. There have been some indications about a uniaxial lattice expansion in ion-implanted silicon studied by x-ray diffraction and ion-channeling experiments.[8] However, its magnitude was found substantially larger than was predicted in uniaxially strained crystalline silicon (c-Si), indicating possible contributions from other sources.

Both theoretical and experimental investigations show that the defects in pure amorphous silicon are analogous to those in crystalline silicon.[8,9] Although the direct identification of a particular defect species in pure a-Si has been difficult, Mossbauer studies have provided evidence for vacancies in a-Si.[10] Direct evidence for vacancy clusters in a-Si has also been obtained from Positron annihilation spectroscopy (PAS).[11–13] However, implications of such results have not been correlated with different physical properties of pure a-Si. For instance, a density deficit of 1.7% in a-Si in comparison to c-Si has been found from swelling studies.[3] However, the contribution of defects to the change in density has not been understood. Recent analyses on the structure factor of a-Si before and after annealing show undercoordination of Si atoms, and this was believed to be due to the presence of vacancy-type defects.[2] Room temperature implantation on diamond was believed to have vacancy-rich regions contributing to the volume expansion.[14] Therefore, such increasing evidence for the presence of vacancies in a-Si is expected to shed light on the mechanism of swelling and the density change in Si during the process of amorphization.

We report the study of swelling in self-ion implanted silicon, using atomic force microscopy (AFM) and transmission electron microscopy (TEM), for a wide range of fluence and postimplant annealing conditions. The fluence dependence and the annealing characteristics of the swelling suggest the involvement of vacancy clusters in the amorphized region. We discuss the mechanism of swelling in low energy ion-implanted silicon in the light of the results from several supporting experiments. The relative density of a-Si with respect to c-Si is evaluated from the measured swelling.

Czochralski grown Si(100) wafers were implanted with 80 keV Si^+ ions in the dose range $6\times10^{14}-6\times10^{16}$ cm^{-2}. Implantations were performed through photoresist masks of varying widths (0.2–5.0 μm) on Si wafers to produce alternating strips of a-Si and c-Si regions. The step height at the boundary between implanted and unimplanted regions was measured using AFM imaging after chemical etching of the photoresist mask. The thickness of the amorphous layer and the presence of extended defects

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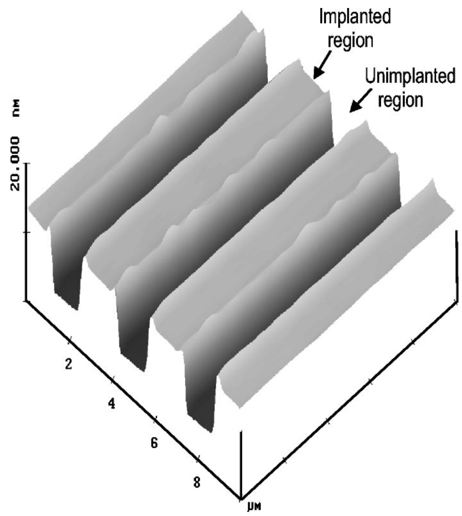

FIG. 1. An AFM image of the swelling observed in 80 keV Si^+ implanted Si at room temperature, with fluence 6×10^{15} ions/cm^2. Unimplanted region corresponds to masked region during implantation.

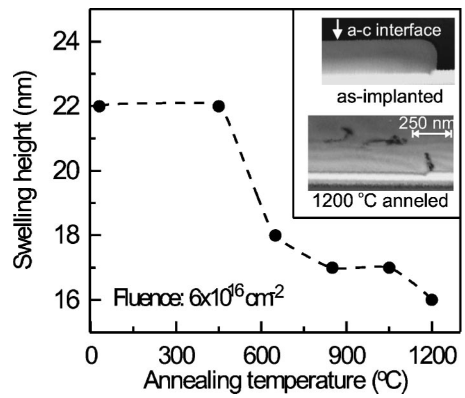

FIG. 2. The saturated step height as a function of postimplantation isochronal annealing at various temperatures, shown for 6×10^{16} ions/cm^2 implanted sample. Inset shows the XTEM images of the as-implanted and 1200 °C annealed samples, respectively.

were determined by cross-sectional TEM (XTEM) imaging. Postimplantation isochronal annealing was carried out at various temperatures in the range 450–1200 °C in steps of 200°C in flowing N_2 gas and the residual step-height was measured after each step of annealing performed for 1 h.

Figure 1 shows a typical AFM-image of the Si^+-implanted (fluence 6×10^{15} cm^{-2}) Si wafer after removal of the mask. The implanted region shows a distinct step with respect to the unimplanted region due to swelling. Typically, several nanometers of swelling were observed for different fluences. The rippled inflated structure at the edge of the implanted region is due to the residual photoresist layer at the boundary. The swelling height was obtained by using the flat region of the image and averaging the data taken from several strips.

