Extended Abstracts of the 1996 International Conference on Solid State Devices and Materials, Yokohama, 1996, pp. 172-174 **Sympo. IV-2**

Nanometer-Scale Local Oxidation of Si Using SiN Islands Formed in the Early Stages of Nitridation

Takeshi YAMAMOTO and Michiharu TABE

Research Institute of Electronics, Shizuoka University
3-5-1 Johoku, Hamamathu 432, Japan

We have proposed and studied nanometer-scale local oxidation of Si (LOCOS) using silicon nitride (SiN) island formed by thermal nitridation. The SiN islands appear as dark regions in STM images and the average size increases with increasing nitridation temperature. When the nitrided surface is successively oxidized in the etching mode, the SiN islands turn to bright regions by selective etching of the clean 7x7 regions and the brightness (height) increases with increasing etching time. Thus the microscopic LOCOS process is demonstrated and nanometer-scale Si pillars are fabricated.

1. INTRODUCTION

Nanometer-scale line, pillar and dot structures of Si have been of great interest in exploring the new Si fields of optical devices and quantum effect devices. So far, various fabrication methods have been reported focusing on reducing their dimensions, where electron beam (EB) lithography and successive dry or wet etching are commonly used.[1)~5)] However, it is difficult to realize high density structures over a large area.

For fabrication of high density nano-structure over a large area, we have proposed and experimentally studied a new method, nanometer-scale local oxidation of Si (LOCOS), using silicon nitride (SiN) islands formed by thermal nitridation. Conventional LOCOS has been one of the most important processes in LSI fabrication,[6)] where SiN regions work as oxidation masks due to extremely slow oxygen diffusion in SiN. The nanometer-scale LOCOS proposed is based on the same idea as the conventional one and consists of the following steps; first, SiN islands are formed without lithography in the early stages of thermal nitridation in vacuum with N_2, and then the nitrided surface is oxidized also in vacuum without exposing the sample to the air. However, it is not known whether small SiN islands with high density are successfully formed nor whether the SiN island, which will be extremely thin, sustains the mask effect during oxidation. The purpose of this work is to examine the topographic features of the nitrided Si (111) 7x7 surface and the masking capability of the SiN for subsequent oxidation.

2. EXPERIMENT

Sample preparation and measurements of X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) were performed in an ion-pumped ultra-high vacuum (UHV) apparatus. A Si (111) sample (n-type, 0.1 Ω cm) was resistively heated at 1200°C for a few seconds to obtain a clean 7x7 surface. The clean Si surface was exposed to N_2 of 1×10^{-5} Torr at various temperatures for certain durations (≤ 150s), and the sample was cooled down to room temperature after evacuating N_2. Then, measurements of XPS and STM were performed at room temperature. Some of the nitrided samples were oxidized at 755°C by O_2 with a pressure of 1×10^{-6} Torr and observed by STM again. It is well known that the O_2 pressure-temperature plane is divided into the etching and growth oxidation modes, and that the etching mode lies in the region of relatively low O_2 pressures and high temperatures.[7)] The oxidation condition (O_2 pressure and temperature) in this works was determined to lie in the Si etching mode with a chemical reaction, $Si + O_2 \rightarrow SiO\uparrow$, instead of SiO_2 growth mode, because the resultant surface topography can be observed by STM. Although we can choose SiO_2 growth mode conditions, STM cannot be used due to the presence of thick non-conducting SiO_2 regions.

3. RESULTS AND DISCUSSIONS

Figure 1 shows previously reported relative nitrogen coverage, I_N/I_{Si}, on Si (111) as a function of nitridation temperature measured by XPS.[8)] It is clearly seen that in the 1x1 temperature range, nitrogen coverage is significantly suppressed to negligible amounts. This indicate that the 1x1 surface is much less reactive than the 7x7 surface, and thus we focused only on the 7x7 temperature range for nitridation in the following.

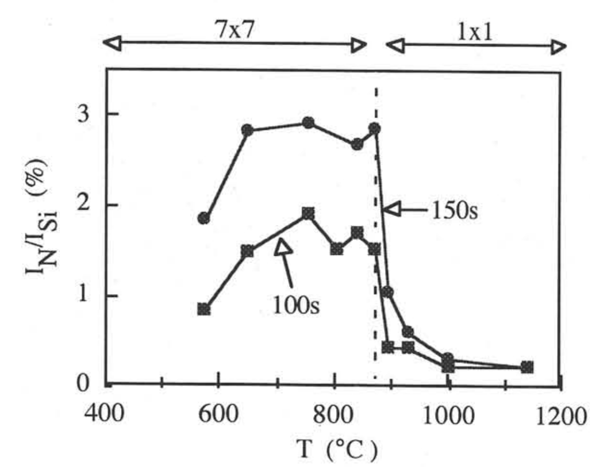
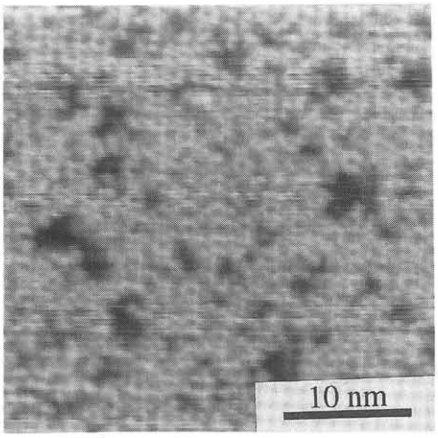


Fig. 1 Relative nitrogen coverage, I_N/I_{Si}, as a function of nitridation temperature at t_{exp} of 100 and 150s for Si (111).

