Roughening of the Si/SiO₂ interface during SC1-chemical treatment studied by scanning tunneling microscopy

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The Si/SiO₂ interface morphology is observed with subnanometer resolution by an ultrahigh vacuum scanning tunneling microscope (STM). We analyze the roughness of the Si/SiO₂ interface for a chemical oxide film formed by a wet chemical process (NH₄OH/H₂O₂/H₂O treatment). The oxide film is selectively removed by irradiating a field emission electron beam extracted from a STM tip at a temperature of 300–350 °C. We find that during the chemical process the roughness of the Si/SiO₂ interface increases with the treatment time. © 2000 American Vacuum Society.

I. INTRODUCTION

Most Si wafer cleaning processes have been used on conventional RCA cleaning. ¹ The SC1 treatment (NH₄OH/H₂O₂/H₂O), which is the first step of the RCA treatment, is particularly effective for removing surface contaminants by etching the Si substrate. However, it has been reported that the surface microroughness increases in wet cleaning processes. ² Such microroughness degrades device performance more significantly as the characteristic dimensions of devices decrease. ³ Despite the technological importance, the mechanism of roughening for wet chemical processes is poorly understood, in particular from the microscopic viewpoint.

In NH₄OH/H₂O₂/H₂O solutions, etching and oxidation occur simultaneously, while keeping the thickness of the chemical oxide constant. ⁴ To understand the nature of the roughening during the treatment on the local atomic scale, it is necessary to directly observe the buried Si/SiO₂ interface. Gibson and co-workers pioneered the investigation of interface roughness, imaging the interfacial steps by plan-view transmission electron microscopy. ⁵, ⁶ Watanabe et al. also observed interfacial steps using scanning reflection electron microscopy. ⁷, ⁸ Although these imaging techniques are powerful methods used to characterize the interface roughness and to study the oxidation mechanism, their lateral resolution is limited to a structural scale of the order of a nanometer. In this article, we report an alternate method to observe buried Si/SiO₂ interface structures with subnanometer resolution using ultrahigh vacuum scanning tunneling microscopy (UHV-STM). ⁹ With this method the oxide films are removed under UHV by a locally confined, low-energy electron beam extracted from a STM tip which is used as well to observe the interface morphology. ¹⁰, ¹¹ This is effective in avoiding contamination and damage to the interface compared to the chemical etching normally used to remove the oxide films. In this article we study the microscopic roughness of the Si/SiO₂ interface for a Si(001) wafer treated by a wet chemical process.

II. EXPERIMENT

We performed experiments in an UHV chamber with a base pressure of 3.0×10⁻⁸ Pa equipped with a variable temperature STM (JSTM-4610 from JEOL). Samples were cut from n-type, (001)-oriented Si wafers. The Si(001) substrate was first cleaned by flashing to 1200 °C in order to prepare an atomically flat, clean surface; it was then thermally oxidized at ~600 °C for 1 min in oxygen at a pressure of 2.0×10⁻⁴ Pa to form a thin oxide overlayer. The oxide layer protects the interface during transfer of the sample through air for further treatment in SC1 solutions (NH₄OH/H₂O₂/H₂O). The mixing ratio of the solution was NH₄OH:H₂O₂:H₂O=1:1:10 and the treatment temperature was 72 °C. Finally, the sample was rinsed in flowing ultrapure water at room temperature before transferring it again into the UHV chamber. The sample was first degassed at 420 °C for 12 h and the oxide film was removed by a field emission electron beam from the STM tip at a sample voltage of 100 V and field emission currents of 100–400 nA while heating the sample (Fig. 1). Subsequently the exposed Si surface was observed with the same tip at a sample bias voltage of 3 V.

III. RESULTS AND DISCUSSION

Figure 2 shows a STM image of the thermally oxidized Si(001) surface in which two circular openings are formed by the field emitted electron beam irradiation at 450 °C for 10 (top left) and 20 s (bottom right). A sample bias voltage of 100 V and a field emission current of 100 nA were used. The Si(001) surface was, as noted in Sec. II, cleaned by flashing in UHV prior to thermal oxidation. Since the oxide film is ultrathin, the atomic steps can be observed not only on the clean Si surfaces in the open windows where alternate S A and S B steps are revealed, but they are seen as well on the oxide surface. Note that the exact oxide thickness cannot be measured from the STM image, but it is believed to be a few monoatomic layers. In Fig. 2, each step in the open window is continuously connected to the step on the oxide surface, and we find no scooped-out ditches and holes in the open

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windows. Thus we consider the perturbation at the interface structure due to oxide removal to be negligible under the process conditions.

