

In-Depth Profiling of Suboxide Compositions in the SiO₂/Si Interface by Angle Resolved X-ray Photoelectron Spectroscopy

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A clean silicon surface was oxidized in a UHV chamber and in-depth profiling of suboxide compositions was carried out by using angle resolved x-ray photoelectron spectroscopy. Implication of the existence of Si-H bonds near the oxide surface is obtained because the background hydrogen in the UHV system reacts with the oxide surface. This hydrogenated Si bond looks like Si³⁺ in the Si_{2p} core level spectrum. It is also shown that the SiO₂/Si interface is atomically abrupt.

1. Introduction

The atomic scale control of MOS gate oxide thickness is needed for near future ULSI. It is also important to know the microscopic structure of the SiO₂/Si interface. X-ray photoelectron spectroscopy (XPS) has extensively been used to characterize the suboxide compositions and chemical bonding features in the SiO₂/Si interface^{1,6)}. As for the SiO₂/Si interface analysis by XPS, the SiO₂ surface has often been assumed to be identical to the bulk SiO₂. However, in-depth profiling of the oxide compositions using a chemical solution²⁾ must results in the surface chemical bond formation such as Si-F and Si-H, and hence the Si_{2p} chemical shift will be more or less influenced with fluorine or hydrogen bonds. The surface of very thin oxide grown on a clean Si surface^{3,4)} is not necessarily identical to the oxide produced at atmospheric pressure because of relatively high hydrogen background in the UHV system. This paper describes the chemical bonding features of the SiO₂/Si system studied by the angle resolved XPS of

very thin oxide (<10Å) formed in UHV.

2. Experimental

P-type Si(100) and Si(111) wafers were used as substrates. After RCA cleaning of a wafer, a protective oxide layer was formed in the boiling solution consisting of H₂O₂:HCl:H₂O=1:1:6. The wafer was heated at about 830°C for 15~20 minutes at a pressure of less than 2×10⁻⁸ Torr to obtain the clean Si surface. The background pressure was 6×10⁻⁹ Torr. The oxidation was carried out at 750°C and in-situ XPS analysis was made at the photoelectron take-off angle range from 30° to 81°.

3. Results and Discussion

The Si_{2p} spectra for the SiO₂/Si system prepared at 750°C with 1200 Langmuir (L) oxygen exposure or 5000 L to the clean Si surface are shown in Fig. 1, where the Si_{2p} signal from the clean Si surface is subtracted. The resulting spectrum is deconvoluted to three suboxide spectra Si¹⁺, Si²⁺, Si³⁺ and Si⁴⁺ by noting that the Si_{2p} chemical shift is basically

proportional to the electronegativity sum of the nearest neighbor atoms for Si. In the figure, the Si^{1+} intensity is reduced for the surface sensitive configuration at a high take-off angle and the Si^{2+} intensity is very weak, reflecting the $\text{SiO}_2/\text{Si}(111)$ interface structure. In Fig. 2 the suboxide intensity ratio is plotted as a function of the photoelectron take-off angle θ . The Si^{3+} signal intensity tends to increase with decreasing the effective photoelectron escape depth, while the Si^{1+} and Si^{2+} signals decrease. This implies that the Si^{1+} and Si^{2+} suboxide states are existing near the SiO_2/Si interface and Si^{3+} exists more predominantly near the SiO_2 surface rather than near the SiO_2/Si interface region. It is possible to assume that the SiO_2/Si system is composed of the triple

