

Initial Stage of Oxidation of Hydrogen-Terminated Si(100)-2 × 1 Surface

T. Aiba, K. Yamauchi, Y. Shimizu, N. Tate*, M. Katayama* and T. Hattori

Musashi Institute of Technology, 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158

*Shin - Etsu Handotai Co. Ltd., 2-13-1 Isobe, Annaka, Gumma 379-01

It is shown from the present study that an atomically flat SiO₂/Si interface can not be prepared even by the oxidation of an atomically flat H-terminated Si(100)-2 × 1 surface in dry oxygen with a pressure of 1 Torr at 300°C and by the subsequent oxidation in the same oxidation atmosphere at 600 and 800°C.

1. INTRODUCTION

Nearly 5 nm thick silicon oxide film will be used as gate oxide for metal-oxide-semiconductor-field-effect-transistor in 1 Gbit dynamic random access memory, which is expected to appear at the end of this century. In order to form such ultra-thin film with high quality, it is necessary to prepare an atomically flat and ultra-clean Si surface and to control oxidation reaction in atomic scale. An atomically flat Si(100) surface can be obtained by annealing in hydrogen with pressure higher than 0.2 Torr at 700°C.¹⁾ H-terminated Si(100)-2 × 1 surface was found to exhibit clear reflection high-energy electron diffraction pattern even after the exposure to air with relative humidity of 28%.²⁾ Furthermore, 0.4 nm thick oxide film formed on Si(100) surface in dry oxygen at 300°C, which is called preoxide in the following, is stable in ultra-dry argon even at 900 °C.³⁾ Through 0.5 nm thick preoxide formed at 300°C the periodic changes in the interface structures appear with the progress of oxidation and can be understood as layer by layer of thermal oxide on Si(111) surface at 800°C in dry oxygen.⁴⁾ It is the purpose of present paper to study the initial stage of H-terminated Si(100)-2 × 1 surface by measuring oxidation induced changes in Si 2p photoelectron spectra

using ESCA-300 manufactured by Scienta Instruments AB, which has high sensitivity and high resolution.⁵⁾

2. EXPERIMENTAL DETAILS

H-terminated Si(100)-2 × 1 surface was prepared on a 0.5 × 51 × 52.5 mm 10-20 Ωcm n-type Si(100) wafer with 45 degrees bevels on each of the short sides by epitaxial growth of Si in a hydrogen atmosphere at 1100°C for 10 minutes, after removing 200-nm-thick thermal oxide films, which were formed on Si(100) surface in dry oxygen at 1000°C, by using 1% hydrofluoric acid solution. Multiple internal reflection spectroscopy was used as a sensitive tool to determine the microscopic arrangement of H-terminated Si(100) surface.

The changes in chemical structures at the initial stage of oxidation was investigated by measuring Si 2p photoelectron spectra, which are excited by monochromatic AlK α radiation, at photoelectron take-off angles of 15, 30 and 90 degrees with an acceptance angle of 3.3 degrees. The samples were oxidized by optical heating in dry oxygen with a pressure of 1Torr at 300, 600 and 800 °C. After the oxidation the samples were cooled down to room

