

Invited

XPS Characterization of SiO₂/Si Interfaces

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The important results necessary for the control of the SiO₂/Si interface structure in atomic scale have been obtained recently. In the present paper the structural imperfections in the ultrathin oxide, which can not be determined uniquely by XPS, in addition to the early stage of interface formation are discussed. The Si2p photoelectron spectra arising from Si-H bonds in the oxide was confirmed by FT-IR-ATR spectroscopy. The Si2p photoelectron spectra arising from Si-Si bonds in the oxide was confirmed from the measurement of reflectance in vacuum ultraviolet.

1. INTRODUCTION

In order to control the interface structure in atomic scale, it is necessary to minimize the effects of the unintentionally formed oxide and the surface microroughness on the thermally grown oxide film.¹⁾ Recently the following results important for the formation of high quality ultrathin oxide have been obtained; 1) The coexistence of oxygen and water is necessary for the formation of silicon oxide.²⁾; 2) If the silicon surface is terminated with hydrogen, the contamination free surface is obtained and the formation of native oxide can be suppressed.³⁾ The hydrogen termination can be achieved not only by the treatment⁴⁾ in dilute HF or that⁵⁾ in NH₄F, but also by the treatment⁶⁾ in boiling water; 3) one molecular oxide layer formed in dry oxygen at 300 °C is stable in ultradry argon gas even at 900 °C.⁷⁾ This seems to be quite different from the native oxide formed during wet chemical treatments. The ultrathin thermal oxide formed in dry oxygen at 900 °C through this preoxide has high electrical insulating performance.⁷⁾; 4) The microroughness of silicon surface can be maintained,⁸⁾ if the amount of NH₄OH is decreased in the cleaning solution of NH₄OH; 5) The atomically flat surface can be obtained on Si(111) by the treatment⁵⁾ in NH₄F or that⁶⁾ in boiling water.; 6) The chemical structure of the ultrathin oxide film is affected by the microroughness at silicon surface.⁹⁾

Therefore, it is important to form high quality preoxide on contamination free hydrogen terminated silicon surface. In the following XPS studies on the initial stage of oxidation on hydrogen terminated Si(111) surface at 300 °C and the structural imperfections in ultrathin oxides are discussed.

2. INITIAL STAGE OF INTERFACE FORMATION

The initial stage of SiO₂/Si interface formation on Si(111) surface were investigated¹⁰⁾ at 300 °C in dry oxygen with a pressure of 133 Pa by measuring Si2p, O1s spectrum with high surface sensitivity using ESCA-300 manufactured by Scienta Instruments AB¹¹⁾. The SiO₂/Si interfacial transition layer is formed in three steps characterized by three oxidation rates. Also, during each oxidation time intervals characterized by three oxidation rates, the ratio of O1s photoelectron spectral intensity with respect to that Si2p photoelectron spectral intensity does not exhibit smooth change. This implies that the distortion of the oxide structure is produced during each oxidation time interval by the incorporation of oxygen atoms into backbonds of silicon atoms in the topmost layer in order to relax the stress at the interface.

3. Si-H BONDS IN ULTRATHIN OXIDE

The hydrogen atom can not be identified by XPS, but can be detected indirectly through the measurement of the chemical shift in Si2p core level induced by Si-H bond. In order to identify the hydrogen atom the infrared absorption arising from Si-H bonds was measured. It was found that the native oxides formed during wet chemical treatments can be characterized by the amount of Si-H bonds in the native oxides.^{12,13)} Recently it was found that the amount of Si-H bonds in the oxide and at the interface in the native oxide formed in H₂SO₄/H₂O₂ (abbreviated in the following as H₂SO₄) solution is negligibly small.¹³⁾ By combining this fact with highly sensitive photoelectron detection by ESCA-300,¹¹⁾ it is possible to obtain a

difference of photoelectron spectrum denoted by Si^{x+} in Fig. 1(b). Here, the 40% NH_4F treated atomically flat surface, which is confirmed by the infrared absorption arising only from silicon monohydrides on Si(111) terrace as shown in Fig. 2(a), is used for the formation of native oxides. The infrared absorption arising from Si-H bonds in native oxide formed in HNO_3 measured by FT-IR-ATR is shown in Fig. 2(b) and gives almost the same amount of Si-H bonds with that determined from Fig. 1(b). Based on such assignment of Si^{x+} , it is now possible to determine the distribution of Si-H bonds in ultrathin oxide film.

