

## Early Stages of Oxidation of Clean Si(111)-7x7 and Si(100)-2x1 Surfaces Studied by In-Situ High Resolution X-Ray Photoelectron Spectroscopy

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Systematic study of Si<sub>2p</sub> core level spectra for clean Si(111)-7x7 surfaces exposed to molecular oxygen has shown that O<sub>2</sub> molecules adsorb on adatom and rest atom dangling bond sites as peroxy radicals. This unstable configuration is followed by the dissociation of the O<sub>2</sub> molecule, i.e. one oxygen atom ties up to the adatom dangling bond and the second oxygen to the first neighbour dangling bond which corresponds to the rest atom. Thus the Si<sup>1+</sup> suboxides are formed on the surface, whereas the back-bond oxidation leading to the Si<sup>2+</sup> suboxide formation does not take place at this stage. As the oxidation reaction proceeds on the surface, Si<sup>2+</sup>, Si<sup>3+</sup>, and Si<sup>4+</sup> units are formed without any indication of bulk Si oxidation. Saturation in the oxidation reaction is reached once the entire 7x7 surface dangling bonds and most of the back-bonds are oxidized. In the case of oxidation of clean Si(100)-2x1 surfaces, similar saturation is observed when the dimers are fully oxidized and most of the second atom layer is also reacted.

### 1. INTRODUCTION

The better understanding of atomic-scale reaction kinetics in the early stages of oxidation of clean Si surfaces is important for finding a relevant way to control the ultrathin SiO<sub>2</sub>/Si interface structures. For oxidation of Si(111)-7x7 surfaces, various models have been proposed for the initial reaction of O<sub>2</sub> molecules with the 7x7 unit cell, based on the appearance of dark and bright sites in scanning tunneling microscopy (STM) images. Avouris et al.<sup>1)</sup> suggested the formation of two reaction products, consisting of an O atom tying up an adatom dangling bond with a second O atom inserted in one of the adatom back-bonds for STM dark sites, i.e. formation of one Si<sup>2+</sup> and one Si<sup>1+</sup> unit in terms of XPS Si<sub>2p</sub> core-level spectrum, and the other adatom whose dangling-bond state remains unchanged while the oxygen atom is inserted in one of its back-bonds for STM bright sites, i.e. formation of two Si<sup>1+</sup> units. Pelz and Koch<sup>2)</sup> claimed that the early oxidation product consists of an adatom back-bonded to one (two Si<sup>1+</sup> units) or two O atoms (two Si<sup>1+</sup> and one Si<sup>2+</sup> units). In both cases, the oxidation process shows a preference for the faulted half of the unit cell. Other study<sup>3)</sup> reports that room temperature oxidation proceeds uniformly over the entire surface in contrast with the formation of islands for high-temperature oxidation. On the other hand, the initial oxidation of Si(100)-2x1 surfaces has been explained by a preferential O insertion to the dimer back-bond from scanning tunneling spectroscopy (STS) and high-resolution electron energy loss spectroscopy (HREELS) observations<sup>4)</sup>.

In this paper we report on the surface composition of clean Si(111)-7x7 and Si(100)-2x1 surfaces after various O<sub>2</sub> exposures as revealed by the structure of the corresponding Si<sub>2p</sub> core-level spectra.

### 2. EXPERIMENTAL

The high-resolution XPS measurements were performed using a Scienta ESCA-300 instrument with monochromatic AlK $\alpha$  radiation and an acceptance angle of 3.3°, a take-off angle of 5° in order to enhance surface sensitivity, and at a background pressure of 5x10<sup>-10</sup> Torr. The Si<sub>2p</sub> core-level peaks have been deconvoluted into the Si<sub>2p3/2</sub> and Si<sub>2p1/2</sub> components with an intensity ratio of 0.5 and an energy separation of 0.61 eV. The reconstructed surfaces were obtained by heating the Si substrate to a temperature around 1200°C with an infrared lamp in the XPS preparation chamber. The clean Si surfaces were then exposed in-situ to pure O<sub>2</sub> (1-68 L) at room temperature. The success in this investigation arises from the capability of an accurate deconvolution of the Si<sub>2p</sub> core-level spectra for the clean Si(111)-7x7 and Si(100)-2x1 surfaces.

