

Silicon-Hydrogen Bonds in Native Oxides Formed during Wet Chemical Treatments

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The existence of Si-H bonds in native oxides were confirmed from the measurement of highly resolved Si 2p photoelectron spectra and Fourier transformed infrared attenuated total reflection. The amount of Si-H bond in native oxides formed in a hot solution of HNO₃ is much larger than that formed in native oxides formed in a mixed solution of NH₄OH and H₂O₂. The amount of Si-H bond in native oxides formed in a hot solution of HNO₃ is evaluated to be $2.7 \times 10^{14} \text{ cm}^{-2}$.

1. Introduction

Experimental technology and performance of 0.1 μm gate-length low temperature operation MOSFETs was reported in the preceding conference¹⁾, where the thickness of gate oxide film was 3.3 nm. In order to form such gate oxide with reliable quality, it is necessary to control the initial stage of oxidation in atomic scale. Then, the silicon surface must be cleaned before the oxidation and is usually cleaned by the wet chemical treatments. However, thin native oxides are formed during the wet chemical treatments. Therefore, it is necessary to clarify the chemical structures of such native oxides.

The chemical structures of such native oxides were studied from the measurements of Si 2p photoelectron spectra²⁾. Also, the structural stabilities of such native oxides were studied from the measurement of thermal desorption of SiO from native oxides. Following understandings were obtained from the measurement of Si 2p photoelectron spectra: Firstly, the distribution of Si³⁺ in

the native oxide depends on the wet chemical treatments²⁾. Later, Si³⁺ was found to be separated into Si³⁺ and Si^{x+}³⁾. Secondly, the amount of Si^{x+} in the native oxide formed in a hot solution of HNO₃ is much larger than that in a mixed solution of NH₄OH and H₂O₂³⁾. Thirdly, Si^{x+} was tentatively correlated with Si-H bond based on the concept of local electronegativity³⁾. However, because of the excess noise in the Si 2p photoelectron spectra, the appreciable errors must be included in the evaluation of chemical shift and intensity of Si^{x+} spectrum.

It is the purpose of the present paper to confirm the existence of Si^{x+} spectrum from the measurement of highly resolved Si 2p photoelectron spectra and to correlate Si^{x+} with Si-H bond from the measurement of infrared absorption spectra.

2. Experimental Details

The native oxides studied were formed as follows: After treatment of a 3 ~ 5 Ωcm n-type (100) oriented silicon wafer in a hot solution of NH₄OH and H₂O₂ for 5 minutes

followed by cleaning in deionized water for 10 minutes, treatment in a 3% HF solution for 1 minute was performed, followed by cleaning in deionized water for 10 minutes. Next, treatment in a solution of HNO_3 maintained at $45\sim 60^\circ\text{C}$ for 5 minutes or treatment in a solution with composition $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1.4 : 4$ maintained at $63\sim 80^\circ\text{C}$ for 10 minutes were performed. These were followed by 10 minutes of cleaning in deionized water. Finally, the specimens were dried in a hot nitrogen atmosphere.

The chemical structures of the native oxides were investigated from nondestructive measurements of highly resolved Si 2p photoelectron spectra using Surface Science Instruments SSX-100. The infrared absorption spectra were measured using a Bruker IFS-113V vacuum type Fourier transform infrared spectrometer equipped with a Model-9 ATR attachment manufactured by Wilks Co. The

specimens used in ATR study were (100) n-type Si wafers (10 ohm-cm) with optically polished faces covered with native oxides. The wafers were cut in trapezoidal shape with 52.5 mm in length, 20 mm in width and 0.5 mm in thickness. The angle of incidence was 45 degrees, which resulted in about 100 internal reflections. Other experimental details are the same as those described previously⁴⁾.

