A medium energy ion scattering analysis of the Si–SiO₂ interface formed by ion beam oxidation of silicon

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Abstract

The Si–SiO₂ interface formed by 3 keV O⁺ ion bombardment on silicon at room temperature and 600°C was studied by in situ medium energy ion scattering spectroscopy (MEIS). The amorphization process at the initial stage of the oxygen ion bombardment and the subsequent formation of the suboxide layer and the disordered silicon layer at the Si–SiO₂ interface were studied as a function of the ion dose from 2.5 × 10¹⁵ atoms/cm² to 5 × 10¹⁷ atoms/cm² at room temperature and 600°C. After reaching the steady state, below a ~ 6 nm SiO₂ layer, a ~ 2 nm suboxide layer and a ~ 3 nm disordered Si layer were observed at the Si–SiO₂ interface. The annealing effect at 600°C decreased the number of disordered silicon atoms and the suboxide silicon atoms, which make the Si–SiO₂ interface more abrupt, was more clearly observed at the initial stage of the bombardment.

Keywords: Ion beam oxidation; Si–SiO₂ interface; Defects; SOI; Medium energy ion scattering spectroscopy

1. Introduction

The oxidation of silicon by energetic oxygen ions is a very important subject in surface analysis and semiconductor technology. In secondary ion mass spectroscopy (SIMS) analysis, oxygen ion beam is widely used because surface oxidation enhances the positive ion yield by orders of magnitude [1]. In the semiconductor processing, accelerated oxygen ions are used to fabricate a silicon-on-insulator (SOI) structure which has a great potential for very large scale integration (VLSI) and other device applications [2].

However, the details of the surface oxidation process due to the low energy oxygen ions were not fully understood, which are very important to study the matrix effect and depth profiles in SIMS especially for mobile impurities such as Cu and Au in silicon [3–6]. The broadening of SIMS depth profiles for the elements has been explained by oxygen implantation-induced segregation of the impurity atoms due to SiO₂ layer formed by primary oxygen beam [5,7]. In the formation of SOI by oxygen ions, reduction of defect density is still an essential problem [8,9]. Especially, the defects at the Si–SiO₂ interface is closely related to the electronic properties of the SOI device.

Therefore, the oxygen build-up process near the silicon surface during bombardment, the stoichiom-
etry and the thickness of the oxide and the structure of the Si–SiO₂ interface should be further investigated. The Si surface oxidation with low energy oxygen ion bombardment has been studied by SIMS, Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS) [10–13]. However, there are relatively few reports on the Si–SiO₂ interface because the observation of the interface requires the high depth resolution for the interface located below the surface. The oxygen stoichiometry and the amorphous layer formation at the Si–SiO₂ interface by low energy oxygen beam at elevated temperatures have not been reported.

In this experiment, we investigated the silicon oxidation process by 3 keV O²⁻ ions at room temperature and 600°C with in situ MEIS. MEIS can probe the composition and the structure of interfaces with the depth resolution better than 1 nm [14,15]. The details of the Si–SiO₂, such as the change of the oxide layer and suboxide layer and the disordered silicon layers were studied by comparison of the measured MEIS spectra and the simulated spectra.

2. Experiment

A 5 mm × 20 mm size Si(001) wafer was mounted in a MEIS analyzing chamber and then heated to 1250°C by direct resistive heating to clean the native oxide [16]. After checking the cleanness and the crystallinity of the silicon surface by MEIS spectrum, the sample was bombarded by 3 keV O²⁻ ion beam (effectively 1.5 keV O⁺) produced by a Penning discharge ion gun. The beam was normal to the silicon surface and the current density of the ion beam was about 5 μA/cm² which was measured by a biased plate near the sample. After bombardment, the sample was analyzed in situ by MEIS using 100 keV proton beam. A double aligned condition (11T) to (001) was used to distinguish the oxygen peak from the silicon peak with the scattering angle of 125.3°. The oxygen ion bombardment and the MEIS analysis of the bombarded sample were repeated sequentially for the oxygen ion doses from 2.5 × 10¹⁵ atoms/cm² to 5 × 10¹⁷ atoms/cm². For 600°C experiment, the sample was heated by direct resistive heating and the temperature was measured by an optical pyrometer. The temperature was sustained during bombardment by control the heating current. The base pressure of the MEIS chamber was 8.0 × 10⁻⁸ Pa but, increased to 1.3 × 10⁻⁴ Pa during oxygen ion bombardment. Details of the MEIS system are given elsewhere [14].

