Early Stage of Silicon Oxidation Studied by \textit{in situ} X-ray Photoelectron Spectroscopy

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A clean silicon surface was oxidized in a UHV chamber and the surface suboxide compositions were analyzed by using \textit{in situ} x-ray photoelectron spectroscopy. It is shown that the predominant suboxides are Si\(_2\)O\(_3\) and SiO irrespective of crystallographic orientations in the early stage of oxidation. This is interpreted in terms of a significant number of atomic steps existing on the clean Si surface.

1. INTRODUCTION

The chemical and physical structure of the Si\(_2\)O\(_3\)/Si interface has been extensively studied by using x-ray photoelectron spectroscopy (XPS). Based on the chemical shift in Si(2p) XPS core level spectrum, various models for the Si\(_2\)O\(_3\)/Si interface structure have been proposed. For instance, Ishizaka et al.\(^1\) have observed an intermediate chemical states in the interface and concluded the abrupt connection of Si\(_2\)O\(_3\) with Si crystal within a monomolecular layer. They have extracted the interface signal through subtracting the Si(2p) signal of bulk Si and of Si\(_2\)O\(_3\) from the measured spectrum whose background was approximated by a straight line. Whereas, Hattori and Suzuki\(^2\) have deconvoluted the measured spectrum by using separately measured Si(2p) spectra from bulk Si and Si\(_2\)O\(_3\) without any assumption on the background of the spectra. Hollinger et al.\(^3\) have shown from the synchrotron radiation spectroscopy of Si\(_2\)O\(_3\)/Si system that the suboxide states of Si\(_2\)O\(_3\), SiO and Si\(_2\)O\(_3\) are existing in the Si\(_2\)O\(_3\)(5 ~ 20 A thick)/Si interface and independent of surface orientation as well as oxide thickness. While Grunthaner et al.\(^4\) have investigated the depth profile of Si\(_2\)O\(_3\)/Si system by etching the oxide using HF/ethanol solution and indicated that interface suboxide compositions depend on the surface orientation. However, it should be noted that when the etched Si\(_2\)O\(_3\) surface is hydrogenated and/or weakly fluorinated by the etching solution, chemically shifted Si(2p) signal will appear at energies close to the interface signal. It was also shown that the top surface of Si\(_2\)O\(_3\) is slightly silicon rich\(^5\). In this paper, a clean silicon surface was oxidized in a UHV system and the surface suboxide layer was characterized by \textit{in situ} XPS.

2. EXPERIMENTAL

P-type Si(100) (4\(\times\)6\(\times\)cm) and Si(111) (1.5\(\times\)3\(\times\)cm) wafers were used as substrates. After the chemical etching, a protective oxide layer (\(\times\)10 A thick) was formed on the
wafer in a boiling solution consisting of \( \text{H}_2\text{O} : \text{H}_2\text{O}_2 : \text{HCl} = 6 : 1 : 1 \). The wafer was heated at about 830°C for 15~20 min to obtain the clean surface. An in situ XPS system with an MgKa x-ray source (1253.6 eV) was used in this study (Fig. 1). The base pressure was \( 6 \times 10^{-9} \) Torr. The Si(2p) or O(1s) spectra from a silicon surface exposed to 10 Langmuir oxygen at room temperature and 120L at \( \sim 700^\circ \text{C} \) were measured.

Fig. 1 A schematic diagram of an in situ XPS system.

3. RESULTS AND DISCUSSION

Typical spectra of oxidized Si(111) surfaces are displayed in Fig. 2, where the bulk Si(2p) signal at 99.3 eV was subtracted by using the measured Si(2p) signal from a clean Si(111) surface. The resulting spectrum (solid curve) was deconvoluted to four spectra arising from the corresponding molecular units, \( \text{Si}_2\text{O}_3 \), SiO, \( \text{Si}_2\text{O}_3 \), and \( \text{SiO}_2 \) by the use of the Si(2p) spectrum of a rather thick oxide as a reference. The binding energies of the suboxides were determined by noting that the chemical shift is proportional to the electronegativity sum of the nearest neighbor atoms for Si(2). As illustrated in Fig. 2, 10L oxygen exposure results in the formation of suboxides of \( \text{Si}_2\text{O}_3 \), SiO, and a little \( \text{Si}_2\text{O}_3 \). While 120L \( \text{O}_2 \) exposure at \( \sim 700^\circ \text{C} \) leads to predominant suboxides of \( \text{Si}_2\text{O}_3 \) and SiO. Similar result was obtained also for Si(100) surface oxidation as summarized in Table 1. Here, the effective oxide thickness was calculated from the integrated intensity ratio of Si(2p) signal from substrate Si to that from oxide. The result of Table 1 shows that suboxide compositions are basically