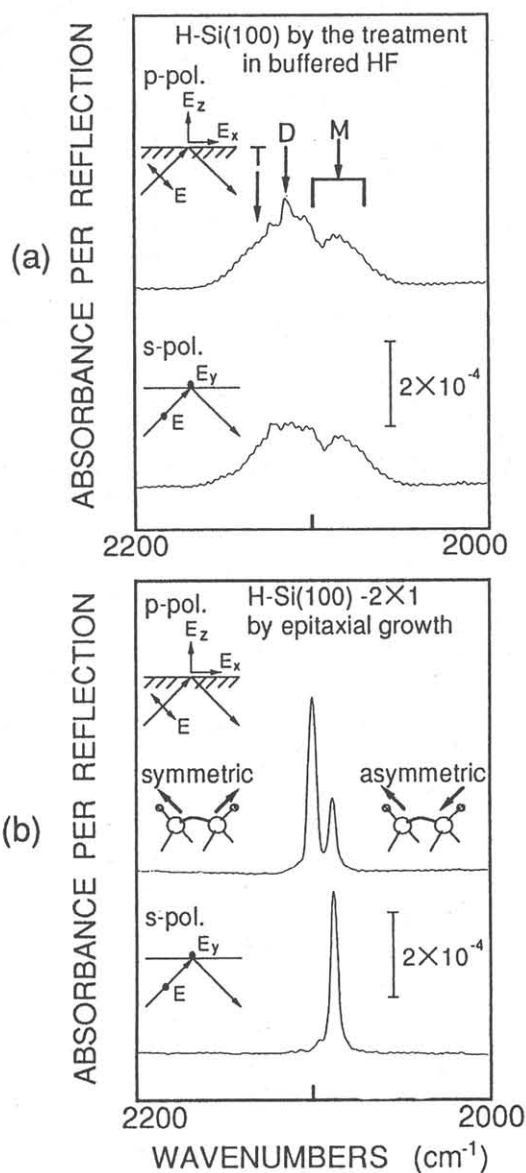


Fig. 1 Infrared absorption spectra of H-terminated Si(100) surface prepared by : (a) treatment in buffered HF; (b) epitaxial growth.

temperature in dry nitrogen with a pressure of 1 Torr. The dew points of both nitrogen and oxygen gases used in the present oxidation process are below -93°C .

3. RESULTS AND DISCUSSIONS

Fig.1(a) shows the vibrational spectra observed in the silicon-hydrogen stretching bands for H-terminated Si(100) surface, which was prepared by the treatment in buffered HF solution, measured for p- and s-polarized

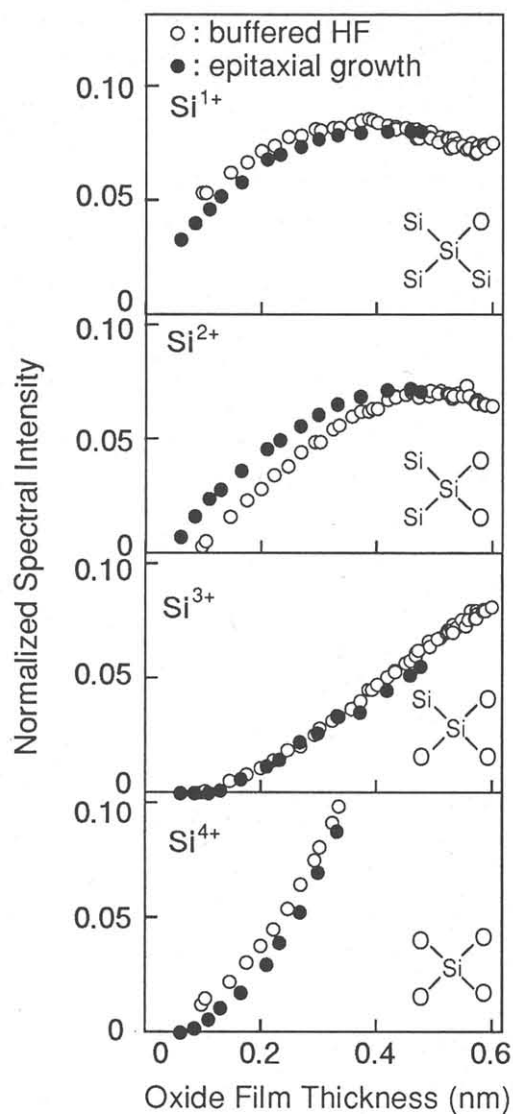


Fig. 2 Formation of suboxides and Si^{4+} during the progress of oxidation.

infrared. According to this figure, Si surface is covered with mono-, di-, and tri-hydrides. Therefore, Si surface is not atomically flat. Fig.1(b) shows the infrared absorption spectra of H-terminated Si(100)- 2×1 surface. This figure can be explained such that Si surface is covered only with pairs of monohydride, each of which is coupled with a Si dimer.⁶⁾ Therefore, Si surface in this case is atomically flat. The oxidation induced changes in chemical structures of these two surfaces were studied by measuring Si 2p photoelectron spectra and the spectral intensities of suboxides obtained from the analysis of

