FT-IR-RAS Analysis of Native Oxide Grown on Si(111)

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Native oxide growth on an atomically flat Si(111) surface formed in pure water was observed by Fourier-Transform Infrared Reflection Absorption Spectroscopy (FT-IR-RAS). The shape of the LO phonon peak of the native oxide grown in pure water is different from that of an oxide layer grown in HNO₃ solution independently of oxidation time. The shape and behaviour of the LO phonon peak for the oxide grown in the pure water correspond to that calculated assuming the oxide was insular. This means that the native oxide did not grow layer-by-layer.

1. Introduction

Determination of the structure and clarification of the growth process of a native oxide are very important to understand the mechanism of oxidation and to develop new semiconductor process technologies. Through the observation of the early stage of native oxidation with XPS, a theory that the oxide grew layer by layer was advocated¹). However, XPS shows us the number of oxygen connecting with Si and the chemical state of Si in the oxide etc., but does not tell us the shape of oxide. Thus we examined the shape of the native oxide grown on a atomically flat Si(111) surface in pure water by Fourier-Transform Infrared Reflection Absorption Spectroscopy (FT-IR-RAS).

2. Experimental

A both sides polished FZ-Si(111) wafer (P type 80-120 cm, off angle 0°) which a surface flattened atomically by treatment in NH_4F solution²) was oxidized in pure water (dissolved oxygen concentration about 8ppm) at room temperature. We observed the change in native oxide structure with

oxidation time by FT-IR-RAS (incident angle: 80°, P-polarized, resolution: 8cm⁻¹).

3. Results and Discussion

Figures 1 and 2 show FT-IR-RAS spectra of the native oxide on a Si(111) surface. Two peaks are observed on every RAS spectra of longer than 440min oxidized wafers. The broad peak at about 1170cm⁻¹ was assigned to LO phonon polariton (LO phonon) and another at about 1080cm⁻¹ was assigned to TO phonon polariton (TO phonon). The TO phonon peak was detected at the usual wave numbers. However, the LO phonon peak shifted from about 1110cm⁻¹ to 1170cm⁻¹ at 320min to 860min. After 860min oxidation, the position of the LO phonon peak was constant. Fig. 3 is the IR-RAS spectra of a native oxide of a Si(111) surface grown in a HNO3 solution. The shape of this spectra was very similar to that of thermally grown oxide films (Fig.4) and the area of peaks in this spectra was almost the same as that of the 19165min oxidation spectra in Fig. 2. (The peak are is proportional to the number of resonance oscillators even in the RAS spectra when the oxide thickness is very thin.)

However, the shape of the spectra and the position of the LO phonon peak in Fig. 3 was different from that in Fig. 2.

To clarify the above difference of the LO phonon peak position and shape, we calculated the IR-RAS spectra assuming that native oxide was growing insularly in the water. If the native oxide is insular, the surroundings of the oxide island on the Si surface is similar to the oxide precipitation in the Si bulk. A calculation method of IR transmission spectra of the oxide precipitation in the Si bulk has been reported³). In the calculation, an insular oxide particle at the Si surface is approximated by a small ellipsoid with axes a_1 , a_2 , a_3 . Since the direction of the electric field of the P-polarized light is perpendicular in our case, a_1 is parallel to the electric field. Then the tensor of polarization of the oxide becomes a scalar (g):

 $g = \epsilon_m / [L_1 \epsilon_p + (1 - L_1) \epsilon_m].$ (1)

L is the depolarization factor.

 $L_1+L_2+L_3=1$, $L_1:L_2:L_3=1/a_1:1/a_2:1/a_3$ ε_m and ε_p are the complex dielectric constants of Si and SiO₂. The oxide has the shape of needle sticking perpendicularly to the Si surface at L=0 and becomes a layer at L=1. The dielectric constant of the surface layer containing the oxide particles was cal-

electric constant. $\epsilon_{av}=1+\{(1-f)(\epsilon_m-1)+f(\epsilon_p-1)g\}/\{(1-f)+fg\}$ (2) "f" is the volume fraction of the insular oxide in the

culated from the continuum theory of average di-

matrix. In the actual calculation, ε_p was calculated from the Drude model⁴). The we used oscillator mode numbers of quartz glass as those of the native oxide⁵). This was because, we assumed that ε_p was isotropic. Though TO phonon peak in the IR-RAS spectra calculated from Drude model using the oscillator numbers of the quartz glass is much higher than that of the real measured spectra, LO phonon peak in Drude model spectra is almost the same as that in the measured spectra (Fig. 4). Thus Drude model is enough to examine the shape of LO pho-

non peak. The IR-RAS spectra was calculated us-

ing Fresnel formula⁶⁾. Fig. 5 shows the results of

calculation. In Fig. 5, the LO phonon peak shift from 1130 to 1250cm⁻¹ with the change in oxide shape and the LO phonon peak of a layered native oxide (L=1) has a similar shape to the LO phonon peak of the native oxide grown in HNO₃ and thermally grown oxide. Moreover, the shape of the LO phonon peak of the native oxide grown in water is similar to that of calculated spectra at L=0.9. This shows that the native oxide grows insularly on the Si(111) surface in pure water.

REFERENCES

- 1) M.Hirose, Oyo Butsuri, 61, 1124 (1992), in Japanese.
- P.Dumas, Y.Chabal, and G.Higashi, Phys.Rev.Lett., 65, 1124 (1990).
- 3) S.M.Hu, J.Appl.Phys., 51, 5945 (1981).
- 4) B.Harbecke, B.Heinz, and P.Grosse, Appl.Phys.A, 38, 263 (1985).
- 5) P.Grosse, B.Harbecke, B.Heinz, R.Meyer, and M.Offenberg, Appl.Phys.A, 39, 257 (1986).
- S.Fujimura, K.Ishikawa, and H.Mori, Proc.Symp. 181st Meet. Electrochem. Soc., St.Louis (The Physics and Chemistry of SiO2 and the Si-SiO2 Interface) in press.



Fig. 1 FT-IR-RAS spectra of native oxide grown in pure water (40- 860min).



Fig. 2 FT-IR-RAS spectra of native oxide grown in pure water (1245-100220min).



Fig. 3 FT-IR-RAS spectra of native oxide grown in HNO₃ solution.



Fig. 4 Measured FT-IR-RAS spectra of a thermally grown oxide layer and a calculated spectra from Drude model using oscillators of quartz glass.



Fig. 5 Calculated FT-IR-RAS spectra of insular oxide particles grown on a Si surface. (f=40%, Thickness of oxidized layer is 5A)