Fig. 2 Si(2p) signal from oxidized surfaces (solid curve) and the deconvoluted spectra (dashed curves)

<table>
<thead>
<tr>
<th>OXIDE THICKNESS</th>
<th>( \text{SiO}_2 )</th>
<th>( \text{Si}_2\text{O}_3 )</th>
<th>SiO</th>
<th>SiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111) 3.5A</td>
<td>10.7</td>
<td>46.2</td>
<td>30.3</td>
<td>12.7</td>
</tr>
<tr>
<td>4.6A</td>
<td>23.2</td>
<td>49.5</td>
<td>18.2</td>
<td>9.1</td>
</tr>
<tr>
<td>5.4A</td>
<td>5.1</td>
<td>64.7</td>
<td>18.6</td>
<td>11.6</td>
</tr>
<tr>
<td>(100) 2.7A</td>
<td>8.0</td>
<td>54.1</td>
<td>21.0</td>
<td>17.0</td>
</tr>
<tr>
<td>5.1A</td>
<td>18.3</td>
<td>48.2</td>
<td>23.7</td>
<td>3.8</td>
</tr>
<tr>
<td>5.2A</td>
<td>12.9</td>
<td>48.0</td>
<td>28.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>
irrespective of the surface orientation. Hattori and Suzuki have demonstrated that the predominant interface suboxides are Si$_2$O and SiO and that SiO$_3$ is located not only in the interface but in the oxide. Ourmazd et al. have recently observed TEM lattice images of the SiO$_2$/atomically flat MBE grown Si(001) system and shown the existence of an ordered crystalline oxide layer with a thickness of about 5 A in the interface between amorphous SiO$_2$ and crystalline Si. Their structural model predicts that possible interface suboxides are Si$_2$O and/or SiO. In the present experiment, UHV cleaning of Si produces a wide variety of surface atomic steps. As shown in Table 1, the effective oxide thickness varies from 3 to 5 A and this fluctuation might arise from the extent of reproducibility of the surface atomic steps. Such surface roughness, if exists, changes the apparent compositions of surface suboxides because microscopic oxidation kinetics at atomic steps is different from the case of atomically flat Si surface. This is a possible reason why the suboxide compositions in this study are different from the TEM result and also explains that the interface suboxide compositions are independent of crystal orientation.

Concerning the O(1s) signal, the peak energy moves toward higher binding energy side with increasing the oxide thickness as shown in Fig. 3. It is well known that the Si(2p) peak energy exhibits the chemical shift toward higher binding energy. If the partial charge transfer from silicon to oxygen causes the chemical shift of Si(2p) and O(1s), the O(1s) peak shift must be opposite to the direction of the Si(2p) shift. However, the result of Fig. 3 apparently contradicts with this prediction. This puzzle could be solved when the second nearest neighbor atoms for each oxygen atom are taken into account and the local electronegativity for oxygen is employed to calculate the O(1s) chemical shift instead of using the conventional electronegativity sum of the nearest neighbor atoms. Figure 4 represents a plot of O(1s) peak energy versus local electronegativity for oxygen. In the figure, the surface suboxide state at 2L oxygen exposure corresponds to Si$_2$O because the surface coverage of oxygen at 2L O$_2$ exposure is about 0.38. By interpolating measured O(1s) binding energies for Si$_2$O and SiO$_2$, the O(1s) peak energies for SiO and SiO$_3$ are estimated. The oxygen exposure of 10 L at room temperature yields the O(1s) binding energy corresponding to a suboxide state in between Si$_2$O and SiO. 120 L oxygen exposure at 700°C causes further chemical shift of the O(1s) signal which corresponds to a mixture of SiO and Si$_2$O$_3$ suboxides. This is consistent with the results of Fig. 2 and Table 1. Such behavior of O(1s) signal is reproduced also for the case of Si(100). Therefore, the valence charge transfer model

![Fig. 3 The O(1s) peak energy as a function of oxide thickness](image-url)
can explain the positive chemical shifts of both Si(2p) and O(1s).

In conclusion, we have shown the existence of the surface and interface suboxides by observing Si(2p) spectra and parallel chemical shift of O(1s) and Si(2p) in the early stage of oxidation. The absence of crystal orientation dependence of the suboxide compositions could be attributed to atomic steps on clean Si surfaces treated in UHV environment.

REFERENCES