3. Results and Discussion

Fig. 1 shows the Si 2p photoelectron spectra measured for two typical native oxides. These spectra were measured for the take off angle of 90 degrees and the spin-orbit doublet was removed. In this figure the deconvoluted spectra are also shown. Here, the chemical shifts of suboxides Si^{1+} and Si^{3+} determined for 0.5 nm thick thermal oxides⁵⁾ and the chemical shifts of Si^{2+} and Si^{4+} determined from the present study were used. It was found from such deconvolution that unknown spectrum expressed by Si^{x+} is included in the observed spectrum. If the chemical shift was calculated based on the concept of local electronegativity developed by Lucovsky^{6,7)}, the observed chemical shift of Si^{x+} is quite close to the calculated chemical shift of 3.26 eV for Si-H bond in silicon dioxide. Therefore, Si^{x+} can be correlated with Si-H bond in SiO_2 network. Here, the calculated chemical shift of Si^{2+} and Si^{3+} localized at the SiO_2/Si interface is 1.87 and 2.61 eV, respectively and is quite close to the observed chemical shift⁵⁾ of 1.75 and 2.48 eV, respectively.

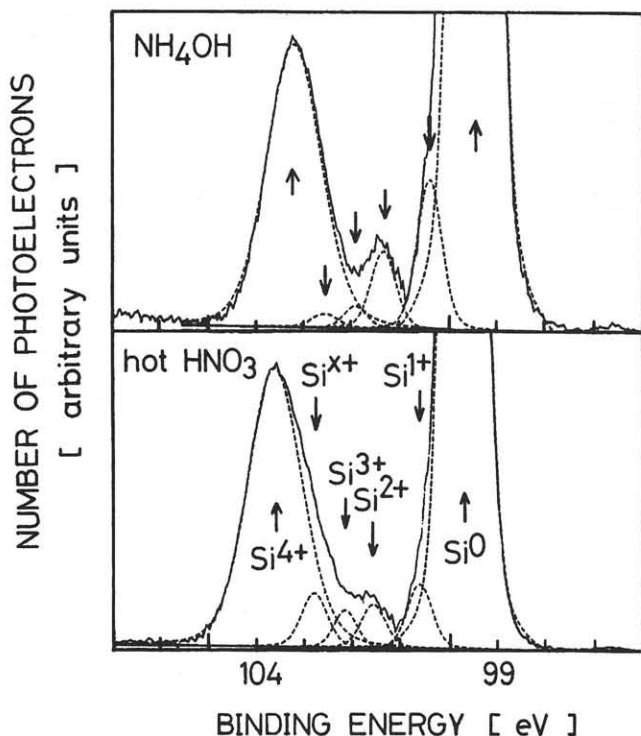


Fig. 1 Si 2p photoelectron spectra and their deconvoluted spectra for native oxides formed in a hot solution of HNO_3 and in a mixed solution of NH_4OH and H_2O_2 .

In order to find out the distribution of Si^{x+} in the oxide film formed in a hot solution of HNO_3 , photoelectron spectra for three take off angles shown in Fig. 2 were measured. In this figure the deconvoluted spectra are also shown. Because it can be

