Energy Dependence of Radiation Damage in Sb-Implanted Si(100)

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Extended defects formed by antimony ion implantation in Si(100) are investigated as a function of the implant energy. After implantation, spike annealing and furnace annealing are performed to examine the evolution of defects. The amorphization/recrystallization of the implanted layer is examined by transmission electron microscopy (TEM), photothermal characterization, and Raman spectroscopy. Secondary-ion mass spectroscopy is employed to identify the dopant distribution before and after annealing. Cross-sectional TEM reveals that, at a dose of \(1 \times 10^{16} \text{cm}^{-2}\), 20 keV Sb implantation is sufficient to induce an amorphous-like layer in Si(100). After spike annealing, the amorphous-like layer restores to the crystalline state, but defects are observed when the Sb implantation energy is greater than 50 keV. For 70 keV implantation, extended defects appear at the near-surface and the end-of-range (EOR) regions. It is observed that near-surface defects diminish after spike annealing at temperatures higher than 980°C, while the EOR defects become coarse at 1095°C. A comparison between the spike annealing and the furnace annealing for the sheet resistance and the EOR defect is also addressed.

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Experimental

Single-crystal silicon (100) wafers (Czochralski grown 8–12 Ω cm, p-type) with 26 Å thick screen oxide were implanted using an Applied Materials XR80S high-current implanter by varying the implant energy from 10 to 70 keV at a dose of \(1 \times 10^{11} \text{cm}^{-2}\). The 26 Å thick screen oxide was grown by rapid thermal oxidation. Singly-charged ions (Sb+) were implanted with energies of 10, 20, 30, 40, and 50 keV, while doubly-charged ions (Sb2+) were implanted with energies of 50, 60, and 70 keV. The beam current was \(\sim 1.25 \text{mA}\) for Sb+ species, and \(\sim 2.50 \text{mA}\) for Sb2+ species. The Sb used in the ion source was the elemental metal, which was heated to 420°C for vaporization. The tilt/twist angle settings were 0°/22°. A water-cooling system was employed in the wafer holder to reduce the heat generated during implantation. After implantation, spike annealing was performed using an Applied Materials Radiance Centura chamber in a nitrogen ambient for dopant activation at 950, 980, 1050, and 1095°C. Samples were first ramped from 350 to 650°C at a rate of 15°C/s and then ramped to the target temperature at a rate of 250°C/s. Furnace annealing was also conducted at 900°C for 15, 30, 45, and 60 min with 100 sccm flowing N2.

Two nondestructive methods were used to characterize the lattice damage. Implanted wafers, before and after spike annealing, were measured by a Thermo-Probe 500. A pump laser with a wavelength \(\lambda = 532 \text{nm}\) was modulated at a frequency of 1 MHz. At this frequency, the thermal diffusion length was about 5.3 μm in silicon (thermal diffusivity of silicon = 0.9 cm²/s). The intensely modulated light beam on the sample surface and the subsequent energy dissipation creates a time-dependent response field. A probe laser at \(\lambda = 670 \text{nm}\) was focused on the sample surface to measure the thermal wave (TW) induced changes in the reflectivity. The magnitude and a phase shift of the TW are sensitive to the doping level and lattice damage. The crystallinity of Si was characterized at room temperature by a Coherent Innova 90 Raman spectroscopy using the 514.5 nm line of an argon-ion laser. The signal of Raman spectroscopy was from the nonlinear scattering of laser beams. The probing depth is about 770 nm beneath the Si surface with the Ar+ laser, which in our case was sufficiently deep to detect the shallow junc-
The signal of Raman spectroscopy at 521.0 cm\(^{-1}\) is related to the defect-free Si single crystal. The attenuated intensity was related to lattice damage as well as the dopant substitution. Laser power and focusing condition were kept the same during the measurement. Four-point probe using a Tencor OmniMap RS75 apparatus quantified the dopant activation after postimplantation annealing. Depth profiles of the Sb\(^{121}\) and Sb\(^{123}\) isotopes were measured with secondary ion mass spectrometry (SIMS) using an Atomika 4000 instrument. O\(^{2+}\) ions were used as the primary ion beam for SIMS depth profiling. A Phillip TECNAI F20 transmission electron microscope (TEM) operating at 200 kV was employed to characterize the crystal defects in cross-sectional view.