In Fig. 2 (a) and (b), we show empty-state STM images of surfaces nitrided at 650 and 755°C, respectively. In 650°C-nitrided surfaces (Fig. 2 (a)), irregularly-shaped dark regions, exhibiting no atom resolution, are the main features of the nitrided surface and the clean 7x7 atom arrangement remains for the rest. (The words "dark" and "bright", which appears later, are used with reference to clean 7x7 regions having a medium height.) Since the area fraction of the dark regions monotonously increases with N_2 exposure time, we ascribe the dark regions to reacted Si sites with nitrogen. Here, it should be noted that the dark regions would not be topographically depressed but rather protruded, because the darkening in this case must be a result of reduced density of states near the Fermi level in the nitrided regions. In 755°C-nitrided surface (Fig. 2 (b)), dark regions are more condensed (larger in lateral size) forming nearly a triangular shape with the apexes pointing in the $\langle \bar{1}\ \bar{1}\ 2 \rangle$ directions. At or above 755°C, the dark regions exhibited characteristic atom arrangement for relatively high sample bias, as shown in Fig. 3, which is identical to previously assigned SiN islands showing "8x8" low-energy electron diffraction (LEED) pattern.[9] Thus, the triangular dark regions are confirmed to be nitrides, while those in Fig. 2 (a) are probably precursors of the "8x8" nitrides. From this experiment, it is found that the average diameters of SiN islands and their spacings can be extensively varied by changing nitridation temperature from 3 to 10 nm and from 6 to 30 nm, respectively. Furthermore, more detailed analysis of STM images in conjunction with X-ray photoelectron spectroscopy (XPS) result suggests that thickness of the SiN islands is deduced to be a few angstroms at most.

(a)



(b)

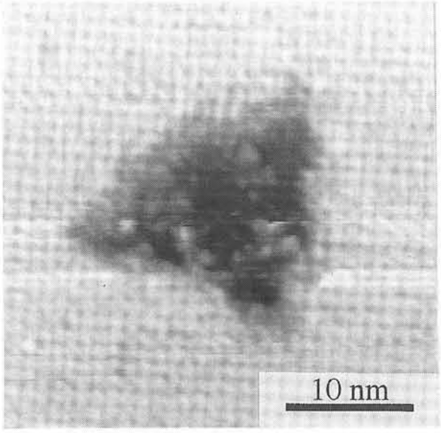


Fig. 2. (a) An STM image of 100s-exposed surface with N_2 at 650°C. The sample bias is 1.2 V and the scanning area is 35x35 nm^2. (b) 50s-exposed-temperature at 755°C. The sample bias is 2.0 V and the scanning area is 35x35 nm^2.

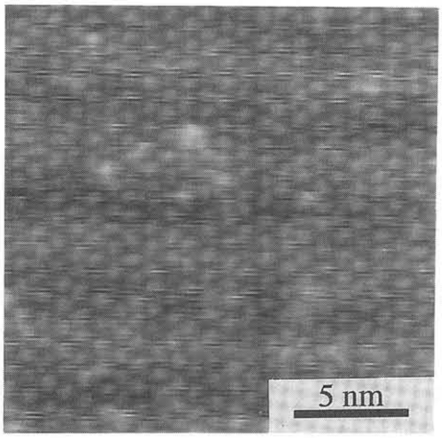


Fig. 3. An atom resolution STM image of dark region formed by 870°C-nitridation for 100s. The sample bias is 2.5 V and the scanning area is 20x20 nm.

Next, we proceeded to etching-mode oxidation of the nitrided surface. The result shows that the original "8x8" dark regions formed by nitridation at 755°C (Fig. 4) now turn to bright regions after 50 s oxidation at 755°C (Fig. 5 (a)). (Note that observation positions on the surface are different from each other, and therefore the correspondence between the original dark regions and the bright regions after etching is tentatively assumed from a comparison of their shapes and densities, but clearly evidenced by coincidence of their atom arrangements as described below.) For prolonged etching as in Fig. 5 (b) , the STM tip does not properly trace the surface topography and the apparent pillar density is doubled due to pronounced double-tip effects, but we can still roughly estimate the height of the SiN regions. We have found that, even after etching, the bright region shows the same "8x8" arrangement in a close-up view as before etching (see Fig. 3). This fact indicates that the SiN islands are not altered by oxidation and effectively work as oxidation (etching) masks, and that only the clean 7x7 regions are retracted by etching. In addition, according to XPS results, the nitrogen coverage is not reduced at all by the etching-

