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Atomic Scale Characterization of Nitridation Process on Si(100)-2x1 Surfaces by Radical Nitrogen

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I. Introduction

A reduction of device dimensions of metal-oxide-semiconductor field-effect transistors (MOSFET's) requires thin gate oxide films with reduced thicknesses in the devices. Simultaneously, the reliability of the devices, which is characterized by, for example, leakage current and time-dependent dielectric breakdown (TDDB) characteristics, must be kept high. It has been reported that nitridation treatments after the oxide formation are effective in improving the MOSFET reliability [1]. However, the role of nitrogen atoms and atomic scale reaction-process have not been fully understood yet. Therefore, it is essential to clarify the relationship between the atomic configuration and the local electronic states of nitride films for the realization of well-defined thin gate dielectric films.

As a first step of understanding the nitridation processes on Si substrates, we have studied the initial nitridation of clean Si (100)-2x1 surfaces at low temperatures (~350°C) using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) [2]. The nitridation has been shown to be controllable on an atomic scale by using radical nitrogen sources. In this study, we perform high temperature nitridation (~850°C) of Si(100)-2x1 surfaces by the ragical nitrogen using STM and STS. We discuss the initial nitridation process on the Si(100) surfaces on the basis of STM images and STS spectra.

II. Experimental

Experiments were carried out in an ultrahigh vacuum system which consisted of a main chamber equipped with STM/STS and Auger electron spectroscopy (AES), and a sample-preparation chamber. These chambers had a base pressure less than $1x10^{-10}$ Torr. A Si(100) substrate was chemically cleaned and successively introduced into the preparation chamber. In order to obtain clean surfaces, the substrate was resistibly heated at 1200°C for a few second at a pressure below $1x10^{-9}$ Torr after degassing at 650°C for five hours. After this treatment, the Si(100) surface was confirmed to have a 2x1-reconstructed structure by STM observations and the amount of C and O contaminants on the surface were below the detection limit of AES measurements.

The nitridation was performed by exposing the clean surface to radical nitrogen at $1x10^{-5}$ Torr at a substrate temperature of 850°C. The radical nitrogen was formed by discharging molecular nitrogen with a radio frequency of 13.56 MHz and charged species were removed by an ion-trap system. The nitride thickness in monolayer (ML) units, which is defined as the ratio of the number of adsorbed nitrogen atoms to that of surface Si atoms, was determined by AES measurements.

III. Results and Discussion

Figure 1 shows a STM image of a clean Si(100)-2x1 surface. The image was obtained at a sample bias of +2.0 V, reflecting an unoccupied states. In this image, a monolayer step and dimer rows can be clearly seen. Moreover, there are some bright spots on the surface. We confirmed that the bright spot images turned into dark dots in occupied-state STM images at a sample bias of -2.0 V in the same area. This characterizes a C-type defect on a Si(100)-2x1 surface [3], in which a Si atom between two adjacent dimers is missing. Accordingly, the bright spots shown in Fig. 1 correspond to the C-type defect.

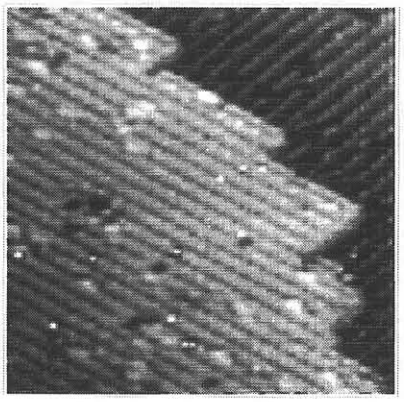

Fig. 1 STM image of a Si(100)-2x1 clean surface. The image was obtained at a sample bias of +2.0 V. The scan area was 20 nm x 20 nm.

Figures 2(a) and (b) show respectively unoccupied and occupied state STM images after exposing to radical nitrogen of about 1 L at 850°C. Many bright spots can be seen in Fig. 2(a) while they appear as dark dots in Fig. 2(b) (see white circles A in both figures). Therefore, C-type defects have been formed on the Si surface due to the exposure of the radical nitrogen. This result means that the detachment of surface Si atoms occurred similarly to the case of low-temperature nitridation [2]. Furthermore, linear defects along the direction perpendicular to the dimer rows were frequently observed, as one example surrounded by white rectangular B in Fig. 2(a) and (b). We confirmed that this type of defect morphology was not observed when the substrates were annealed at 850°C without radical nitrogen. Therefore, we deduce that the nitrogen atoms promote the migration of surface Si atoms and this resulted in the rearrangement of the individual defects on the surface.