**Results and Discussion**

**Amorphization and dopant distribution in Sb-implanted Si.**—The threshold for amorphization depends on the mass of the implanted species, the implant energy, the dose and dose rate, as well as on the sample temperature.\(^{25-28}\) Since antimony has a larger ion mass than silicon, the ion-solid interaction will lead to a dense collision cascade, which is an efficient process of amorphization. Hence, the a/c interface is expected to form at a depth beyond the projected range. Figure 1 shows the cross-sectional TEM view of 20 and 70 keV Sb-implanted samples. Both micrographs show an amorphous-like layer (a-Si), a transition region (TR), and the undamaged crystalline Si (c-Si). Figure 1 suggests that 20 keV Sb implantation is sufficient to produce an amorphous-like layer at the surface of Si(100). Note that the amorphization may be incomplete near the Si surface for the 70 keV implantation, and the incomplete amorphization will lead to the near-surface defects upon annealing. This is discussed in the section on Defects evolution with postimplantation annealing. The amorphous-like layer extends from the top of the transition region to the Si surface and the thicknesses are ~177 Å for the 20 keV implantation and ~473 Å for the 70 keV implantation, respectively. The roughness at the a-Si/TR/c-Si interface increases with the increasing implant energy. In consequence, for the same dose, higher energy implants are shown to have a thicker amorphous-like layer and a thicker transition region.

**Figures 2a and b show SIMS depth profiles of 20 and 70 keV Sb-implanted wafers before and after spike annealing at 1095°C. The projected ranges (\(R_p\)) of the 20 and 70 keV Sb implantations are around 138 and 371 Å, respectively. The peak concentrations of the 20 and 70 keV Sb implantations are about \(6.75 \times 10^{19}\) and \(2.74 \times 10^{19}\) atom/cm\(^3\). SRIM\(^{29}\) simulations predicted that \(R_p\) equals 159 Å for the 20 keV, and 402 Å for the 70 keV Sb implantation, respectively. The peak concentrations were calculated to be 7.82 \(\times 10^{19}\) atom/cm\(^3\) for the 20 keV and 3.19 \(\times 10^{19}\) atom/cm\(^3\) for the 70 keV implantation, respectively. In consequence, the \(R_p\) and peak concentration values predicted by SRIM were both found to be larger than those from the SIMS results.**

**Figures 2a and b also show SIMS depth concentration profiles of Sb dopants for 20 and 70 keV Sb implanted wafers before and after spike annealing at 1095°C. It is found that spike-annealing treatments do not change the dopant profile very much. However, dopant diffusion still occurs after the short-duration thermal cycle. The peak concentration decreases from \(6.75 \times 10^{19}\) to \(4.65 \times 10^{19}\) atom/cm\(^3\) (~31% reduction) in Fig. 2a and from \(2.74 \times 10^{19}\) to \(2.55 \times 10^{19}\) atom/cm\(^3\) (~7% reduction) in Fig. 2b. The high peak concentration in the sample implanted at 20 keV exhibits a more significant reduction than the one implanted at 70 keV. This implies that the dopant diffusion increases as the concentration increases.**\(^{30}\)
Effect of implant energies on the formation of EOR defects.—

The defects in the samples implanted with Sb at energies ranging from 10 to 70 keV were characterized by using cross-sectional TEM. Previous studies on the nature of dislocation loops produced in the ion-implanted Si after annealing concluded that the dislocation loops were generated by the recoil of Si interstitials in the amorphous layer. In the present study, given the implant dose of $1 \times 10^{14}$ cm$^{-2}$ and the spike annealing temperature at 1095°C, we do not observe extended defects in the Si wafers implanted at energies of 50 keV or lower. Figure 3a and b show that there are no conspicuous defects in either 50 keV singly-charged or 50 keV doubly-charged Sb-implanted samples. However, a defect density of 1.86 defects/μm, which were counted under TEM observation in a zone of 8 μm in length, is observed in the 60 keV Sb-implanted samples, as shown in Fig. 3c. The average depth of EOR defects is around 69 ± 5 nm, and their diameter is less than 32 nm. Accordingly, the threshold energy for defect formation should be between 50 and 60 keV.

Defect evolution with postimplantation annealing.— We examined the evolution of defects after spike annealing at various temperatures and the result is summarized in Table I. Figures 4a-d show the defect evolution of 70 keV Sb implantation after spike annealing.