### 3. RESULTS AND DISCUSSION

The deconvolution of the Si<sub>2p</sub> spectra shown in Figs. 1 and 2 was carried out according to previous synchrotron studies<sup>5,6)</sup> on the values of energy shifts and intensity ratios. For the Si(111)-7x7 surface, we can identify S2 (rest atoms), S4 (defects or subsurface), S1 (pedestal atoms) and S3 (adatoms) peaks together with the bulk peak (B). For Si(100)-2x1 surfaces, we could separate the S (dimer up atoms), C (defects), SS (dimer low atoms), S' (subsurface) and A (not identified) peaks.

In the case of Si(111)-7x7, O<sub>2</sub> exposures lower than 2 L (see Fig. 3) lead to a distribution of suboxide states in which Si<sup>1+</sup> is clearly dominant. For these exposures, surface Si peaks

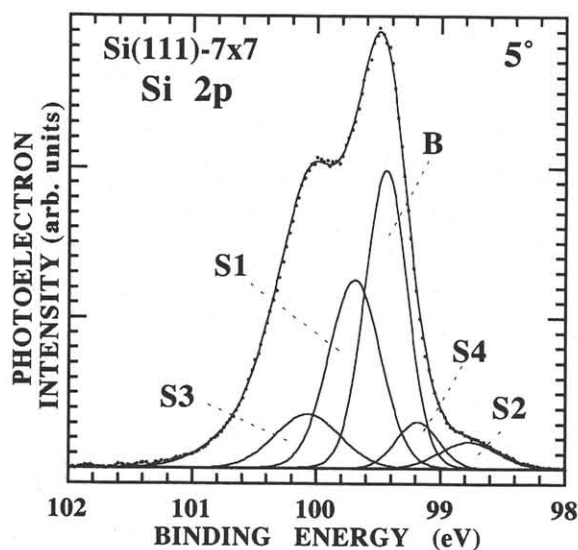


Fig. 1.  $\text{Si}_{2p}$  core-level spectrum from a  $\text{Si}(111)\text{-}7\times 7$  surface. For the sake of clarity in the deconvolution only the  $\text{Si}_{2p3/2}$  components are indicated in Figs. 1, 2, 3, and 4. Five peaks, S1 (pedestal atoms), S2 (rest atoms), S3 (adatoms), S4 (defects or subsurface) and B (bulk) are identified.

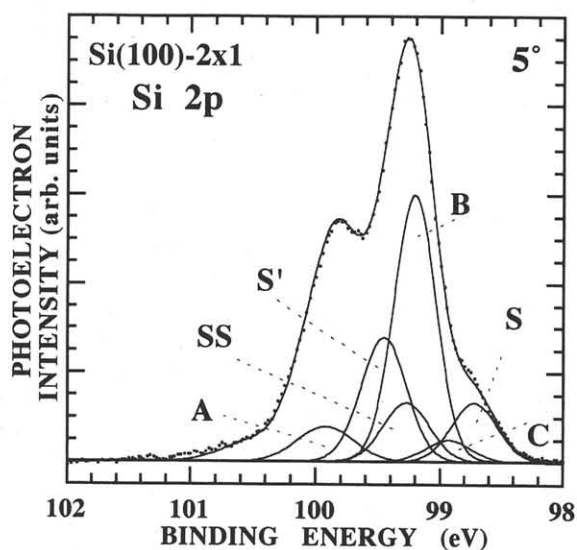


Fig. 2.  $\text{Si}_{2p}$  core-level spectrum from a  $\text{Si}(100)\text{-}2\times 1$  surface together with the deconvoluted  $\text{Si}_{2p3/2}$  components. Five peaks, B (bulk), S (dimer up atoms), SS (dimer low atoms), S' (subsurface) and C (defects) are indicated together with an unidentified peak A.

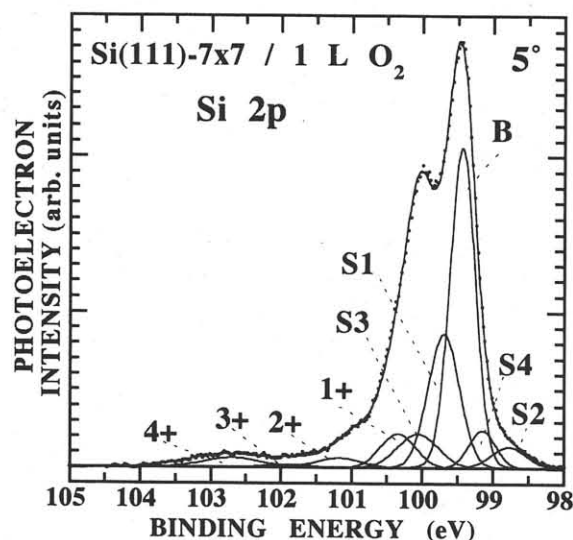


Fig. 3.  $\text{Si}_{2p}$  core-level spectrum from a  $\text{Si}(111)\text{-}7\times 7$  surface exposed to 1 L  $\text{O}_2$  together with the deconvoluted  $\text{Si}_{2p3/2}$  components. 1+ to 4+ refer to  $\text{Si}^{1+}$  to  $\text{Si}^{4+}$ .