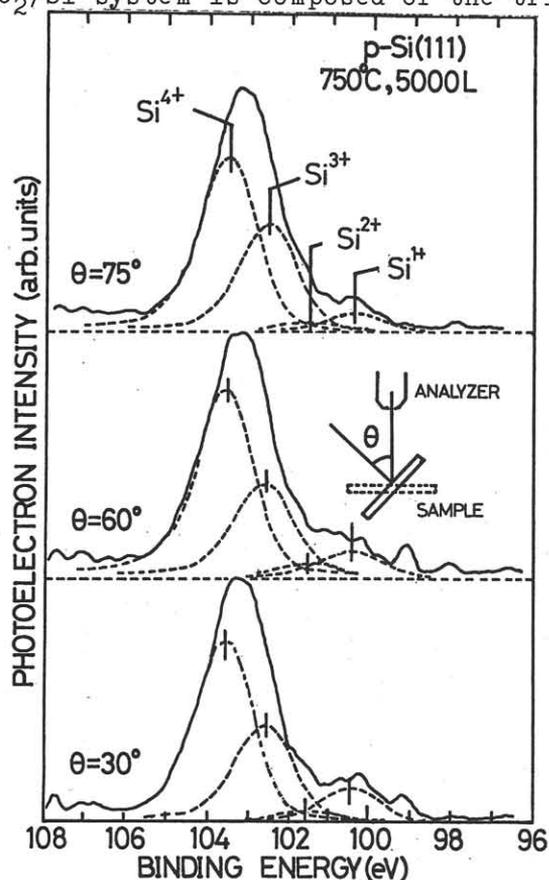


Fig. 1 Si_{2p} spectra from an oxidized surface (solid curves) and the deconvoluted spectra (dashed curves). The Si_{2p} signal from the substrate is subtracted.

layered structure, i.e., the surface layer mainly consisting of Si^{3+} , the bulk SiO_2 and the interface suboxide layer composed of Si^{1+} and probably Si^{2+} as illustrated in Fig. 3. Based on this model the suboxide intensity is calculated as a function of θ

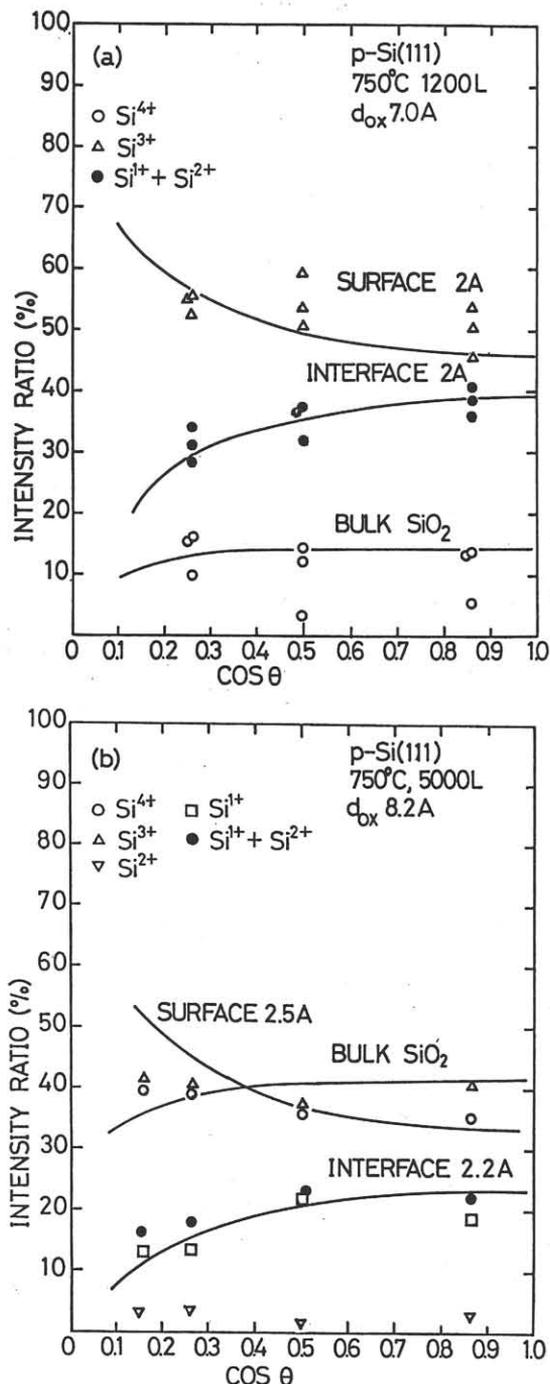


Fig. 2 Suboxide signal intensity ratio as a function of the photoelectron take-off angle θ for (a) 1200L O_2 exposure and (b) 5000L O_2 exposure to clean $\text{Si}(111)$.