![Figure 3. TEM images of (a) 50 keV singly-charged, (b) 50 keV doubly-charged, and (c) 60 keV Sb-implanted Si after spike annealing at 1095°C.](https://example.com/fig3)

![Figure 4. TEM images of 70 keV implanted Si after spike annealing at (a) 950, (b) 980, (c) 1050, and (d) 1095°C. The cross-sectional views of spike-annealed samples show crystal defects in the near-surface and the EOR region.](https://example.com/fig4)

<table>
<thead>
<tr>
<th>Energy</th>
<th>Spike annealing (°C)</th>
<th>Defect density</th>
<th>Dislocation center from surface (nm)</th>
</tr>
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<tbody>
<tr>
<td>70 keV Sb$^{2+}$</td>
<td>950</td>
<td>Continuous TDs and DLs</td>
<td>≈ 9</td>
</tr>
<tr>
<td>980</td>
<td>Many DLs</td>
<td>≈ 22</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>3.70 defects/μm</td>
<td>≈ 23</td>
<td></td>
</tr>
<tr>
<td>1095</td>
<td>1.90 defects/μm</td>
<td>≈ 32</td>
<td></td>
</tr>
</tbody>
</table>

Table I. Defect density, diameter, and depth in 70 keV Sb implant Si, as a function of spike-annealing temperatures, observed by cross-sectional TEM.
less damaged. The near-surface defects are likely to originate from an incomplete amorphization near the surface. Besides, they may disappear by dissolution in the vicinity of the oxide/silicon interface at high annealing temperatures. Fair and Kim have demonstrated that the shallow near-surface defects are more easily removed than the deep EOR defects. The average depth of the EOR defects is around 69 ± 5 nm under the Si surface, which lies deeper than the a/c interface (about 47 Å in Fig. 1). In this region, two defect structures are observed in the 950°C spike-annealed samples. One is a rod-like dislocation line along the (110) direction in the (111) lattice plane, referring to threading dislocations (TDs). The others are small circular-shaped dislocation loops (DLs), which resulted from the transformation of (311) defects. It is found that the samples exhibit no TDs but only DLs (Fig. 4b-d) after spike annealing at 980°C and above. The DL densities are 3.70 defects/μm for the 1050°C spike-annealed sample and 1.90 defects/μm for the 1095°C spike-annealed one. In comparison, the size of the DLs is found to be larger than that of the near-surface defects. On the other hand, it is seen that the size of the EOR defects increases from 9 to 32 nm when the temperature is increased from 950 to 1095°C.

From the aforementioned result, it is shown that defect densities are reduced when the annealing temperature increases. Coarsening of defects is observed as the annealing temperature increases, which can be attributed to the Oswald ripening effect. According to the Gibb-Thomson equation, the concentration of Si interstitials near a DL decreases as its size increases. Therefore, there would be a concentration gradient in the Si matrix which drives Si interstitials to diffuse from the small DLs to the large DLs, so that the large DLs grow at the expense of small ones that shrink. The oversaturation of Si interstitials during annealing will result in transient enhanced diffusion of boron or phosphorous. For Sb dopants, the enhanced diffusion is very small (see Fig. 2), because Sb diffuses mainly via a vacancy-mediated mechanism.

Characteristics of Sb-implanted Si before and after spike annealing.—The sheet resistance (Rₛ) of Sb-implanted Si as a function of the implant energy was measured after spike annealing at 1095°C, as shown in Fig. 5a. It was observed that the Rₛ decreases as the implant energy increases. Lower implant energies at the same dose will result in a shallower junction and a higher doping concentration. Therefore, the presence of more dopant atoms in the Si lattice will lead to a more intensive scattering. As a result, the sheet resistance increases owing to the reduced mobility of electrical carriers in the case of low-energy implantation. Other factors might be the dose-loss effect after removal of the screen oxide, and/or the precipitation of Sb (not activated since the solubility is exceeded) in low-energy implantation. Figure 5b suggests that the Rₛ decreases as the spike annealing temperature increases. The reduction of Rₛ upon spike annealing is due to the further activation of dopant and the partial elimination of EOR defects. The dopant activation appears to be saturated at 1050°C, and higher annealing temperatures result in nearly the same Rₛ value.

Average TW values as a function of the implant energy before and after spike annealing at 1095°C are shown in Fig. 6a. For as-implanted samples, it is observed that TW values increase with increasing implant energies. It can be attributed to the deeper buried amorphous-like layer and the wider transition region, as shown in Fig. 1. The higher the implant energy, the more damage it causes. After spike annealing at 1095°C, the amorphous-like layer is recovered to the single-crystalline structure, and TW values are reduced to 300-450. However, the TW value for a virgin Si wafer is only 21-22. Residual defects (such as vacancies and interstitials) and electrically activated dopants in Si would alter the thermal and electrical properties, such as thermal conductivity, surface energy state density, and excess carrier lifetime, etc. Consequently, the depth distribution of dopants and residual defects contribute to the change of the photothermal properties in the annealed samples. That is the reason why the TW value cannot recede to the value of a virgin Si wafer.