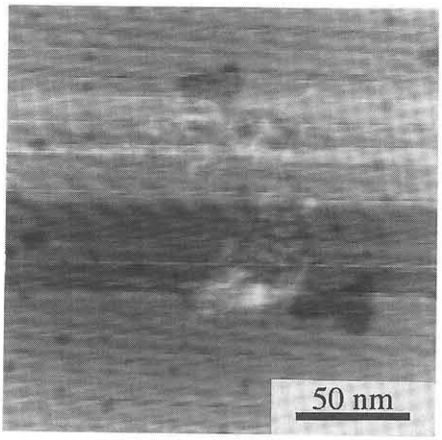
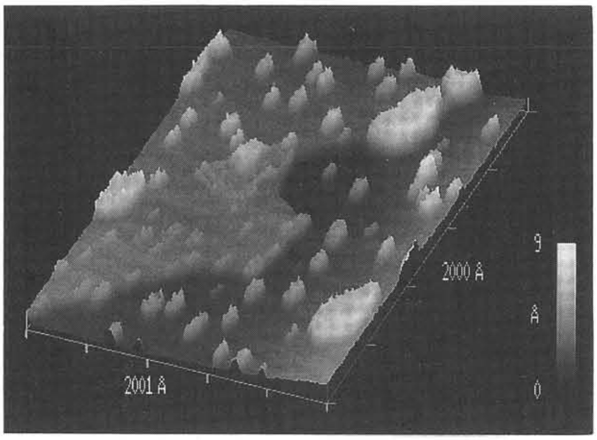


Fig. 4. An STM image of 100s-exposed surface with N_2 at 755°C before oxidation. The scanning area is 200x200 nm^2. Small and large dark SiN regions are seen. Unfavorable vibration noises are superimposed.

oxidation, supporting the STM results. The etched amounts of Si regions were estimated to be 0.31 and 0.55 nm for Fig. 5 (a) and (b), respectively, resulting an etching rate of about 0.006 nm/s in the present condition.

(a)



(b)

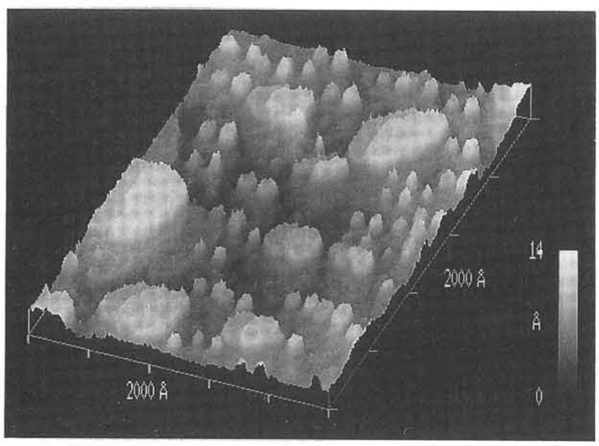


Fig. 5. (a) A bird's-eye view of 50s-oxidized (etched) surface. (b) A bird's-eye view of 100s-oxidized surface.

Thus, we have fabricated Si nano-structures with the average diameter of 5 nm and the height of 0.3~0.6 nm, depending on etching time but limited by multi-tip effects of STM observations, and with the average spacing of 20 nm.

4.CONCLUSION

We have proposed and demonstrated nanometer-scale LOCOS process for high density ultra small Si structures. At first, we have studied SiN island formation on the Si (111) 7x7 surface in the early stages of thermal nitridation by N_2, and found that dimensions of SiN regions are sensitive to nitridation temperature, i.e., more condensed with increasing temperature. Second, we have demonstrated that the SiN islands work as oxidation masks in the experiment that etching mode oxidation was employed for STM observations.

ACKNOWLEDGMENT

This work was partly supported by a Grant-in-Aid for General Scientific Research (No. 07455137) from the Ministry of Education, Science and Culture, and by the Murata Science Foundation.

REFERENCES

1) W. Chen and H. Ahmed, Appl. Phys. Lett. **63** (1993) 1116.
2) P. B. Fischer and S. Y. Chou, Appl. Phys. Lett. **62** (1993) 1414.
3) P. B. Fischer, K. Dai, E. Chen and S. Y. Chou, J. Vac. Sci. Technol. B **11** (1993) 2524.
4) A. Nakajima, H. Aoyama and K. Kawamura, Jpn. J. Appl. Phys. **33** (1994) L1796.
5) H. Namatsu, M. Nagase, K. Kurihara, K. Iwadate, T. Furuta and K. Murase, J. Vac. Sci. Technol. B **13** (1995) 1473.
6) E. Bassous, H. N. Yu and V. Maniscalco, J. Elctrochem. Soc. **123** (1976) 1729.
7) F. W. Smith and G. Ghidini, J. Electrochem. Soc. **129** (1982) 1300.
8) M. Tabe, Jpn. J. Appl. Phys. **34** (1989) L1375
9) E. Bauer, Y. Wei, T. Müller, A. pavlovska and I. S. T. Tsong, Phys. Rev. B **51** (1995) 17891.