and compared with the measured intensities in Fig. 2. The surface and interface layer thicknesses are estimated to be about 2Å in this model. Similar analysis has also been done for Si(100). The agreement between the measured and calculated results are not satisfactory although the relative intensities of the respective suboxides are consistent with the calculated result. A significant difference of the interface width between the 1200 L oxide and 5000 L might be explained by assuming that the lateral oxidation rate of Si is considerably high compared to the rate of the vertical oxidation at a high oxygen exposure. The existence of Si^{3+} on the oxide surface originates in the fact that the background gas in the UHV system is mostly hydrogen whose pressure is 5×10^{-9} Torr. The oxidation at 750°C proceeds at an oxygen pressure of 2×10^{-6} Torr, so that the hydrogen/oxygen ratio is in the range of 10^{-3} . This molecular hydrogen reacts with the heated oxide surface to produce Si-H bonds, some of which remain stable on the surface when the substrate is cooled down. The electronegativity of hydrogen is close to the value of Si, so that the Si-H bond looks like Si-Si in the Si_{2p} spectrum. Predominant suboxide compositions in the ideal interface are thought to be Si^{1+} on Si(111) and Si^{2+} on Si(100). It is known

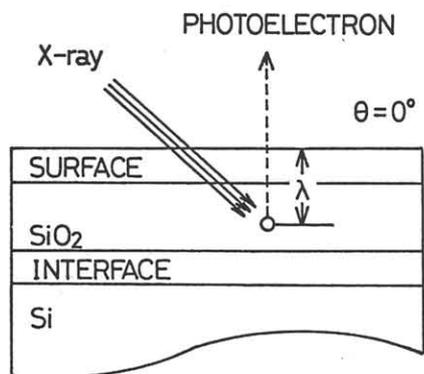


Fig. 3 A triple layer model in the SiO_2/Si system.

that there are a number of atomic steps on the Si surface. This introduces Si^{2+} on Si(111) and Si^{1+} on Si(100) as schematically illustrated in Fig. 5. Also it should be noted that Si-Si bonds indicated by arrows in the figure are easily cleaved by oxygen to produce Si^{3+} and/or Si^{4+} because the