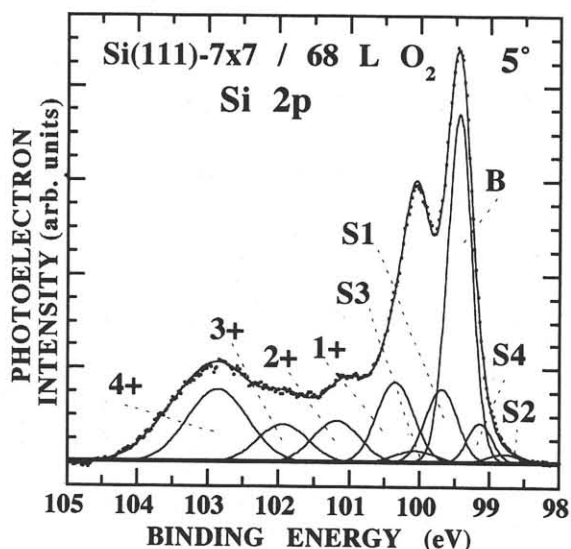


Fig. 4.  $\text{Si}_{2p}$  core-level spectrum from a  $\text{Si}(111)\text{-}7\times 7$  surface exposed to 68 L  $\text{O}_2$  together with the deconvoluted  $\text{Si}_{2p3/2}$  components.

corresponding to rest (S2), adsorbed (S3) and pedestal (S1) atoms remain observable, indicating that most of the surface is still reconstructed and only limited local oxidation takes place on it. For larger  $\text{O}_2$  exposures (Fig. 4),  $\text{Si}^{4+}$  and  $\text{Si}^{3+}$  turn to be dominant among the four oxidation states, whereas all peak intensities arising from the  $7\times 7$  unit cell states become significantly weak. The oxidation reaction apparently saturates at exposures of about 68 L since no significant

increase in oxygen adsorption or variation in the suboxide signal intensity is observed for the higher exposures. Correspondingly, the surface oxide composition is kept almost unchanged as due to saturation in the Si-O bond formation reaction at room temperature.

From the core-level peak fittings it is possible to derive a correlation between the increase in relative intensity of the various oxide states ( $\text{Si}^{1+}$ ,  $\text{Si}^{2+}$ ,  $\text{Si}^{3+}$  and  $\text{Si}^{4+}$ ) and the decrease

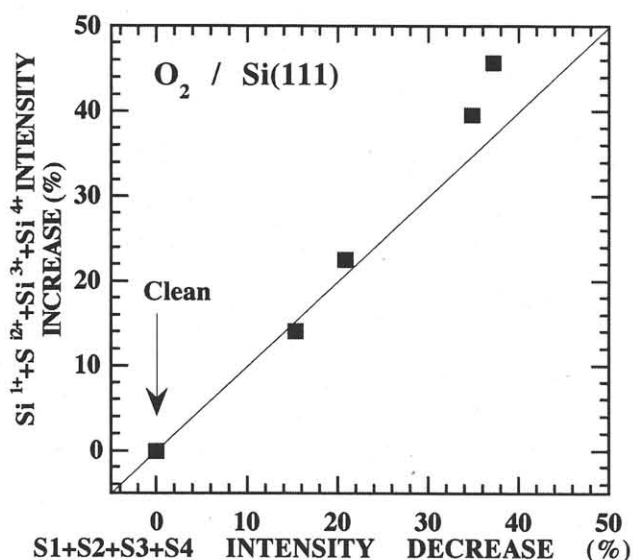


Fig. 5. Increase of oxide and suboxide intensity as a function of the decrease of all peaks arising from the 7x7 unit cell.