The swelling height perpendicular to the Si surface was studied for various strip widths. For high-fluence implantation (6×10^{16} cm^{-2}), the step height increases with the strip width and a saturation in swelling is reached for a width of 3.0 μm. For lower fluences ($\sim10^{15}$ cm^{-2}), no strip-width dependence was detected. This strip-width dependence of swelling implies that for shorter widths (comparable to the range of the implanted ions), the defects in the adjacent amorphous layers interact due to their close proximity and thus affect the swelling. A similar observation has been made for the swelling of He^+-implanted silicon.[15] We have used the saturation values of swelling in each case for analyzing the fluence dependence and annealing characteristics.

The effect of isochronal annealing on the swelling is shown in Fig. 2. For different fluences, identical decay characteristics for swelling were observed with step-by-step annealing at various temperatures. Annealing up to 450 °C does not give rise to any measurable change in the step height. However, a marked reduction in the swelling is observed upon annealing at 650°C, and the step-height reduces further upon annealing up to 1200 °C. Note that for the highest fluence (6×10^{16} cm^{-2}), the residual step height (16 nm) after annealing is larger than the height (12.1 nm) contributed by the implanted Si ions assuming their rearrangement on a perfect crystalline Si lattice. This extra height in the annealed sample can be related in part to the presence of the extended defects at the amorphous/crystalline (a-c) interface. XTEM imaging of the as-implanted sample shows a uniform amorphous layer and a sharp a-c interface; upon annealing up to 1200 °C extended defects such as dislocations are formed at the original a-c interface, as shown in the inset of Fig. 2. During the high-fluence implantation, point defects that escape recombination form clusters due to their close proximity and may contribute to the structure of a-Si in the subnanometer scale. These defect clusters show high thermal stability, in particular the vacancy clusters. Recent studies on vacancy clusters in silicon show that depending on the implantation fluence, higher order vacancy clusters can be stable up to as high as 800 °C.[16,17] Theoretical studies predict that the hexavacancy (V_6) is one of the most stable structures found in silicon.[18] Most of the experiments using PAS indeed find higher order vacancy clusters besides a low concentration of divacancies in the disordered and amorphous Si. Direct evidence for the dominance of V_5 and V_6 clusters has been obtained in pure a-Si from positron lifetime studies.[13] In the present case, the annealing behavior shown in Fig. 2 also suggests that higher order vacancy clusters in pure a-Si are responsible for the relatively high thermal stability of swelling.

The swelling data obtained for different fluences are shown in Table I and exhibit a sublinear dependence on fluence. The damage evolution leading to amorphization in Si is also known to vary sublinearly with fluence. In order to isolate the mechanism for swelling in excess of the height added by the implanted ions, the ions contribution was subtracted from the measured swelling. To look for a functional dependence of the excess swelling on the fluence, in Fig. 3 the excess swelling is plotted as a function of cube root of the fluence. Sputtering effect has been taken into consideration in the calculation of the excess height. The experimental data are shown with symbols, while the dashed line represents a linear fit to the data and passes through the origin.

TABLE I. Calculated relative density (ρ_c/ρ_a) of amorphous Si obtained for different fluences of 80 keV Si^+-implanted Si at room temperature.

Fluence (ions/cm^2)	a-Si thickness (nm)	Measured swelling (nm)	Calculated height due to implanted ions (nm)	Excess swelling (nm)	Calculated ρ_c/ρ_a
6.0×10^{14}	128	4	0.12	3.92	1.030
1.6×10^{15}	196	6	0.32	5.68	1.030
6.0×10^{15}	209	7.5	1.21	6.76	1.032
1.8×10^{16}	232	12	3.63	9.79	1.042
3.6×10^{16}	236	17	7.26	12.59	1.052
6.0×10^{16}	248	22	12.10	14.65	1.058

This fit indicates that the excess swelling follows approximately a cube root dependence on the fluence.

Recent studies of high-fluence B^+-implanted silicon show that the concentration of vacancy type defects increases in proportion to the square root of the fluence.[11] Sealy *et al.* observed a similar behavior for the integral strain measured for Si by x-ray diffraction.[19] Such a square root dependence of the damage on fluence is typical for defect evolution via a homogeneous nucleation process. However, for self-ion implantation, the density of vacancies is reduced due to extra interstitials, which easily recombine with the vacancies. Therefore, the vacancy concentration in self-ion implanted silicon grows more slowly than the square root of the fluence. Experimentally, a cube root dependence of vacancies on the fluence has been observed in self-ion implanted silicon.[20] This striking similarity of the fluence dependence for vacancy concentration and excess swelling in self-ion implanted Si strongly suggests that excess vacancies in amorphous Si are most likely to be responsible for the excess swelling. In heavily damaged Si, Eichler *et al.*[11] provided evidence for large vacancy clusters which were stable up to 580°C. A similar fluence dependence of defects was found from Rutherford backscattering spectroscopy (RBS) measurements as well as from the estimation of displaced atom density in Si. The annealing behavior of swelling shown in Fig. 2 is qualitatively similar to the annealing of open volume defects in heavily damaged silicon.[20]