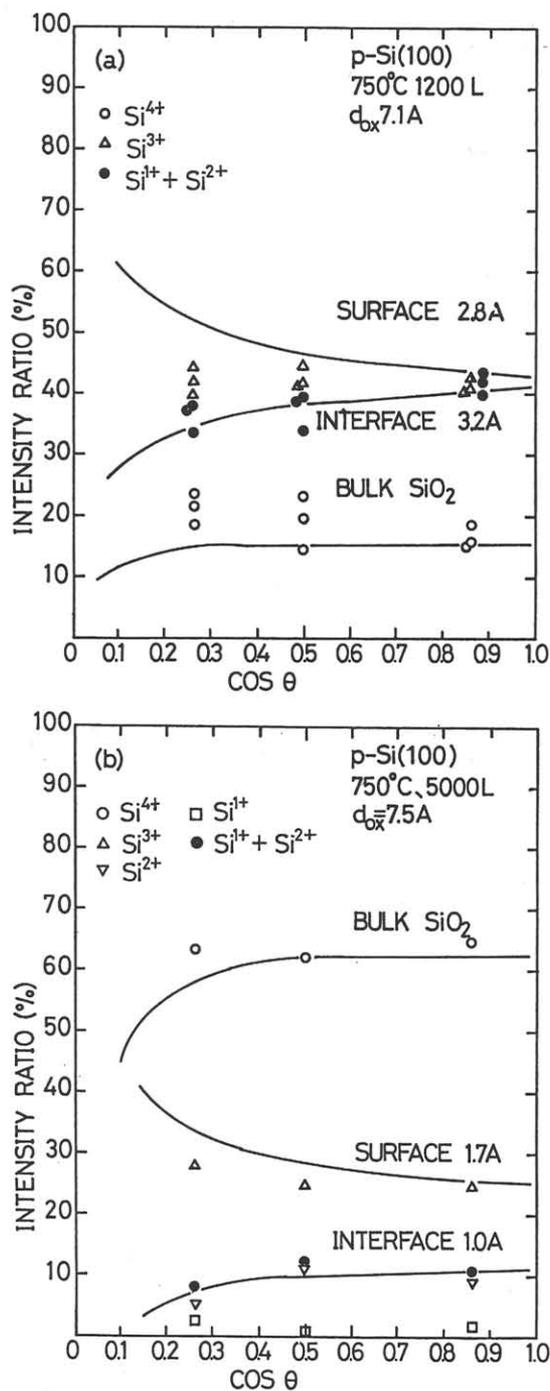


Fig. 4 Suboxide signal intensity ratio as a function of photoelectron take-off angle for (a) 1200L O_2 exposure and (b) 5000L O_2 to clean Si(100).

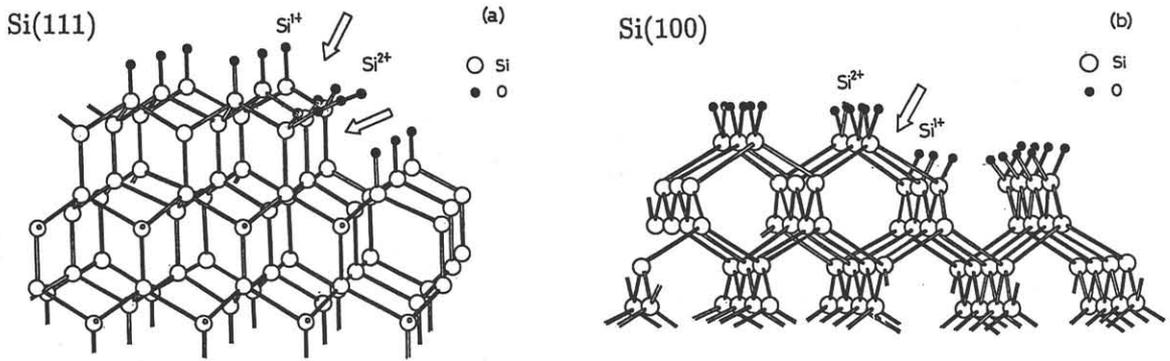


Fig. 5 Surface steps on Si(111) (a) and Si(100) (b).

valence electron transfer from Si to oxygen weakens the corresponding Si-Si bond at or near the step edge. Hattori et al.¹⁾ have observed the sub-monolayer Si^{3+} state existing in the SiO_2 side of the interface in the thermal oxide thicker than 25Å. They eliminated the influence of the surface chemical bonds by using the Si_{2p} spectrum of a thick oxide treated with the similar process as a reference. Ohdomari et al.⁶⁾ have proposed a possible structure by minimizing the strain energy in the $\text{SiO}_2/\text{Si}(100)$ interface by taking into account the suboxide ratios obtained by XPS measurements. Himpsel et al.⁷⁾ also proposed a similar SiO_2/Si interface model. In these models, the interface thickness is about two monolayers and Si^{3+} exists in the bulk SiO_2 side near the interface. In the present experiment the amount of Si^{3+} is larger than one monolayer, implying the presence of Si^{3+} also on the surface in UHV oxides. If Si^{3+} exists in the interface in the present case, the take-off angle dependence of Si^{3+} becomes less pronounced in consistence with Figs. 2 and 4. The SiO_2/Si interface width estimated by the suboxide intensity appears to be very abrupt for 5000L O_2 exposure at 750°C and close to the ideal transition

width of about 1.2Å.

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