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Scaning Tunneling Microscopy of Initial Nitridation Processes on Oxidized Si(100) Surface with Radical Nitrogen

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1. Introduction

In recent years, ultra-thin silicon nitride and silicon oxynitride have become attractive as a gate dielectric film and a reaction barrier layer at high-k-material/Si substrate interfaces, both of which are used for the next-generation Si ultral-large scale integrated circuits. It is well known that, because of the denser structures of silicon nitride and silicon oxynitride compared to SiO_2, boron diffusion from poly-Si gate electrode is effectively suppressed when those materials are applied to the gate insulator films. Furthermore, it has been reported that they improve the interfacial endurance such as hot electron immunity and breakdown strength[1-3].

Elucidation of atomistic reactions which occur during the nitridation process is crucial for the control of film morphology. However, the atomic scale oxnitridation process has not been clear yet. Recently, scanning tunneling microscopy (STM) has been demonstrated to be a powerful tool for clarifying atomistic process in the initial stage of radical nitridation on Si(100) clean surfaces[4]. In this paper, we have used STM and investigated an initial oxynitridation process on Si(100) using a radical nitrogen source. Detailed film evolution stage of silicon oxynitride films, concomitant with defect formation and surface step modification, have been examined on an atomic scale.

2. Experiment

Experiments were carried out using an ultrahigh vacuum chamber equipped with a STM system. P-type Si(100) substrates were chemically cleaned. And then, in order to obtain clean surfaces, the substrate was resistively heated at 1200℃ for a few minutes at a pressure below $1x10^{-9}$ Torr after degassing at 650℃ for 6 hours. After this treatment, a 2.3-monolayer-thick silicon oxide layer was formed on the clean surface by exposing to dry oxygen at 700℃ or room temperature (hereafter we call 700℃-oxide and RT-oxide layers, respectively). Next the oxide layers were exposed to radical nitrogen at a pressure of $1x10^{-5}$ Torr at 850℃. The radical nitrogen was formed by discharging molecular nitrogen with radio frequency of 13.56 MHz and charged species were removed by an ion-trap system. The thicknesses of the nitride and oxide layers were determined by Auger electron spectroscopy (AES) mesurement.

3. Results and Discussion

Figure 1 shows a STM image of the 700℃-oxide layer formed on the Si(100) surface. Since a monolayer step on the surface is clearly observed, a thin oxide film is found to grow layer by layer. Similar surface morphology was also observed in the case of the RT-oxide layer.

Figure 2(a) shows a STM image of the 700℃-oxide layer after exposure to the radical nitrogen of about 1 Langmuir (L) at 850℃. Bright regions which form islands are observed as well as flat terraces separated by monolayer steps. Figure 2(b) shows scanning tunneling spectroscopy spectra taken from the islands and terrace regions of the same sample as that shown in Fig. 2(a). The energy gap in the density of states taken from the islands is larger than that from the terraces, indicating that the island regions should be more nitrized than the terrace regions. As seen in Fig. 2(a), step morphology around the nitride islands are slightly changed from the regular alignment shown in Fig. 1. We have previously confirmed a drastic change of Si step structures during radical nitridation on clean Si(100)-2x1 surfaces and this comes from the detachment of Si atoms from the step edges[4]. Since the degree of the structural change is lower in the present case than the clean surface case, the oxide layer essentially suppresses such Si detachment caused by the nitrogen atoms. Figure 2(c) shows a 1-L-nitrogen-exposed RT-oxide layer where a comparatively rough surface with no regularity of steps was formed and multilayer steps are also observed. This result means that nitrogen-induced modification of the film is critically influenced by the performed silicon-oxide structure.

Figure 3(a) shows STM image of the 700℃-oxide layer subjected to the 10 L radical nitrogen exposure. Compared to the island morphology in the case of the clean surface shown in Fig. 3(b) [4], larger nitride islands with higher surface coverage are formed on the surface. Furthermore, 2x1 reconstructed structures, which indicate Si clean surface exposure, were hardly observed on the terraces in the present case. This is effectively suppressed on the oxide layer, leading to the formation of a continuous film morphology.

4. Summary

We have investigated by STM the initial nitridation process on thin silicon oxide layers formed on Si(100) surfaces using radical nitrogen. STM observation revealed that the thin oxide layer can suppress the changes of original Si step structures during nitridation, and this effect critically depends on the growth conditions of the oxide layers. Comparison of the nitride island morphology to the case of the clean surface suggests that the migration of the precursor during nitridation is suppressed by the oxygen in the layer.

References

[1] S. V. Hattangady, H. Niimi and G.Lucovsky: Appl. Phys. Lett. **66**, 3495(1995).
[2] M. L. Green et al Appl. Phys. Lett. **65**, 848(1994).
[3] T.Hori: IEEE Trans. Electron Devices **37**, 2058(1990).
[4] D. Matsushita et al: Jpn. J. Appl. Phys. **40**, 2827(2001).

