Observation of Solution/Si Interface Using IR Spectrochemical Cell During Wet Chemical Oxidation

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We investigated the early stage oxidation of hydrogen terminated Si(100) and (111) surface in solution using *in situ* infrared internal reflection spectroscopy (IR ATR) and the conventional IR transmission spectroscopy. *In situ* observation reveals that oxidation starts with the insertion reaction of oxygen atoms to the back bonds of the top most silicon atoms. We presented a model of the dependence of this oxygen reaction on surface orientation. We also suggested relationship between the redox potential of an oxidizing solution and oxidation including island-growth of oxide. Our model were confirmed by the results of IR experiments, demonstrated a faster oxidation process on (100) than on (111), and island-growth of oxide in surfaces of both orientation.

Introduction

The existence of any oxide on Si wafer surface degrades the electrical properties of the substrate, when low resistance metal contact and high dielectric constant capacitor are formed on the surface. In device fabrication, HF acid is widely used to produce oxide-free H-terminated Si surfaces.¹) However, it is well known that the treated surface may be oxidized during the subsequent rinse in water containing dissolved oxygen²). It is widely accepted, based on the experimental evidence obtained by *ex situ* techniques, that oxidation of H-terminated Si surface begins with oxygen attachment to the back bond of surface Si atoms when the oxidation occur in water containing dissolved oxygen and when in dry oxygen atomosphere.²⁻⁷)

In surface cleaning process, oxidant such as H_2O_2 and O_3 are intentionally added to the cleaning solution to oxidize the surface previously treated in HF acid. Little of the oxidation chemistry is known about such solution where the redox-potential is large. In the present study, we investigated surface oxidation in H_2O_2 solution and ozonized water both are nearly neutral but differ from each other in redox potential. The progress of oxidation and the consumption of the Si-hydrides structure were monitored using both *in situ* and *ex situ* infrared spectroscopies.⁸) We experimented with two types of surfaces, (100) and (111), to examined the relationship between oxidation reaction and the surface structure.⁹) The effect of solution redox potential on oxidation, and the aspect of the oxide growth are also discussed in this paper.

Experiments

We examined the surfaces using an FT-IR-ATR spectrometer with a specially designed chemical cell, as shown in Figure 1.⁸) We used both (100) and (111) samples cut from both-side-polished wafers. After mounting a precleaned sample in the chemical cell, we introduced 0.5% HF solution to the cell. The surface oxide was then removed and the surface Si bonds were terminated with hydrogen atoms. Then, we introduced an oxidizing solution for a certain duration. To allow sufficient time for the spectrum accumulation (10 min/1000 times typically), we exchanged the oxidizing solution with water to stop the oxidation reaction. This procedure was repeatly doen. We used a 3% H_2O_2 solution (pH 5.5, NHE. +0.5~0.7 V) and a 2 ppm ozonized water (pH 6-7, NHE. +1.0~1.2 V) as the oxidizing solutions.

Ex situ infrared spectroscopic analysis were performed using a incidence angle of 70° under p-polarized and spolarized conditions. Both LO and TO phonons from Si-O-Si asymmetric stretching were observed, as predicted by Berreman.¹⁰)



Fig. 1 Schematic of a spectrochemical cell for IR-ATR. The cell was made of poly-tetra-fuloro-ethylene (PTFE) that is resistant to HF solution. Si ATR prism was assembled with O-ring seal. The ATR prism was $53x53 \text{ mm}^2$ in size and the cell volume was 15 cm^3 . The IR beam incidence angle used was 45° . The typical solution flow rate was 100 cc/min.



Fig. 2 P-polarized ATR spectra of Si-H stretching on Si(100) surface in solution. The reference was Si(100) with the native oxide formed in a boiling H_2SO_4 / H_2O_2 solution. The native oxide was then removed using 0.5% HF then oxidized using 3% H_2O_2 . De-ionized water was introduced during the spectra recording.