Fig. 3 shows the change in Si2p photoelectron spectrum with decrease in thickness of thermally grown oxide film.¹⁴⁾ Here, 4.5 nm thick as-grown oxide film, which was formed by ultraclean oxidation method,¹⁵⁾ was chemically etched to obtain 3.6, 2.7 and 1.4 nm thick oxide films. It should be noted that Si^{x+} spectrum is not observed for 1.4 nm thick chemically etched oxide film, while Si^{x+} spectrum is observed for 1.5 nm thick as-grown oxide film grown at the same oxidation condition used for the formation of 4.5 nm thick oxide film.¹⁶⁾ Therefore, the amount of Si-H bonds near the interface is smaller for thicker oxide film formed by the ultraclean oxidation method.

4. Si-Si BONDS IN ULTRATHIN OXIDE¹⁴⁾

The solid lines in Fig. 4 show the change in the optical absorption coefficient with the decrease in oxide film thickness. Here, the oxide film used to obtain these spectra is the same as that used for the spectra in Fig. 3. The dashed lines in this figure show the optical absorption coefficient of fused quartz. According to the analysis of Fig. 4, it can be shown that the optical absorption below the fundamental absorption edge of fused quartz arises from structural imperfections in the oxide film within 1.4 nm of the interface. The optical absorption at 7.8 eV can be ascribed to that arising from the Si-Si bond in the oxide film. The amount of this Si-Si bonds in the oxide roughly agrees with that of Si^{3+} estimated from Fig. 3. The optical absorption at 6.5 and 8.8 eV may be ascribed to that arising from the Si-Si-Si and Si-O-O-Si, respectively.

5. SUMMARY AND FUTURE PROBLEMS

The cleaning without destroying the flatness, the suppression of native oxide formation, and the formation of high quality preoxide at 300°C have been developed and useful for the control of the interface structure in atomic scale. It is then necessary to investigate the structural imperfections introduced during the interface formation in dry oxygen at 300°C. The structural imperfections in ultrathin oxide have been studied in the case of the native oxide formed during wet chemical treatments, which were found to be characterized by the amount of Si-H bonds in the native oxides. It is shown that the Si-O bonds, the

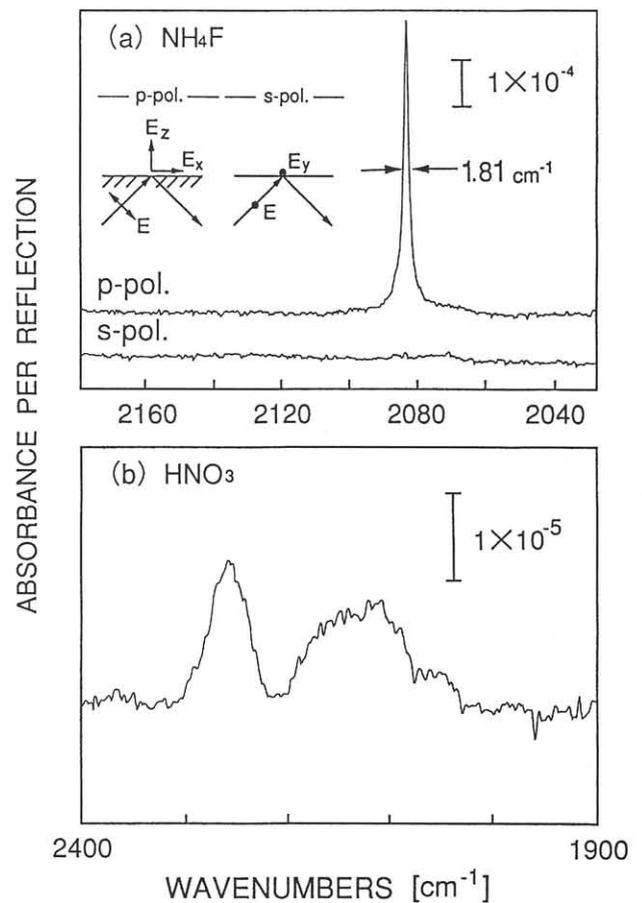


Fig. 1 infrared absorption spectra for (a) NH_4F treated Si(111) surfaces; (b) native oxide formed in HNO_3 .