Figure 3 shows STM images of the Si(001) surface which is thermally oxidized after flash cleaning in UHV and a region where the oxide film is removed by field emitted electron beam irradiation at 350 °C with scanning the STM tip at a sample bias voltage of 100 V and a field emission current of 200 nA over the 260 nm × 260 nm square region. The scanning time was 90 s, which corresponds to an area dose of 2.7 × 10^4 C/cm^2. In Fig. 3(b), one can see that the terrace and step structure which had been formed by flashing prior to thermal oxidation is retained at the interface after thermal oxidation, although the roughness of the steep edge and the density of islands seem to be larger compared to a typical flash cleaned surface. This result may suggest that the oxide film growth accidentally corresponds to completion of oxide layers according to the previously reported layer-by-layer oxidation of Si surfaces. The root-mean-square (rms) roughness of the exposed Si surface is 0.13 nm, which is comparable with that of the clean Si surfaces. Study of the dependence of the thermal oxide interface roughness on oxide thickness is in progress. We used such well-controlled surfaces covered by thin thermal oxide layers as starting surfaces for chemical oxidation by the SC1 treatment.

In SC1 solutions, etching and oxidation of the Si surface occur simultaneously. The thickness of the chemical oxide is about 6 Å, independent of the concentration of NH_4 OH and H_2 O_2. Figure 4(a) shows a typical STM image of the chemically oxidized Si(001) surface after the SC1 treatment for 15 min. Figures 4(b) and 4(c) show STM images of the Si/SiO_2 interfaces exposed by electron beam irradiation for the samples treated by the SC1 for 1 and 15 min, respectively. To remove the chemical oxides, the 260 nm × 260 nm square regions were scanned by the STM tip at a sample bias voltage of 100 V and a field emission current of 400 nA, while heating the samples at 300 °C. The scanning time was 180 s, which corresponds to an area dose of 1.1 × 10^5 C/cm^2. Figure 5 shows cross sections of the surfaces along the lines in
Figs. 4(b) and 4(c). In the STM images in Figs. 4(b) and 4(c), we cannot find terrace and step structures, but, instead, microscopic undulation. As the treatment time increases, the interface roughness increases by coarsening of the microscopic undulation.

To quantify the roughness from the STM data we measured the rms roughness (surface width) \( \sigma(L) = \left( \frac{1}{L} \int_{0}^{L} [h(r) - \langle h(r) \rangle]^2 \, dr \right)^{1/2} \), where \( h(r) \) is the surface height at position \( r \) and \( L \) is the horizontal length measured. Figure 6 shows the rms roughness plotted as a function of length-scale \( L \) for the samples treated by SC1 for 1 and 15 min. The rms roughnesses saturated at larger length are 0.18 and 0.29 nm for the 1 and 15 min SC1 treatments, respectively, showing that the interface roughness increases with the length of the chemical treatment. It is known that SC1 cleaning increases the surface microroughness and that the rms roughness for the 15 min SC1 treatment is comparable with the values previously reported.\(^{12}\) In Fig. 6, the correlation length, at which the rms roughness reaches a constant, increases with the length of chemical treatment, implying that the lateral characteristic

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**Fig. 4.** 250 nm×245 nm STM images of (a) the chemically oxidized Si(001) surface and (b) and (c) regions where the oxide films formed by the SC1 treatment for 1 and 15 min are removed by field emitted electron beam irradiation at 300 °C, respectively.

**Fig. 5.** Cross sections of the surfaces along the lines in Figs. 4(b) and 4(c).

**Fig. 6.** Scaling analysis of the chemical oxide interface roughness for the chemical oxides treated for 1 and 15 min.
scale of the roughness also increases due to the prolonged treatment. The results shown in Fig. 6 suggest that the interface roughness follows scaling behavior. Detailed analysis of the scaling behavior is in progress to determine the roughening mechanism for the wet chemical process.

IV. CONCLUSION

In conclusion, our STM based method for observation of buried Si/SiO₂ interfaces, in which oxide films are removed under UHV conditions by low-energy electron beam irradiation at 300–350 °C, is effective for measuring the microscopic interface roughness. Using this method, we have measured the roughness of the Si/SiO₂ interface caused by the SC1 treatment and found that the interface roughness increases with the treatment time.

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