Results

Figure 2 and Figure 3 show oxidation of (100) and (111) surfaces in H2O2 solution. While the Si-H stretching frequencies in Figs. 2 and 3 were almost the same at observed by ex situ analysis, the peaks are broader as was already explained in terms of the interaction of SiH with water.8) It can be clearly seen from these figures that the increase of O_xSi_vH_z (x=1-3, x+y+z=4) structures were accompanied by decrease of SiHz (z=1-3) structure.11) In the (100) surface, the O₃SiH structure was the dominant structure even at very early stage of the oxidation process (less than 0.5 mono-layer), indicating that the O₂SiH_z (z=1-2) and the OSiH_z (z=1-3) structures were unstable. In contrast, these were clearly observable in the (111) surface, as shown in Fig. 3. The same observation was made when H2O2 was replace with ozonized water, demonstrating that the instability of O₂SiH_z (z=1,2) and OSiH_z (z=1-3) in (100) and the stability of the same structures in (111) is independent of the redox potential of the oxidizing solution.

Fig. 3 P-polarized ATR spectra of Si-H stretching in Si(111) surface in solution. The reference was Si(111) with the native oxide formed in a boiling H_2SO_4/H_2O_2 solution. The native oxide was then removed using 0.5% HF then oxidized using 3% H_2O_2 . De-ionized water was introduced during the spectra recording.

When we consider charge transfer from the back bonds to the chemisorbed oxygen, it may be generally said that oxidation of one back bond weakens the other back bonds. In the case of (111) surface, however, attachment of oxygen to the back bond requires displacement of the top most Si atoms, making the remaining two back bonds stressed as a result. This increases the reaction potential. With (100) surface, the effect is expected to be less significant because oxidation of one back bond requires displacement of top most Si atom, making only one back bond stressed. We think that such stress basically originates from the anisotropy of atomic density in the [111] direction and that this interrupts subsequent oxygen attachment to the back bonds in the (111) surface. This model may explain our result where the back bond oxidation rate in the (100) surface is higher than in the (111) surface.

When ozonized water is used, all Si-hydrides structures disappeared from both the (100) and the (111) surfaces after only a few minute of oxidation. In contrast, a part of O_3SiH and SiH_z structures remained stable in 3% H₂O₂ solution



Fig. 4 Dependence of peak intensity on time measured with *ex situ* IR transmission. The vertical axis is the measured peak intensity of LO Si-O-Si asymmetric stretching phonon with P-polarization.



Fig. 5 IR spectra obtained by glancing incidence transmission with P-polarization. The incidence angle was 70°. The reference was hydrogen terminated Si(100) treated with an HF solution.

even after long term oxidation. It can be said that the stability of Si-hydrides depends on the redox potential of the oxidizing solution. This is consistent with the report that the residual Si-hydrides in native-oxide decreases with the redox potential of the cleaning solution.^{12,13}

Figure 4 shows the dependence of oxide growth on time derived from the intensity of LO peaks. The detection of Si-O stretching bring us the information of the oxygen insertion reaction even at second top and more deeper layers. Oxide growth rates in (100) surface was higher than in (111) surfaces for both oxidizing solutions. The stress interruption mentioned above is supported for oxide growth in a rather thick region. Figure 5 shows p-polarized transmission spectra obtained from (100) surfaces which were oxidized in ozonized water. LO-TO splitting were reinforced with the progress of oxide growth. This is observed in both the (100) and (111) surfaces even when we tested using H_2O_2 . The results suggested that the oxide formed rather island-like based on the observed peak separation¹⁰).

The relatively long time existence of SiH_z (z=1-3), seen in Figure 2 and Figure 3, also implies the island-like oxide growth, because the existence of SiH_z is evident of the existence of un-oxidized area on the surface. All our results **1000** indicate that oxide growth in the oxidizing solutions is imhomogenious and stop when the oxide thickness reaches the diffusion limit of the oxidant.

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