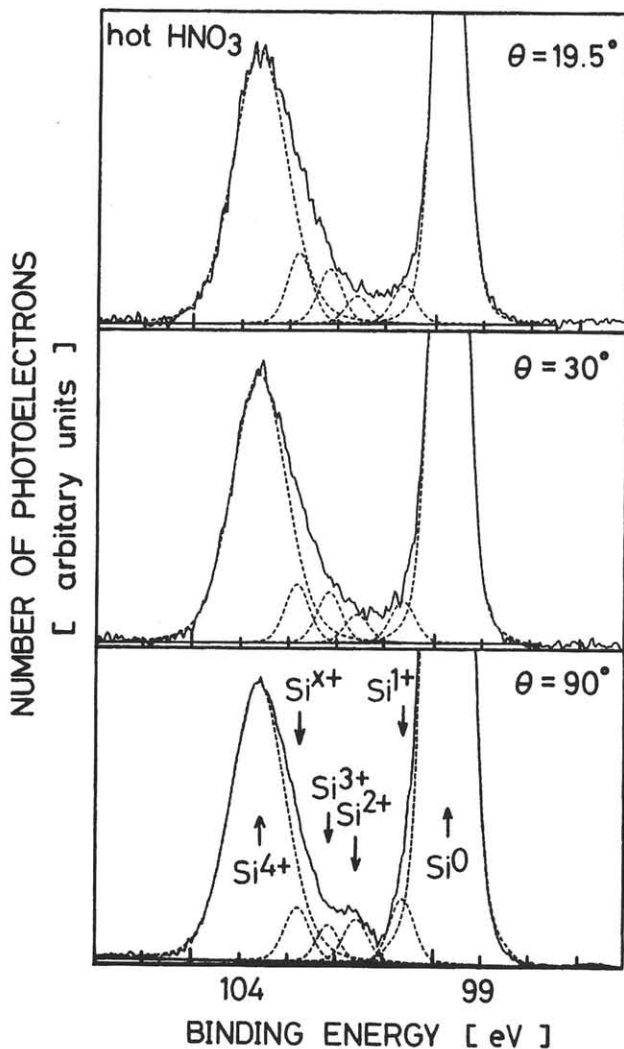


Fig. 2 Si 2p photoelectron spectra and their deconvoluted spectra for three take off angles for native oxide formed in a hot solution of HNO_3 .

seen from this figure that the ratio (NI/NO), that is, Si^{X+} spectral intensity normalized by Si^{4+} spectral intensity, is almost the same for three take off angles, the amount of Si^{X+} must be distributed almost uniformly in the native oxide. Considering that (NI/NO) is 0.092 for 90 degrees take off angle, thickness of one monolayer-silicon dioxide is 0.29 nm and thickness of native oxide measured in terms of silicon dioxide film thickness is 1.3 nm, a value of $2.7 \times 10^{14} \text{ cm}^{-2}$ is obtained for the amount of Si-H bond. This amount is much larger than the amount

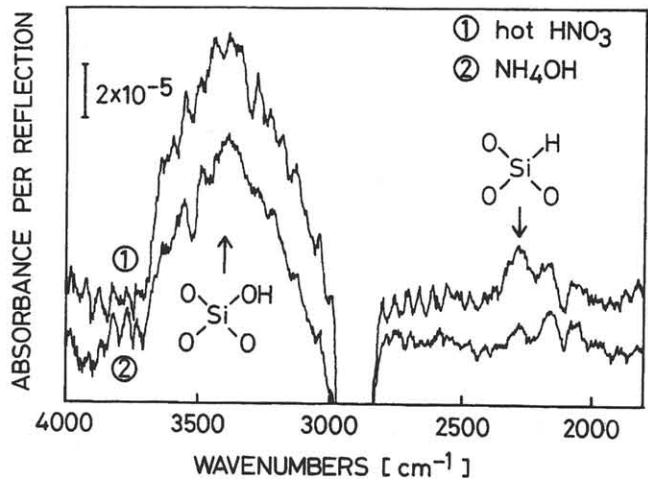


Fig. 3 Infrared absorption spectra of native oxides formed in a hot solution of HNO_3 and in a mixed solution of NH_4OH and H_2O_2 .

of Si-H bond in native oxide formed in a mixed solution of NH_4OH and H_2O_2 as can be seen in Fig. 1.

Fig. 3 shows the infrared absorption spectra for two typical native oxides. Infrared absorption at 2280 cm^{-1} can be correlated with Si-H bonds in silicon dioxide⁸⁾. The amount of Si-H bond in native oxide formed in a hot solution of HNO_3 is much larger than that formed in a mixed solution of NH_4OH and H_2O_2 . This result is the same as that obtained from the measurement of Si 2p photoelectron spectra. Considering that for native oxide formed in a hot solution of HNO_3 absorbance per reflection at 2280 cm^{-1} is 2.6×10^{-5} with FWHM of 120 cm^{-1} , a value of $2.7 \times 10^{14} \text{ cm}^{-2}$ is obtained for the amount of Si-H bond in silicon dioxide and is in excellent agreement with that evaluated from Si 2p photoelectron spectra. Therefore, there is one to one correspondence between Si^{X+} and Si-H bond. Details in the evaluation of the amount of Si-H bond will be published elsewhere⁹⁾.

4. Conclusion

Chemical structures of native oxides were investigated from the measurement of highly resolved Si 2p photoelectron spectra and infrared absorption spectra. The existence of Si^{x+} spectra are confirmed and can be correlated with Si-H bond in silicon dioxide. The amount of this Si-H bond in native oxide formed in a hot solution of HNO₃ is $2.7 \times 10^{14} \text{ cm}^{-2}$, and is much larger than that in native oxide formed in a mixed solution of NH₄OH and H₂O₂.

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