Initial Stage of SiO₂/Si Interface Formation on Si(111) Surface

Yoshinari TAMURA, Kazuaki OHISHI, Hiroshi NOHIRA, and Takeo HATTORI

Department of Electrical and Electronic Engineering, Musashi Institute of Technology 1-28-1 Tamazutsumi, Setagaya-ku, Tokyo 158

The initial stages of SiO₂/Si interface formation on n-type and p-type Si(111) surfaces treated with 40% NH₄F were investigated at 300 °C in dry oxygen with a pressure of 133 Pa. It was found that the larger oxidation rate is obtained for p-type Si and the SiO₂/Si interface formed on n-type Si(111) is close to atomically flat.

1. INTRODUCTION

In order to control the interface structure in atomic scale, it is necessary to minimize the formation of unintentionaly formed oxide and surface microroughness.1) An atomically flat and clean silicon surface can be obtained by a treatment in NH₄F.^{2,3)} It was found from the preliminary studies on the initial stage of oxidation of p-type Si(111) that the interface is formed in three steps characterized by three different oxidation rates.⁴⁾ However, because the amount of contamination remaining on the silicon surface was not negligible, the early state of oxidation was not observed. In the present study the experimental setup was improved to decrease contamination on silicon surface extremely. Also, it is a question that the previous results are reproduced on n-type Si(111) surface. It is therefore the purpose of the present paper to study the initial stage of SiO,/Si inetrface formation on contamination free n- and p-type Si(111) surfaces at 300 °C in dry oxygen with a pressure of 133 Pa.

2. EXPERIMENTAL DETAILS

After removing 200-nm-thick thermal oxide films formed on 2-6 Ω cm n-type and 10-20 Ω cm p-type Si(111) surfaces in buffered hydrofluoric acid, native oxides were formed in HCl-H₂O₂-H₂O solution at 80 °C. By the treatment in 40 % NH_4F followed by a rinse in deionized water, atomically flat H-terminated Si(111) surfaces, which were confirmed by Fourier transformed infrared attenuated total reflection spectroscopy, were obtained. A Si2p photoelectron spectrum measured for these surfaces are bottom spectra in Figs. 1 and 2. A part of the silicon surface, whose area is 20 mm in diameter and the central part of which was used for XPS study, was heated by light guided by a quartz rod.

The initial stages of oxidation were performed by measuring Si2p photoelectron spectra at room temperature after each of the following treatments. By heating the sample in 133 Pa dry nitrogen at 300°C for 20 minutes, the bottom spectra in Figs. 1 and 2 change into the spectra next to the bottom in these figures. Other spectra are obtained after every two minutesheating of sample in 133 Pa dry oxygen at 300 °C. Fig. 3 shows the same kind of spectra obtained for long oxidation time intervals on n-type Si(111). The dew points of nitrogen and oxygen gas are below -93 °C and -85 °C, respectively. The structural change at the initial stage of oxidation is investigated by measuring Si2p and O1s photoelectron spectra with an acceptance angle of 3.3 degrees using an ESCA-300 manufactured by Scienta instruments AB.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

According to Figs. 1 and 2, the initial oxidation rate of p-type Si is larger than that of n-type Si. The amount of suboxide on p-type Si is larger than that on n-type Si at the same oxide film thickness. In other words, the oxide film on p-type Si is more smooth than that on ntype Si. In the following the initial stage of oxidation of n-Si(111) surface is described in details.