Hence, the observed annealing characteristics and the fluence dependence of swelling strongly indicate that the region

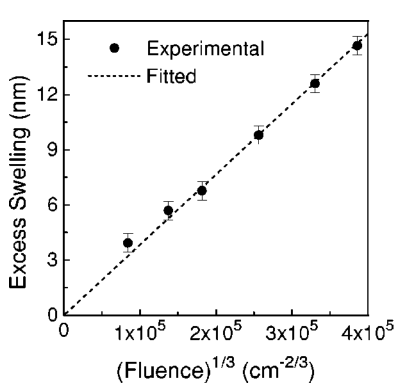

FIG. 3. Excess swelling as a function of cube root of fluence in as-implanted Si. The dashed line represents a linear fit to the experimental data passing through the origin.

directly modified by the ions contains excess vacancies or open volume defects in silicon. Despite the incorporation of extra ions in the lattice during implantation, the presence of excess vacancies in the bulk would imply that a fraction of the displaced silicon atoms must migrate to the surface and will contribute to the swelling. We believe that this is the key point in understanding the swelling for low-energy (keV) ion-implanted silicon. Due to their close proximity to the surface, the displaced atoms can migrate towards the surface and leave excess vacancies in the damaged region. It may be noted that the amorphous Si with vacancies represents a structure where the average Si atoms are undercoordinated[2] and correspondingly more open-volume is available compared to the crystalline structure. The change in average bond length and the distortion in bond angle result in a structure with more open-volume than that present in crystalline Si.[9]

The dependence of swelling on the ion-energy further supports our view on the mechanism of swelling. We observe identical swelling (of 7 nm) for both 40 and 80 keV Si^+ implants at a fluence 6×10^{15} cm^{-2}. For the case of 40 keV implants, though the thickness of the amorphous layer is about half that for the 80 keV implants, identical swelling in both cases implies that lattice expansion in the damaged layer cannot account for the observed swelling and the displaced silicon atoms directly contribute to the swelling.

Further, our studies using 80 keV Si^+ implantation at low temperature (77 K) show a slightly reduced swelling, as expected due to the controlled migration of displaced Si atoms at low temperature. We observe a difference of 2 nm (out of 22 nm in room-temperature implanted Si) for a fluence of 6×10^{16} cm^{-2} on different strips of amorphous silicon. As the self-interstitials are still mobile compared to the vacancies at this temperature, the effective reduction in swelling is not substantial. We also note that at high fluence, the change in thickness of the amorphous layer with fluence is not substantial as compared to the swelling (see Table I). Hence, the swelling is primarily caused by the Si atoms that have migrated towards the surface.

In this context, in a separate study of the microstructure of amorphous silicon layers produced by keV Ar^+ ions, using spectroscopic ellipsometry, we found that in all damaged samples besides the thick a-Si layer produced by the direct beam, there is also a thin amorphous Si layer (of thickness few nm) just above the original Si surface and beneath the native oxide layer.[21] The surface layer thickness increases with fluence. This near-surface amorphous layer can be attributed to the redistribution of Si interstitials produced by the implantation process from the buried damaged region towards the surface and to a subsequent segregation process. This observation further strengthens our model for swelling. A similar observation has been made by Lohner *et al.*[22] in heavy-ion implanted silicon.

It is obvious that the presence of excess vacancies or open volume in the amorphous region can naturally account for the reduced density of the amorphous Si. If the swelling height is very small compared to the thickness of the amorphous layer, the relative density of *a*-Si can be calculated by taking the ratio of the excess step-height and the thickness of the *a*-Si layer, after incorporating the sputtering correction. Table I shows the calculated relative density of *a*-Si for various fluences. We find a density difference of about 3–4 % and this value is somewhat higher than the value of 1.8% reported earlier for MeV implanted Si.[3] Note that the mechanism for swelling is likely to be different for keV and MeV implantation due to the different depths of the defects created. Higher density differences have also been noted in the literature.[4] Nevertheless, the vacancy concentration measured by positron back-diffusion experiment estimates a similar density difference.[20] An average increase in bond length due to vacant sites in *a*-Si can also account for the estimated density difference.[9,21]

In conclusion, we have investigated the phenomenon of swelling in self-ion implanted silicon by studying its dependence on ion fluence, energy and post-implant annealing. Both the fluence dependence and the annealing characteristics of swelling are correlated to the presence of vacancy clusters or nanovoids in the amorphous Si layer. The excess swelling is believed to occur as a result of outdiffusion and segregation of the displaced Si atoms on the surface and thereby leaving corresponding number of excess vacancies in the host material. The presence of excess vacancies or open volume in the amorphous layer accounts for the reduced density of amorphous Si. From swelling studies, we find a density reduction of ~3.1% for the pure amorphous Si with respect to crystalline Si.

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