

Modification of Silicon Surface Produced by Electric Field Enhanced Oxidation Through Native Oxide

Yasunori EJIRI, Masatoshi YASUTAKE*, and Takeo HATTORI

Department of Electrical and Electronic Engineering,
Musashi Institute of Technology

1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158

*Scientific Instruments Division, Development Department,
Seiko Instruments Inc, Takatsuka Unit
Takatsuka-shinden, Matsudo, Chiba 271

It is demonstrated that nearly atomically flat Si surfaces passivated with native oxides can be modified by applying a negative potential to the conducting probe of an atomic force microscope (AFM) with respect to the silicon substrate. It was verified from the detection of O_{KLL} Auger electrons and Si_{LVV} Auger electrons excited by the electron beam that silicon surfaces are modified by the oxidation of silicon. This oxidation is enhanced by increasing the potential applied across the probe and silicon substrate. The fabrication of nanometer-sized structures is demonstrated.

1. Introduction

Recently there have been attempts to fabricate nanometer-scale structures on chemically prepared silicon surfaces using a scanning tunneling microscope.¹⁾ In these attempts voltage pulses imposed across the tunneling gap were used to generate nanometer-sized structures. These attempts were made in electrochemical solution, in air or in ultrahigh vacuum. However, the formation mechanism of these nanometer structures is not clarified yet. Our purpose in the present paper is to report the formation mechanism of nanometer-sized structures obtained by measuring their chemical composition and height using Auger electron spectroscopy and the atomic force microscope (AFM), respectively.

2. Modification of Silicon Surfaces²⁾

The surfaces of nearly atomically flat hydrogen-terminated Si samples, passivated with native oxides, were modified. The samples were prepared as follows. First, 20-nm-thick oxide films were formed on $5 - 8 \Omega \cdot \text{cm}$ n-type silicon (100) surfaces in dry oxygen at 1000°C . Second, these oxide films were etched in buffered hydrofluoric acid. Third, silicon surfaces thus obtained were treated in buffered hydrofluoric acid at $\text{pH}=3.8$ ³⁾

Fourth, these silicon surfaces were passivated with native oxides formed by treatment in hot HNO_3 at $45 - 60^\circ\text{C}$ in order to minimize the effect of contamination on the modification studied here. These native oxide surfaces are quite smooth: their surface microroughnesses, expressed by R_a , are on the order of 0.1 nm over the area of $100 \text{ nm} \times 100 \text{ nm}$.⁴⁾ The silicon surfaces thus prepared were modified by applying negative potential to the conducting probe with respect to the silicon substrate, there by applying a voltage across the native oxides. The conducting probes used for the present study were made of Si_3N_4 and were covered with about 10-nm-thick gold films. The heights of modified silicon surfaces were measured by means of AFM with a repulsive force of nearly 1 nN. It was verified from the detection of O_{KLL} Auger electrons and Si_{LVV} Auger electrons excited by the electron beam that silicon surfaces are modified by the oxidation of silicon.

3. Oxidation Process

The Si(111) surfaces used for the studies on the oxidation process are passivated with native oxides in order to avoid the effect of contamination on the oxidation process. These silicon surfaces are prepared as follows. First, 20-nm-thick oxide films were formed on $2-6 \Omega \cdot \text{cm}$ n-type Si(111)

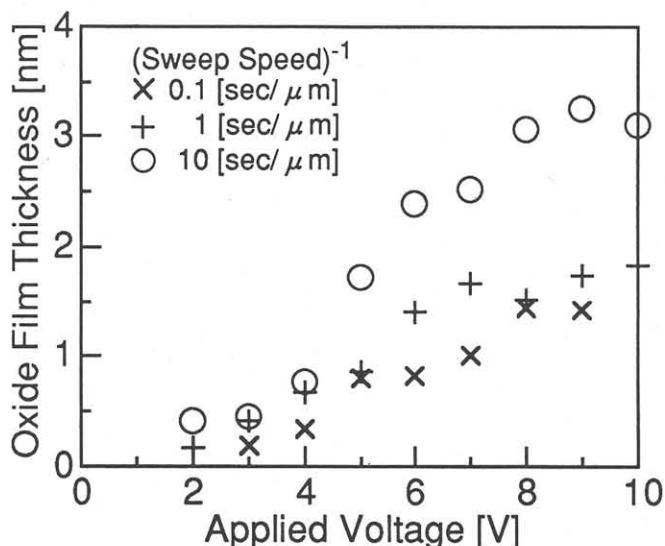


Fig. 1 Dependence of oxide film thickness on applied voltage across probe and silicon substrate.