Figure 6b shows TW values of samples with implant energies of 20 and 70 keV, followed by spike annealing at 950, 980, 1050, and 1095°C. For the 20 keV implanted samples, the TW value does not change much as the spike-annealing temperature increases. However, for the 70 keV implanted samples, the TW value is reduced more significantly when samples are annealed at higher temperatures. From TEM micrographs, one can see that the decrease of defect density and the coarsening of defect size are dependent on the annealing temperature. The EOR defect is a poorer thermal conductor than the Si matrix. Garrido et al. have shown that the amplitude and phase of the thermal wave depend on the density, size, resistance, and depth of buried defect spheres. Hence, evolution of EOR defects may explain the significant change of TW values in the 70 keV Sb-implanted samples.

Samples with various process parameters were also analyzed by Raman spectroscopy. The c-Si peak at 521.0 cm⁻¹ shows nonpolarized Si tetrahedral structures, which is the most intense peak in a c-Si sample. If the Si backbone is destroyed or a Si atom is replaced by a foreign atom like Sb, the intensity would be attenuated. Figure 7 presents the normalized peak height obtained from Raman spectroscopy before and after spike annealing at various temperatures. An unimplanted Si wafer was used as the standard sample for normalization. The as-implanted samples manifest a larger amount of
damaged structures; hence, the peak intensities at 521.0 cm$^{-1}$ of the as-implanted samples are much lower than that of the spike-annealed ones. Figure 7 also shows that the 70 keV samples exhibit lower c-Si peak intensities than the 20 keV samples after annealing, which should be related with the EOR defects observed in 70 keV samples.

Spike annealing vs. furnace annealing.— Figure 8 shows values measured for the sheet resistance $R_s$ of 20 and 70 keV implanted Si samples after furnace annealing at 900°C for 15, 30, 45, and 60 min. The $R_s$ of the samples after furnace annealing is found to be lower than after spike annealing (Fig. 5b). The observation indicates that Sb dopants are activated to a lesser extent by the short-duration spike annealing than by the isothermal furnace annealing. However, Fig. 8 also indicates that the $R_s$ increases as the annealing time increases, and the rate of the $R_s$ increase with annealing time is higher in the 20 keV implanted sample than in the 70 keV one. Takamura et al. have shown that the Sb deactivation becomes increasingly severe as the concentration increases.38 Therefore, the clustering of Sb atoms during furnace annealing, which leads to the deactivation of dopants, may account for the increase in $R_s$.

Figure 9 shows the transmission electron micrograph of the 70 keV-implanted Si after furnace annealing at 900°C for 30 min. The density of EOR defects after furnace annealing is 1.86 defects/$\mu$m, which is comparable to 1.90 defects/$\mu$m after spike annealing at 1095°C. It was also observed that the size of EOR defects after furnace annealing ($\approx$56 nm) is larger than that after spike annealing ($\approx$32 nm). Spike annealing thus results in smaller EOR defects than furnace annealing does. Defects with a large size will probably overlap the depletion region and serve as an additional leakage current path.39 As a result, spike annealing is effective for reducing the size of EOR defects, which may have an important consequence for the reduction of the junction leakage.

Conclusions

In this work, we report on the characteristics of radiation damage induced by Sb implantation with various energies. The radiation damage and its recovery by spike annealing were examined with TEM, TW, and Raman spectroscopy. Cross-sectional TEM micrographs reveal that 20 keV Sb implantation is sufficient to induce an
amorphous-like layer in Si(100). After spike annealing, visible defects were observed in the samples implanted at energies higher than 50 keV. Two discrete layers of defects were found after postimplantation annealing for the 70 keV implantation. The near-surface defects dissolve after spike annealing at and above 1050°C. On the other hand, the density of dislocation loops in the EOR region decreases as the annealing temperature increases, and their size coarseens as well. It was also found that Sb dopants are activated to a lesser extent in the short-duration spike annealing than in the isothermal furnace annealing. On the other hand, the spike annealing is more effective for reducing the size of EOR defects than the furnace annealing.

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