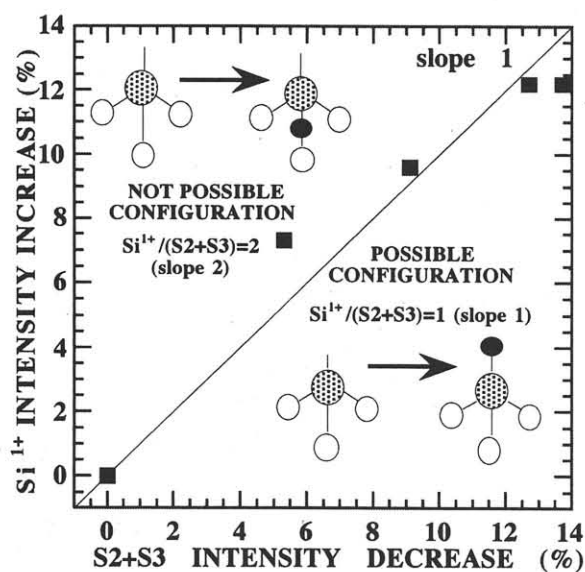


Fig. 6.  $\text{Si}^{1+}$  intensity increase as a function of rest atom ( $\text{S}_2$ ) and adatoms ( $\text{S}_3$ ) intensity decrease.

in the relative intensity of the 7x7 unit cell states ( $\text{S}_1$ ,  $\text{S}_2$ ,  $\text{S}_3$ , and  $\text{S}_4$ ) in order to propose a model for the initial stages of oxidation. As clearly shown in Fig. 5 an increase in oxide and suboxide states in the  $\text{Si}_{2p}$  core-level spectra coincides with an extent of the total decrease in 7x7 unit cell states. This shows that the oxidation proceeds uniformly through the entire surface by forming various oxidation states until most of the 7x7 ordered structure disappears. There is no evidence of any bulk oxidation as expected from the low diffusion coefficient of oxygen at room temperature.

Moreover, as shown in Fig. 6, the  $\text{Si}^{1+}$  (earliest oxidation state) intensity increase is proportional to the intensity decrease of adatoms and rest atoms signals with a slope of unity, indicating that oxygen termination of a surface dangling bond results in the formation of single  $\text{Si}^{1+}$  unit.

The significance of this result is that the oxygen atom ties up the dangling bond of the adatom or rest atom but it is not inserted in the back bond, being different from the result of STM studies<sup>1)</sup>. If the oxygen atom is back-bonded, the disappearance of one adatom (or rest atom) should lead to the formation of two  $\text{Si}^{1+}$ -like-units: One corresponds to the top adatom and another to the low pedestal atom, and hence the slope should be 2 as illustrated in the inset of Fig. 6, being inconsistent with the observed result.

Oxygen exposure to  $\text{Si}(100)\text{-}2\times 1$  surfaces exhibits similar behavior to the case of Fig. 5 for  $\text{O}_2/\text{Si}(111)$ : Intensity increase of  $\text{Si}^{1+} + \text{Si}^{2+} + \text{Si}^{3+} + \text{Si}^{4+}$  coincides with the total decrease in  $2\times 1$  surface unit cell states ( $\text{S}$ ,  $\text{SS}$ ,  $\text{S}'$  and  $\text{C}$ ) although the contribution of unidentified peak A is unclear. Also, saturation in the oxidation reaction is observed at about 68 L  $\text{O}_2$ , when dimers are fully oxidized and most of the second atom layer is also oxidized although very little bulk oxidation occurs. This implies the oxidation of  $\text{Si}(100)\text{-}2\times 1$  surfaces is more complex than  $\text{Si}(111)\text{-}7\times 7$ .

#### 4. CONCLUSIONS

We have proposed a new model for the initial oxidation stages of  $\text{Si}(111)\text{-}7\times 7$  surfaces in which the  $\text{O}_2$  molecules adsorb on adatom and rest atom dangling bond sites as peroxy radicals. This unstable configuration leads to the dissociation of the  $\text{O}_2$  molecule with one oxygen atom tying up to the adatom dangling bond and the second oxygen to the first neighbour dangling bond which corresponds to the rest atom. Hence  $\text{Si}^{1+}$  suboxides are formed on the surface, but back-bond oxidation does not take place at this stage. As the oxidation reaction proceeds on the surface,  $\text{Si}^{2+}$ ,  $\text{Si}^{3+}$  and  $\text{Si}^{4+}$  units are formed but there is no indication of bulk oxidation. Saturation in the oxidation states is reached once the entire 7x7 surface dangling bonds and most of the back-bonds are oxidized. Qualitatively, similar saturation is observed also for  $\text{O}_2/\text{Si}(100)\text{-}2\times 1$ .

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