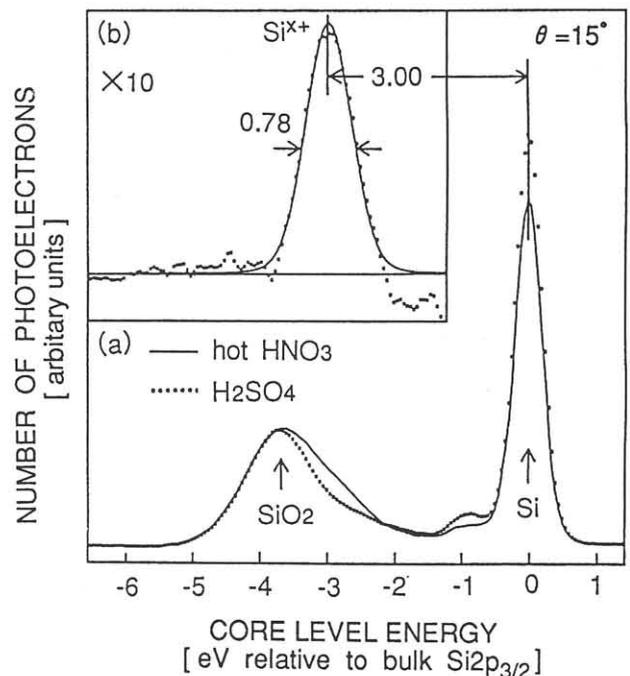


Fig. 2 (a) $\text{Si}2p_{3/2}$ photoelectron spectra for two kinds of native oxides; (b) difference of two spectra in Fig. 2 (a).

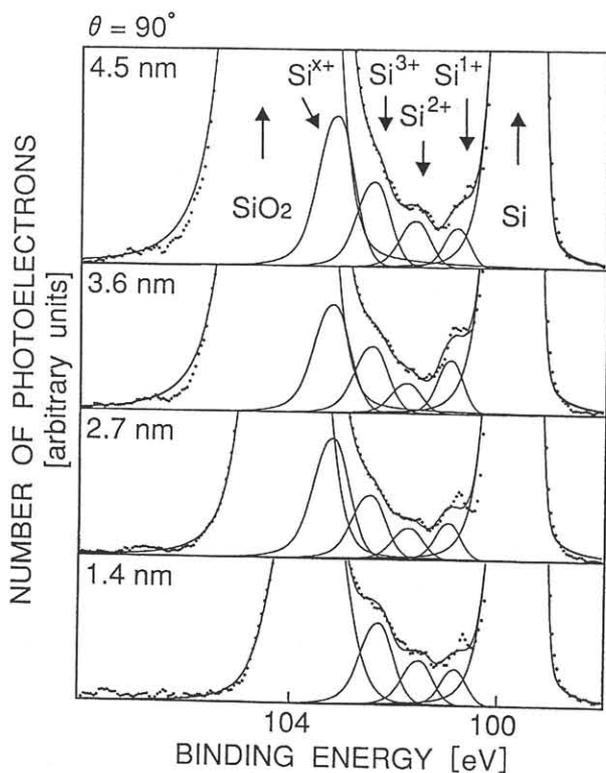


Fig. 3 Change in $\text{Si}2p_{3/2}$ photoelectron spectrum with decrease in thickness of 4.5 nm thick thermal oxide.