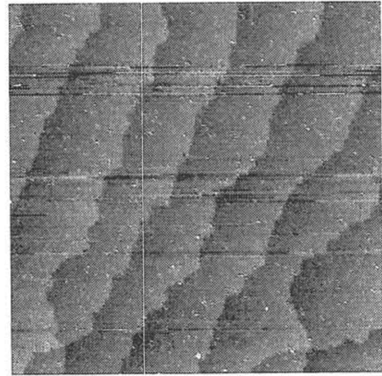

Fig.1 STM image of a Si surface after oxidation at substrate temperature of 700℃. The scan area is 500 nm x 500 nm.

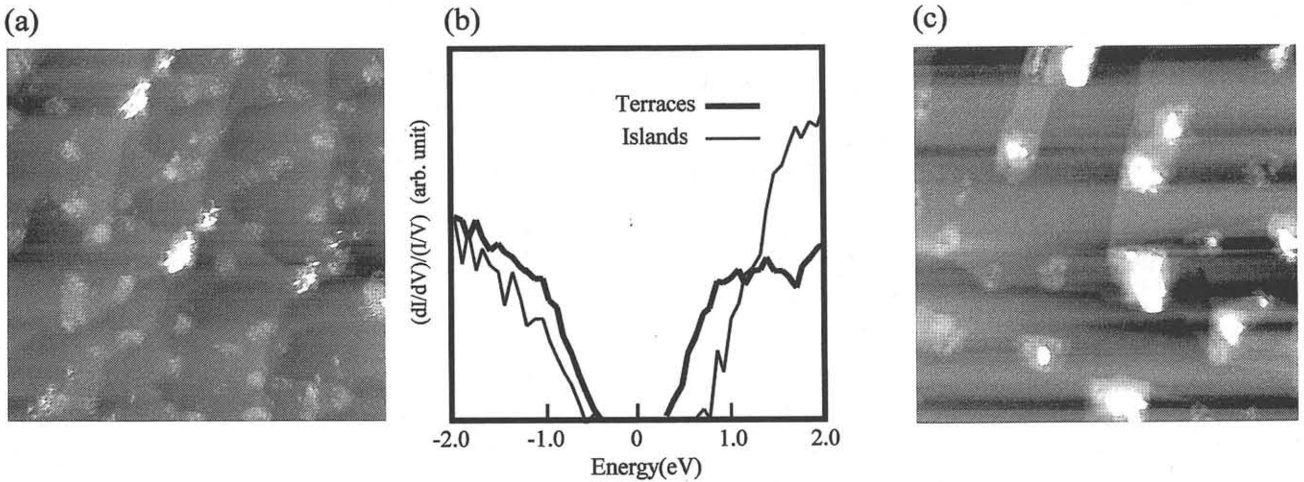

Fig. 2 (a) STM image of a 700℃-oxide layer after exposing to radical nitrogen about 1L at 850℃. (b) STS spectra taken from islands and terrace regions in the sample shown in (a). (c) STM image of a RT-oxide layer after exposing to radical nitrogen about 1L at 850℃. The scan areas are 500 nm x 500 nm.

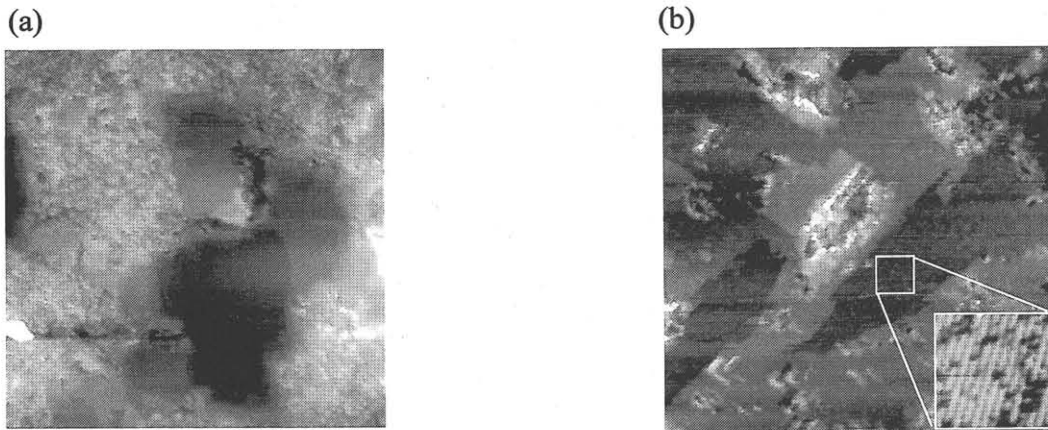

Fig. 3 STM image of (a) a 700℃-oxide layer after exposing to radical nitrogen about 10 L at 850℃. (b) a clean Si surface after exposing to radical nitrogen about 10 L at 850℃. Insert shows a close up image showing a 2x1 structure. The scan areas are 200 nm x 200 nm.