surfaces in dry oxygen at 1000 °C. Second, these oxide films were etched in buffered hydrofluoric acid. Third, silicon surfaces were treated in 40% NH₄F in order to obtain an atomically flat hydrogen-terminated surfaces.⁵⁾ Fourth, these silicon surfaces were passivated with native oxides formed by the treatment in the mixed solution of H₂SO₄ and H₂O₂ at 85-90°C. The surface microroughnesses of native oxides formed, expressed by Ra, are on the order of 0.1 nm over the area of 100 nm x 100 nm so that the oxidation process studied here is weakly affected by the surface microroughness.

Figure 1 shows the dependence of oxide film thickness, which is averaged along the sweep direction of the probe on silicon substrate, on the applied voltage with sweep speed of the probe as a parameter. The thickness of the oxide film is reproducible if the applied voltage is more than nearly 5V. This figure exhibits the enhancement of oxidation by the electric field.⁶⁾ Here, the spacing between oxide stripes is 0.5 μm so that the effect of oxidation on the neighbouring oxide stripes can be neglected. Fig. 2 shows the dependence of oxide thickness, which is averaged along the sweep direction of the probe on silicon substrate, on the sweep speed with applied voltage as a parameter. It is found from this figure that the increase in oxide film thickness is roughly proportional to the square root of sweep time, in other words oxidation time, for oxide film thickness of more than 1 nm. Therefore, the oxidation may be limited by the diffusion

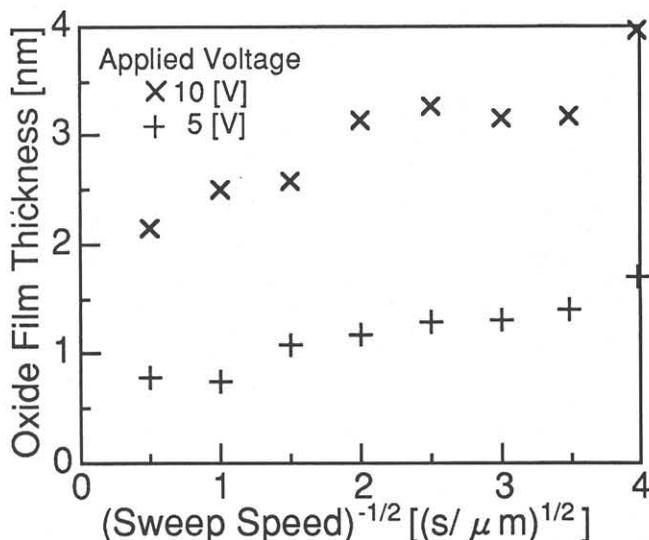


Fig. 2 Dependence of oxide film thickness on sweep speed.

of oxidized species for this thickness range.

4. Fabrication of Nanometer-Sized Structures

Figure 3 shows the nanometer-sized structures fabricated using present oxidation process with applied voltage of 6 V and sweep speed of 1 μm/s. In order to optimize the fabrication conditions of nanometer-sized structures the dependences of oxide-stripe-width on the applied voltage and the sweep time were investigated. Fig. 4 shows the dependence of oxide-stripe-width expressed by Full Width Half Maximum (FWHM) on the applied voltage with the sweep speed of the probe as a

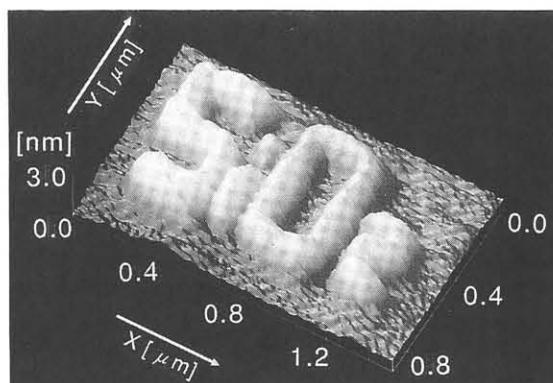


Fig. 3 Nanometer-sized structures fabricated using present oxidation process.

