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Selective thermal decomposition of ultrathin silicon oxide layers induced by electron-stimulated oxygen desorption

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The mechanism of electron-beam-induced selective thermal decomposition of ultrathin oxide layers on Si surfaces was studied by scanning reflection electron microscopy, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. We found that the change in the oxide layer composition caused by electron-stimulated oxygen desorption accounted for the selective thermal decomposition, where nanometer-scale voids were densely generated at a low heating temperature (720 °C). This implies that oxygen desorption from the oxide layers promotes the formation of a volatile oxide (SiO), and generates void nucleation sites. © *1997 American Institute of Physics.* [S0003-6951(97)00834-6]

Silicon dioxide (SiO₂) films grown on Si surfaces are an excellent insulating material, and they are indispensable for the fabrication of Si-based devices. Patterned SiO₂ films are also useful masks for etching and selective growth. These applications suggest that nanometer-scale patterning onto a SiO₂ layer will be an important step towards the development of advanced quantum-effect devices. The use of SiO₂ films for nanofabrication has been proposed,^{1–3} where nanometer-scale patterning onto a relatively thick oxide layer (over 200 nm thick) was realized by using a focused electron beam (EB) and subsequently developing it in a hydrogen fluoride (HF) based solution. Although delineation of SiO₂ films requires a much higher electron dose than is needed with a conventional polymer-based EB resist, the ultrahigh resolution is attractive for the fabrication of nanodevices.

We have previously proposed the application of ultrathin oxide layers on Si surfaces as an atomic-layer mask for nanofabrication.^{4,5} Since it has been confirmed that layer-bylayer oxidation takes place on Si surfaces,^{6,7} highly uniform SiO₂ layers that are only a few monolayers thick (less than 1 nm thick) can be formed. By using a 0.3-nm-thick oxide layer, Fujita et al. demonstrated selective Si epitaxial growth on Si(001) surfaces using disilane (Si_2H_6) as the source material.⁵ Also, our recent study showed that selective thermal decomposition of ultrathin oxide layers less than 1 nm thick could be induced by EB exposure.⁴ In this method, EB irradiation and the subsequent annealing result in local decomposition of the oxide layer at around 720 °C, and reconstructed clean Si surfaces are exposed. Using this technique, a 10-nm-wide open window was formed in the oxide layer by using a focused EB, and pattern transfer was achieved by combining this method with a molecular-beam-epitaxy technique.⁴ These results suggest that a combination of the EB-induced selective thermal decomposition of ultrathin oxide layers with the selective-growth technique is a promising candidate for nanofabrication. However, the reaction mechanism of the selective thermal decomposition of oxide layers has not been clarified. In this letter, we investigate the delineation mechanism by using scanning reflection electron microscopy (SREM), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS).

Our experiments were carried out using an ultrahighvacuum (UHV) surface analysis system that performs scanning electron microscopy (SEM), SREM, AES, and XPS.⁸ These analyses could be performed without sample transfer. A 30 keV EB with a 2-nm-diam and a 0.37 nA current was used for the SREM. SREM images were obtained by using a specular reflection spot. The diffraction patterns [reflection high-energy electron diffraction (RHEED)] were monitored on a fluorescent screen with a charged-coupled-device camera. AES measurements and EB irradiation for the delineation of the SiO₂ layers were performed using an electron gun for microscopy. Because of the low incident angle of the probe beam (about 2° to the sample surface), a highly sensitive AES measurement was achieved.⁸ A Mg $K\alpha$ line was used for the XPS. The oxide thickness was carefully measured by comparing the Si 2p peak intensity from the substrate before and after thermal decomposition of the SiO₂ overlayer in the UHV analysis chamber.⁷

The sample was cut from a highly oriented Czochralski (CZ)-N Si(111) wafer. A Si(111)-7 \times 7 surface was prepared by flash heating with a direct current under UHV conditions. Oxidation of the sample surface was carried out by introducing molecular oxygen into the UHV chamber. XPS measurement showed that a 0.5-nm-thick oxide layer was formed after oxidation at a substrate temperature of 720 °C under a 1×10^{-4} Torr oxygen gas pressure for 2 min. In the photoelectron spectrum, a chemical shift component from the stoichiometric SiO₂ phase (Si⁴⁺) was dominant compared to the intermediate oxide states $(Si^{1+}-Si^{3+})$, which showed that a uniform oxide layer with an abrupt interface was formed. This is consistent with the high selectivity in epitaxial growth.⁵ To study the selective thermal decomposition mechanism, the EB was irradiated over a wide rectangular area $(1.2 \times 6 \text{ or } 0.4 \times 2 \,\mu\text{m})$ with the substrate at room temperature (at a 30 kV acceleration voltage and a 16 nA beam current). The developing procedure was to heat the EBirradiated sample at 720 °C with a direct current. The changes in the SiO₂ film composition during electron expo-

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FIG. 1. Change in oxygen Auger peak intensity of a 0.5-nm-thick oxide layer caused by electron exposure. The spectrum in the inset is from the initial SiO_2 surface. The O *KLL* peak was normalized by the Si *LVV* peak. Selective thermal decomposition was clearly observed when the film composition reached the SiO phase.

sure and the subsequent thermal heating was monitored through the Auger peak intensities. The surface morphology and the reconstruction were observed by SREM and by the diffraction pattern.