3. Results and discussion

Fig. 1 shows the double aligned MEIS spectra as a function of oxygen dose at different temperature. At room temperature, for the low ion dose of 6.7 × 10¹⁵ atoms/cm², the oxygen peak did not appear but the silicon surface was heavily disordered by the oxygen ion beam. The silicon peak height from this region is about two times of that of SiO₂, which indicates that the region becomes amorphous before being oxidized. As the dose was increased, the thickness of the silicon peak increased and the oxygen peak began to grow. With the further ion dose increase, the silicon surface peak height decreases as the SiO₂ layer forms at the surface. Finally, above 1 × 10¹⁷ atoms/cm², the silicon surface is completely oxidized but the disordered layer still remained under the surface oxide layer. This dose dependency is similar to the 8–30 keV O²⁻ ion bombardment on Si [11,12].

At 600°C, however, a quite different shape of the silicon peak was observed compared with room temperature. For the low ion dose of 5.0 × 10¹⁵ atoms/cm², the two separated silicon peaks were observed instead of the broad amorphous peak at room temperature. For the high dose, the change of the MEIS spectra were similar to that of room temperature but the thickness and the height of the silicon peak under the surface oxide layer was quite decreased.

To study these observation in detail, all the MEIS spectra were fitted with the ion scattering analysis program (ISAP) which simulates random and aligned spectra for multielement and multilayered thin film structures [17–19]. It can also simulate the contribution of disordered layers in crystals. Fig. 2 shows the MEIS spectra and the simulated spectra for the initial stage of the oxygen ion bombardment on silicon at room temperature and 600°C. Because oxygen peaks are not observed, the spectra were fitted by considering only the disordered silicon profiles. The thickness of the amorphous layer for the dose of 6.7 × 10¹⁵ atoms/cm² at room temperature is 7.3 nm. All
Fig. 1. The 100 keV H<sup>+</sup> MEIS spectra as a function of the 3 keV O<sub>2</sub><sup>+</sup> ion dose at room temperature (a), and at 600°C (b). The ion dose unit is oxygen atoms/cm<sup>2</sup>.

Fig. 2. The measured MEIS spectra and the simulated curves for the initial stage of the oxygen ion bombardment on Si. A broad amorphous Si peak is observed at room temperature (6.7 x 10<sup>15</sup> atoms/cm<sup>2</sup>, solid circle) but two separated and relatively small peaks are seen at 600°C (5.0 x 10<sup>15</sup> atoms/cm<sup>2</sup>, open square). In the insertion the disorder concentration profiles used to simulate the MEIS spectra are given.
thicknesses in this paper were calculated with the bulk densities. But, at 600°C, the surface peak was fitted with a 1.4 nm thick amorphous layer and the disordered Si peak was fitted by an asymmetric Gaussian distribution. The disordered silicon concentration profile, \( N_{Si} \), used for the fitting was inserted in Fig. 2 without the surface peak. The \( N_{Si} \) and \( N_{D} \) are the number densities of the silicon and the disordered silicon, respectively. This shows that a broad amorphous layer was formed at the silicon surface at the initial stage of low energy oxygen ion bombardment at room temperature. At 600°C, the total number of disordered silicon atoms was greatly reduced. From the MEIS spectra, we can calculate the number of disordered silicon atoms by the oxygen ion bombardment. At room temperature, for the dose from \( 2.5 \times 10^{15} \) atoms/cm\(^2\) to \( 6.7 \times 10^{15} \) atoms/cm\(^2\), one 1.5 keV oxygen ion produce roughly \( \sim 11 \) disordered silicon atoms. But, at 600°C, a 1.5 keV oxygen ion produce \( \sim 3 \) disordered silicon atoms. The annihilation of disorder at 600°C is more efficient than that of room temperature. This behavior of the initial stage oxygen ion bombardment at room temperature and at elevated temperature will be presented in more detail elsewhere.