Figure 3 shows oxidation-induced changes in Si2p photoelectron spectra measured at a photoelectron takeoff angle of 15 degrees with oxidation time as a parameter. Figure 4 shows the oxide film thickness as a function of oxidation time determined from the analysis of Fig. 3. Here, electron escape depth in the silicon substrate and that in silicon dioxide is 2.7 nm and 3.4 nm, respectively.⁶)

The intermediate spectral intensity normalized by the intensity arising from silicon substrate and silicon monohydrides is shown in Fig. 4 as a function of oxidation time. This normalized intensity almost saturates at the oxidation time of 110 min. This saturated value of 0.23 in Fig. 4 is in good agreement with the calculated value of 0.23 as described in the following. The value of (NI/NS), for intermediate states at the interface can be approximately expressed as $N_i/(n_s \Lambda_s \sin 15^\circ)$. Here, N_i is average areal density of interface atoms, n_s is density of silicon atoms in silicon substrate and Λ_s is electron escape depth in silicon substrate. Here, it is assumed that inelastic scattering in the interfacial layer is negligible. Therefore, the formation of an interfacial transition layer may be completed at the oxidation time of 110 min.

Figure 5 shows the Si¹⁺, Si^{y+}, Si²⁺, Si³⁺ and Si⁴⁺ spectral intensity normalized by the intensity arising from silicon substrate and silicon monohydrides as a function of oxidation time. Si^{y+} spectrum may be correlated with hydrogen-related intermediate states.^{5,6)} The chemical shifts of other intermediate states are assumed to have the same values as those determined previously.⁷⁾ According to this figure, the normalized spectral intensity of intermediate states Si^{y+}, Si¹⁺, Si²⁺ and Si³⁺ saturates in this order.



Fig. 1 Si2p photoelectron spectra measured at initial stage of oxidation of NH_4F treated p-Si(111).



Fig. 2 Si2p photoelectron spectra measured at initial stage of oxidation of NH_4F treated n-Si(111).



Fig. 3 Si2p photoelectron spectra measrued at initial stage of oxidation of NH_4F treated n-Si(111) measured after heating in 133 Pa in dry N₂ at 300°C; spectra denoted by c, d, e, f, g and h are measured at the oxidation time of 2, 30, 60, 90, 120 and 150min.



Fig. 4 Oxide film thickness and normalized spectral intensity of oxidation-induced intermediate states as a function of oxidation time.



Fig. 5 Si¹⁺, Si^{y+}, Si²⁺, Si³⁺ and Si⁴⁺ spectral intensity normalized by spectral intensity arising from silicon substrate and silicon monohydrides as a function of oxidation time.

4. SUMMARY

The initial stages of SiO₂/Si interface formation on NH₄F treated n-type and p-type Si(111) surfaces were investigated at 300 °C in dry oxygen with a pressure of 133 Pa. The initial oxidation rate of p-type Si is larger than that of n-type Si. When the amount of suboxides saturate at the oxidation time of 110 min. to complete the interfacial region, the sum of the spectral intensities of Si¹⁺ and Si³⁺ normalized by the spectral intensity arising from silicon substrate and silicon monohydrides reaches 0.17 and at this stage contributes to the interface structure by 72%. This implies that the interface formed on n-Si(111) is close to atomically flat.

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REFERENCES

- T. Ohmi, M. Morita, A. Teramoto, K. Makihara, and K. S. Tseng: Appl. Phys. Lett. 60 (1992)2126.
- G. S. Higashi, R. S. Becker, Y. J. Chabal, and
 A. J. Becker: Appl. Phys. Lett. 58, 1656 (1991).
- T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda, and Y. Nagasawa: J. Appl. Phys. 64, 3516 (1988).
- T. Hattori, H. Nohira, Y. Tamura, and H. Ogawa: Jpn. J. Appl. Phys. 31 (1992) L638.
- Y. Nagasawa, H. Ishida, T. Takahagi, A. Ishitani, and H. Kuroda: Solid-State Electronics 33, Supplement (1990)129.
- N. Terada, H. Ogawa, K. Motiki, A. Teramoto, K. Makihaara, M. Moriki, T. Ohmi, and T. Hattori: J. Appl. Phys. 30, 3584 (1991).
- F. J. Himpsel, F. R. McFeely, A. Talev-Ibrahimi,
 J. A. Yarmoff, and G. Hollinger: Phys. Rev. B38, 6084 (1988).