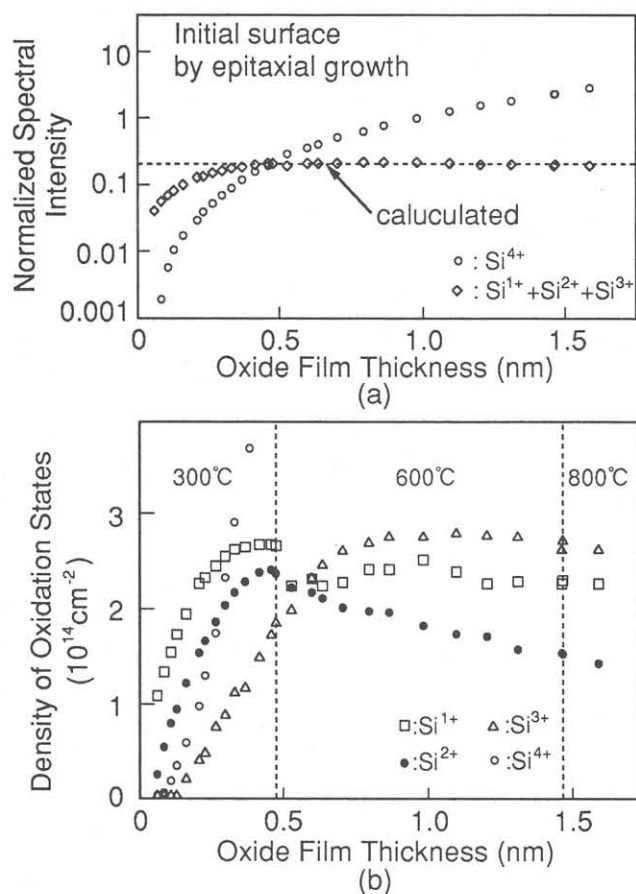


Fig. 3 Changes in interface structures with the progress of oxidation: (a) Dependence of normalized spectral intensities of Si^{4+} and summation of all suboxides on oxide film thickness; (b) Dependence of areal densities of Si^{4+} and suboxides on oxide film thickness.

these Si 2p spectra are shown in Fig.2 as a function of oxide film thickness. Here, the oxidation was performed in oxygen with a pressure of 1 Torr at 300°C. According to Fig. 2, for two kinds of initial surfaces, there is a slight difference in the amount of Si^{2+} at the early stage of oxidation, but there is no distinct difference at the final stage. This implies that an atomically flat interface consisting only of Si^{2+} can not be realized even by the oxidation of an atomically flat H-terminated surface. According to Fig.3(a), the formation of one-atomic-layer thick interfacial transition layer is completed at oxide film thickness of 0.4 nm because at this thickness total amount of suboxides saturates and coincides with that calculated for abrupt interface. Also at this thickness the

amount of Si^{1+} , Si^{2+} and Si^{3+} for two kinds of surfaces become equal with each other. Therefore, the interface structure does not depend on the initial surface morphology of two kinds of H-terminated Si(100) surfaces. By oxidizing these two kinds of surfaces further in the same oxidizing atmosphere at 600 and 800°C, Fig.3 is obtained. According to this figure, at the final stage of oxidation the contribution of Si^{2+} to the interface structure is only 25%. This implies that an atomically flat interface can not be formed even by the oxidation of an atomically flat H-terminated Si(100)- 2×1 surface. However, the composition of suboxides at the interface can be roughly explained by the existence of surface microroughness on the order of one atomic layer.

4. CONCLUSION

It is shown from the present study that an atomically flat SiO_2/Si interface can not be prepared even by the oxidation of an atomically flat H-terminated Si(100)- 2×1 surface in dry oxygen with a pressure of 1 Torr at 300°C and by the subsequent oxidation in the same oxidation atmosphere at 600 and 800°C.

REFERENCES

- 1) T. Ito : Int. Conf. Advanced Microelectronic Devices and Processing, Sendai, 1994, p.45.
- 2) M. Sakuraba, J. Murota and S. Ono: J. Appl. Phys. **75** (1994) 3701.
- 3) T. Ohmi, M. Morita, A. Teramoto, K. Makihara and K. S. Tseng : Appl. Phys. Lett. **60** (1992) 2126.
- 4) K. Ohishi and T. Hattori: Jpn. J. Appl. Phys. **33** (1994) L675.
- 5) U. Gelius, B. Wannberg, P. Baltzer, H. Fellner-Feldegg, G. Carlsson, C.-G. Johansson, J. Larsson, P. Munger, and G. Vegerfos: J. Electron Spectrosc. Relat. Phenom. **52** (1990) 327.
- 6) Y.J. Chabal and K. Raghavachari : Phys. Rev. Lett. **53** (1984) 282.