Figure 1 shows the change in the oxygen Auger peak intensity of the 0.5-nm-thick oxide layer during electron exposure. The Auger electron spectrum (the Fig. 1 inset) was taken from the initial SiO₂ surface, where Si *LVV* and O *KLL* signals were detected. We confirmed that the EB-induced carbon contamination was within the detection limit of our AES measurement. Note that the normalized oxygen Auger peak intensity [(O *KLL*)/(Si *LVV*)] decreased as the electron dose increased, which is attributed to electron-stimulated oxygen desorption (ESD) from the ultrathin oxide layer.^{9,10}

After electron exposure of 50 C/cm^2 , the oxygen peak became half that of the initial SiO₂ surface. This implies that oxygen desorption occurred from inside of the SiO₂ layer, as well as from the uppermost layer, and that the average composition changed to the SiO phase. After EB irradiation, samples were heated in the UHV analysis chamber at 720 °C. The EB-induced selective thermal decomposition was first monitored through the Auger peak intensities. Fig-



FIG. 2. Change in normalized oxygen Auger peak intensities. Open and closed circles, respectively, show the results of the EB-irradiated and the fresh SiO₂ surfaces. The EB was irradiated onto a 0.5-nm-thick oxide layer before annealing at 720 °C.



FIG. 3. SREM images taken during the selective thermal decomposition of the 0.5-nm-thick SiO₂ layers. The electron doses and the subsequent annealing times are shown in (a)–(f). The EB was irradiated onto a $0.4\times1.2 \ \mu m$ area at room temperature. Subsequent annealing was performed at 720 °C.

ure 2 is a typical result. These results clearly suggest that the selective thermal decomposition of the oxide layer occurred only within the EB-irradiated area.

Next we investigated the selective thermal decomposition process by SREM. Figures 3(a)-3(f) are SREM images taken during thermal decomposition of the oxide layers. (The electron doses and the subsequent annealing times are shown in each part of Fig. 3.) As mentioned in our previous report, we could not observe any change in the SREM image after EB irradiation.⁴ Figure 3(a) shows the result of thermal heating at 720 °C for 90 s after electron exposure with a dose of 30 C/cm^2 . The EB-irradiated area is shown by a dotted line. The dark contrast line indicated by the arrow corresponds to an interfacial step at the $SiO_2/Si(111)$ interface.⁷ (Since the amorphous SiO₂ layer on a crystal Si substrate does not contribute to diffraction spots, the SREM method shows interfacial step images.) Within the EB-irradiated area, individual nanometer-scale voids nucleated in the oxide layer appear as dark contrast spots. Further annealing resulted in an increase of the void density as well as a slight lateral growth [Fig. 3(b)]. When the electron dose and annealing time increased [Figs. 3(c) and 3(d)], the voids were densely generated where the SREM images show dark contrast regions. In the case of a 120 C/cm² electron dose [Figs. 3(e) and 3(f)], a bright region appeared within the EB-irradiated area, where we observed a diffuse 7×7 RHEED pattern. Although AES analysis of the bright area in Fig. 3(f) showed the presence of residual oxide (indicated by the arrow in Fig. 2), we confirmed the formation of an open window, where a clean 7 $\times 7$ reconstructed Si(111) surface was exposed after further annealing.

It is well known that the thermal decomposition of oxide layers is mediated by void formation and lateral growth.^{11–13} In our recent study, we showed that Si adatoms that form the volatile SiO phase were supplied by the creation of atomic-

height holes in exposed Si surfaces.¹⁴ The SREM observation in Fig. 3 shows that selective thermal decomposition is also mediated by void nucleation. However, the void density in the EB-irradiated area was much higher than that of common thermal decomposition observed for oxide layers with the same thickness. (As previously reported, the void density also depends on the oxide thickness.¹⁴) In addition, when using a thinner oxide layer (less than 0.3 nm thick), we could not observe the nucleation of individual voids during the EB-induced selective thermal decomposition. This means that the distance between each void is shorter than the resolution limit of the SREM method. These results indicate that a thinner oxide layer is suitable for nanofabrication, and that our previous results⁴ are consistent with the SREM observations.

Our results concerning the oxygen ESD characteristic (Fig. 1) and the selective thermal decomposition property (Fig. 3) suggest that the change in the oxide layer composition (SiO₂ \rightarrow SiO over 50 C/cm²) accounts for the selective thermal decomposition. (The threshold electron dose depends on the oxide thickness, annealing temperature, and time.) It has been reported that the thermal decomposition of oxide layers without electron exposure is mediated by SiO desorption as voids form on the surfaces, where the ratedetermining reaction step in void growth is the creation of mobile Si atoms within the exposed Si surfaces.^{12,13} The high activation energy for SiO formation was attributed to the energy required to pick off Si atoms from the Si substrate. Although we cannot determine whether a uniform SiO phase results from the electron exposure, the decrease in oxygen concentration should promote formation of the volatile SiO phase. This is because the Si atoms required for SiO formation can be supplied from the amorphous oxide layer when the film composition changes to the SiO phase. So, we can expect that an atomically smooth open window can be formed by optimizing the electron dose and oxide thickness. Another possible candidate for the selective-thermaldecomposition mechanism is the creation of void nucleation sites. Although the origin of nucleation sites has not been clarified, we believe that the void-formation energy in the

EB-irradiated oxide layer (the SiO phase) must be lower than in the initial SiO₂ phase, and also locations where Si-O bonds are broken by high-energy electron exposure should act as defect sites for void nucleation. This explains the increase in void density as the electron dose increases. Consequently, nanometer-scale voids are newly generated at a relatively low annealing temperature before any significant void growth. Moreover, since a core-level excitation is required for the oxygen ESD reaction,¹⁰ secondary electrons generated by a primary EB do not blur the patterns, which is essential to attain an ultrahigh-resolution resist material.

In summary, we have investigated the mechanism of EB-induced selective thermal decomposition of ultrathin oxide layers. We found that the selective thermal decomposition was mediated by densely formed nanometer-scale voids in the oxide layers, and that the void growth caused by SiO desorption was promoted by the change in the oxide-film composition induced by electron exposure.

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