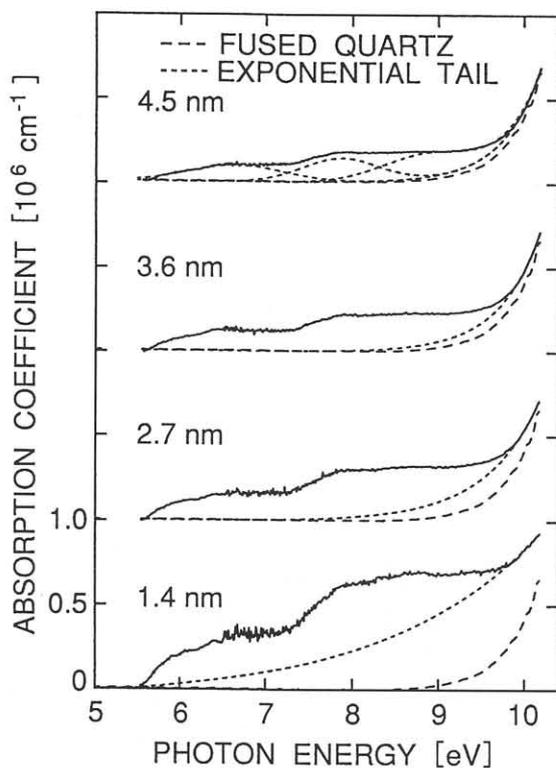


Fig. 4 Change in optical absorption coefficient with decrease in thickness of 4.5 nm thick thermal oxide.

various bonding configurations of which can not be resolved by XPS, seems to be resolved by the reflectance study in the vacuum ultraviolet. The method of stabilizing interface structure,¹⁵ that of controlling structure of oxide, that of measuring chemical structures of silicon surface at atmospheric pressure must be the important subject in the near future. Also the mechanism of SiO_2/Si interface formation in early stage and the surface morphology necessary for the formation of high quality oxide should be clarified in the near future.

REFERENCES

- 1) T. Ohmi: Extended Abstracts of Intren. Symposium on Semiconductor Manufacturing Technology, Tokyo, 1992, p. 3.
- 2) M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and M. Ohwada: J. Appl. Phys. 68 (1990) 1272.
- 3) T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda, and Y. Nagasawa: J. Appl. Phys. 64 (1989) 3516.
- 4) T. Yasaka, K. Kanda, K. Sawara, S. Miyazaki, and M. Hirose: Extended Abstracts of 1991 Intern. Conf. on Solid State Devices and Materials (1991, Yokohama) p.487.
- 5) G. S. Higashi, R. S. Gecker, Y. J. Chabal, and A. J. Becker: Appl. Phys. Lett. 58 (1991) 1656.
- 6) S. Watanabe, M. Shigeno, N. Nakayama, and T. Ito: Jpn. J. Appl. Phys. 30 (1991) 3575.
- 7) T. Ohmi, M. Morita, A. Teramoto, K. Makihara, and M. Ohwada: J. Appl. Phys. Lett. 60 (1992) 2126.
- 8) T. Ohmi, M. Miyashita, M. Itano, T. Imaoka, and I. Kawanabe: IEEE Trans. Electron Devices 39 (1992) 537.
- 9) F. J. Himpsel, D. A. Lapiano-Smith, J. F. Morar, and J. Bevk: Extended Abstracts, Spring Meeting of Electrochem. Soc., St. Louis, 1992, p. 386.
- 10) T. Hattori, H. Nohira, Y. Tamura, and H. Ogawa: Jpn. J. Appl. Phys. 31 (1992) L 638.
- 11) U. Gelius, B. Wannberg, P. Baltzer, H. Fellner-Feldegg, G. Carlsson, C.-G. Johansson, J. Larsson, P. Munger and G. Vegerfors: J. Electron Spectrosc. Relat. Phenom. 52 (1990) 747.
- 12) K. Sugiyama, T. Igarashi, K. Moriki, Y. Nagasawa, T. Aoyama, R. Sugino, T. Ito, and T. Hattori: Jpn. J. Appl. Phys. 29 (1990) L 2401.
- 13) H. Ogawa and T. Hattori: to be published in Appl. Phys. Lett. Vol.61, No. 3 (1992).
- 14) N. Terada, T. Haga, N. Miyata, K. Moriki, M. Fujisawa, M. Morita, T. Ohmi, and T. Hattori: to be published in Phys. Rev. B46 (1992).
- 15) M. Morita, T. Ohmi, and E. Hasegawa: Solid State-Electronics 33, suppl. (1990) 143.
- 16) C. Heimlich, M. Kubota, Y. Murata, T. Hattori, M. Morita, and T. Ohmi: Vacuum 41 (1990) 793.