Fig. 3 shows the MEIS spectra for the high ion doses of \( 3.0 \times 10^{17} \) atoms/cm\(^2\) at room temperature (a) and \( 2.0 \times 10^{17} \) atoms/cm\(^2\) at 600°C (b). The spectra were fitted by three layered structures of a SiO\(_2\) surface oxide, a Si suboxide under the surface oxide and a disordered silicon layer on a crystalline silicon substrate. In all fitting, the interface roughness between each layer were not considered because the roughness effect is not significant in our 125.3° scattering geometry. First, the surface oxide layer and the suboxide layer were used to fit the oxygen peak. In a RBS study, the silicon peak from the layer under the surface oxide was treated as an amorphous layer for 8–30 keV O\(_{17}^+\) bombardment on silicon [11,12]. But, we could not fit the spectra without the suboxide layer between the disordered silicon layer and the surface oxide layer. After the oxygen distribution was fixed, the Si peak was simulated with an additional disordered Si layer below the suboxide layer. At room temperature, the thickness of the SiO\(_2\) layer, the silicon suboxide layer and the disordered silicon layer were 6.7 nm, 2.5 nm and 3.3 nm, respectively. At 600°C, they were 6.5 nm, 1.9 nm, and 3.2 nm, respectively. As can be seen in Fig. 3, the SiO\(_2\) layer thickness did not changed with temperature. But the silicon suboxide and the disordered Si layer showed very clear annealing effect at 600°C. The number of the disordered silicon atoms decreased significantly from \( 14.5 \times 10^{15} \) atoms/cm\(^2\) to \( 6.0 \times 10^{15} \) atoms/cm\(^2\), even though the thickness did not changed at 600°C. The stoichiometry of the simulated suboxide layer was SiO at room temperature. But at 600°C, the oxygen concentration at the suboxide and the surface oxide layer decreased about 20%. This oxygen decrease can be due to the oxygen etching at the vacuum heating [20]. But it needed to confirm this deficiency clearly. Details of the stoichiometry and the shape of each layer will be discussed elsewhere [21].

Another interesting feature in this experiment is the decrease of the disordered layer thickness with the ion dose beyond \( \sim 1.0 \times 10^{17} \) atoms/cm\(^2\) at room temperature as can be seen in Fig. 1(a), in
consistent with former RBS studies for 12 keV and 30 keV $O^+$ ion bombardment on silicon [11,12]. It decreased significantly from 4.4 nm to 3.2 nm with the ion dose increase from $1.0 \times 10^{17}$ atoms/cm$^2$ to $5.0 \times 10^{17}$ atoms/cm$^2$. But, this change was not significant at 600$^\circ$C. Even though a qualitative explanation based on the ion range decrease in SiO$\_2$ compared to Si has been proposed [12], further detailed studies are in progress with Monte Carlo simulation [22].

4. Summary

The Si–SiO$_2$ interface formation by 3 keV $O^+$ ion bombardment on silicon at room temperature and 600$^\circ$C was studied by in situ MEIS analysis. At room temperature, a broad disordered Si layer was observed before a surface SiO$_2$ layer and silicon suboxide layer formed. At the steady state, a 6.7 nm SiO$_2$ layer, a 2.5 nm silicon suboxide layer and a 3.3 nm disordered Si layer were formed. At 600$^\circ$C, the SiO$_2$ layer thickness did not change with temperature. But the silicon suboxide and the disordered Si layer showed very clear annealing effect at 600$^\circ$C. The number of the disordered silicon atoms decreased significantly from $14.5 \times 10^{15}$ atoms/cm$^2$ to $6.0 \times 10^{15}$ atoms/cm$^2$, even though the thickness did not change at 600$^\circ$C. The effect of the annealing at elevated temperature was more clearly at the initial stage of the bombardment.

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References