In-Depth Profiling of Suboxide Compositions in the SiO$_2$/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 Si$^+$ in the Si$_{2p}$ core level spectrum. It is also shown that the SiO$_2$/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 SiO$_2$/Si interface. X-ray photoelectron spectroscopy (XPS) has extensively been used to characterize the suboxide compositions and chemical bonding features in the SiO$_2$/Si interface$^{1,6}$. As for the SiO$_2$/Si interface analysis by XPS, the SiO$_2$ surface has often been assumed to be identical to the bulk SiO$_2$. However, in-depth profiling of the oxide compositions using a chemical solution$^2$ 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 SiO$_2$/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 H$_2$O$_2$:HCl:H$_2$O=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 SiO$_2$/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 Si$^+$, Si$^{2+}$, Si$^{3+}$ and Si$^{4+}$ 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 SiO$_2$/Si(111) interface structure. In Fig. 2 the suboxide intensity ratio is plotted as a function of the photoelectron take-off angle $\theta$. 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 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 $\theta$. 

**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.

**Fig. 2** Suboxide signal intensity ratio as a function of the photoelectron take-off angle $\theta$ for (a) 1200L O$_2$ exposure and (b) 5000L O$_2$ exposure to clean 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$_3^{3+}$ on the oxide surface originates in the fact that the background gas in the UHV system is mostly hydrogen whose pressure is $5\times10^{-9}$ Torr. The oxidation at 750°C proceeds at an oxygen pressure of $2\times10^{-6}$ 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 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$_3^{3+}$ and/or Si$_4^{4+}$ because the

Fig. 3 A triple layer model in the SiO$_2$/Si system.

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).
valence electron transfer from Si to oxygen weakens the corresponding Si–Si bond at or near the step edge. Hattori et al. have observed the sub-monolayer Si\(^{3+}\) state existing in the SiO\(_2\) side of the interface in the thermal oxide thicker than 25 Å. 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. have proposed a possible structure by minimizing the strain energy in the SiO\(_2\)/Si(100) interface by taking into account the suboxide ratios obtained by XPS measurements. Himpel et al. 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

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

**References**