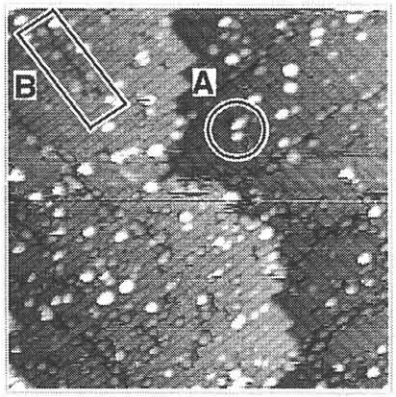

Fig. 2 (a) STM image of a Si surface after exposing to radical nitrogen of about 1 L at 850℃. The image was obtained at a sample bias of +2.0 V. The scan area was 25 nm x 25 nm.

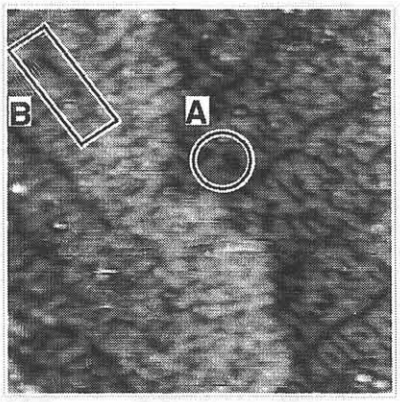

Fig. 2 (b) STM image of a Si surface after exposing to radical nitrogen of about 1 L at 850℃. The image was obtained at a sample bias of -2.0 V. The scan area was 25 nm x 25 nm.

Figure 3 shows a STM image taken after exposing to radical nitrogen of about 10 L at 850°C. The amount of nitrogen on the Si surface was estimated to be about 0.07 ML. It is observed that the step morphology drastically changed in comparison with that on clean surfaces and some steps were pinned by island regions. Compared with STS spectra from the clean surfaces, those taken from the island regions showed remarkable decreases of peaks coming from πd, πd^*, and backbond states. This means that nitridation occurred in these regions.

Figure 4 shows a STM image taken after exposing to radical nitrogen of about 50 L at 850°C. The amount of nitrogen was 0.18 ML. The density of the nitride islands decreases and the size increases. Furthermore, these islands grow preferentially along the <011> direction perpendicular to the Si dimer rows that surround the island and drastic changes of Si step structures are clearly observed. From the comparison between the island area estimated from the STM images and the number of adsorbed nitrogen atoms estimated from AES, we found that the islands have about 1ML-thick nitrogen. This result indicates that the nitridation at 850°C proceeded via lateral growth of two-dimensional nitride islands. On the other hand, nitridation was not observed on the rest regions and these surfaces were typically lower than the island over 7 ML's. This surface morphology would be attributed to the promotion of surface atom migration induced by radical nitrogen exposure.

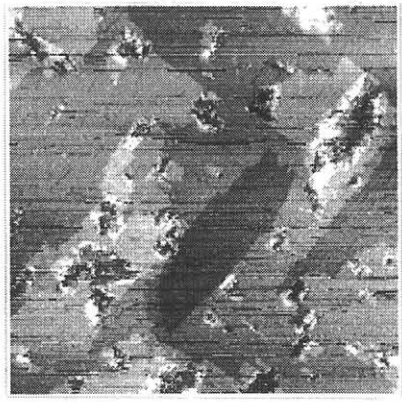

Fig. 3 STM image of a Si surface after exposing to radical nitrogen of about 10 L at 850℃. The image was obtained at a sample bias of +4.0 V. The scan area was 100 nm x 100 nm.

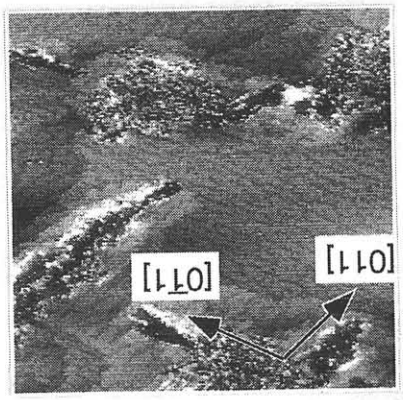

Fig. 4 STM image of a Si surface after exposing to radical nitrogen of about 50 L at 850℃. The image was obtained at a sample bias of +4.0 V. The scan area was 100 nm x 100 nm.

IV. Summary

We have investigated the initial nitridation process on clean Si (100)-2x1 surfaces by radical nitrogen at 850°C using STM and STS. It was found that linear defects perpendicular to dimer rows are formed. The nitridation proceeds via lateral growth of two-dimensional nitride-islands. In this case, the island grows preferentially along the <011> direction perpendicular to the Si dimer rows that surround the island. Drastic changes of Si step structures during nitridation were clearly observed, which results from the promotions of surface atom migration caused by nitrogen atoms.

References

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