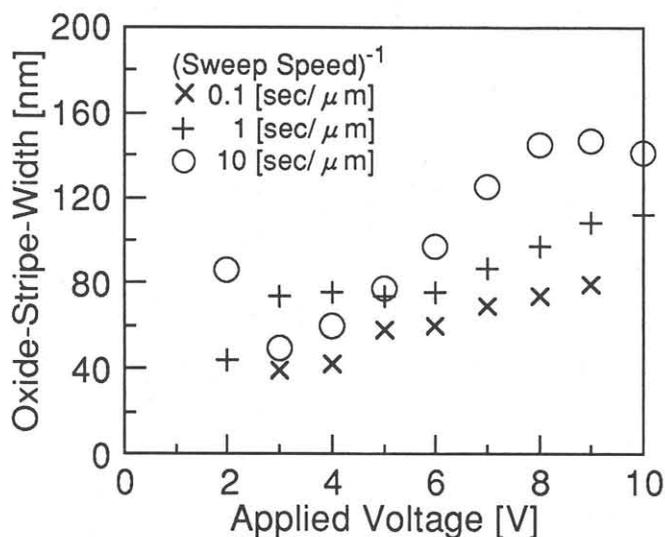


Fig. 4 Dependence of oxide-stripe-width on applied voltage across probe and silicon substrate.

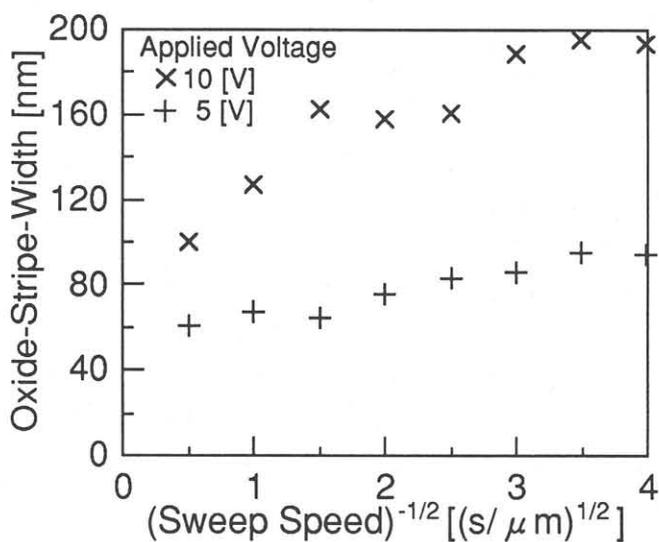


Fig. 5 Dependence of oxide-stripe-width on sweep speed.

parameter. According to this figure, the width increases with the increase in the applied voltage. This suggests that the oxide grows not only along the vertical direction normal to the silicon surface, but also along the horizontal direction parallel to the silicon surface. Fig. 5 shows the dependence of oxide-stripe-width expressed by FWHM on sweep speed with the applied voltage as a parameter. According to this figure, the width increases with sweep time. This also

suggests that the oxidation proceeds not only along the vertical direction normal to the silicon surface, but also along the horizontal direction parallel to the silicon surface.

5. Summary

In summary, it is demonstrated that nearly atomically flat silicon surfaces passivated with native oxides can be modified by applying negative potential to the conducting probe of an atomic force microscope, thereby applying voltage across the native oxide. It was found from the compositional analysis that this modification is produced by the oxidation of silicon. It was also found from height measurement of the modified silicon surface that this oxidation is enhanced by the electric field. The fabrication of nanometer-sized structures are demonstrated together with their fabricating conditions studied.

Acknowledgements

The one of the authors (T. H.) expresses his hearty thanks to Dr. Masatake Katayama of SEH Isobe R & D Center for supplying silicon wafers used in the present study. The authors would like to express their sincere thanks to Mr. Kazuhiro Yanagisawa for his invaluable assistance.

References

- 1) N. Barniol, F. Perez-Murano, and X. Aymerich: Appl. Phys. Lett. 61 (1992) 462 and references therein.
- 2) M. Yasutake, Y. Ejiri, and T. Hattori: to be published in Jpn. J. Appl. Phys. Vol.32, No.7B (1993).
- 3) H. Nezu, Y. Mizue, M. Matsukawa, S. Miyazaki, and M. Hirose: Ext. Abstr. 53rd Autumn Meeting of Japan Society of Applied Physics, Osaka, September, 1992, 16p-ZP-11.
- 4) Y. Shimizu, Y. Ejiri, Y. Tamura, and T. Hattori: Abstr. 40th Spring Meeting of Japan Society of Applied Physics and Related Societies, Tokyo, March, 1993, 31p-ZW-3.
- 5) G. S. Higashi, R. S. Becker, Y. J. Chabal, and A. J. Becker: Appl. Phys. Lett. 58 (1991) 1656.
- 6) P. J. Jorgensen: J. Chem. Phys. 37 (1962) 874.