

High-resolution core-level study of initial oxygen adsorption on Si(001): Surface stoichiometry and anomalous Si 2*p* core-level shifts

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The submonolayer oxygen adsorption on the Si(001) surface is studied by high-resolution Si 2*p* photoemission. Significant intensities of Si 2*p* components due to the Si²⁺ and Si³⁺ species are observed from the very early stage of adsorption at 120 K, which grow linearly with the oxygen coverage. This indicates an active agglomeration of oxygen adsorbates even for submonolayer adsorption at low temperatures. Annealing above ~500 K of oxygen adlayers formed at 120 K induces not only changes of the adlayer stoichiometry but also shifts of the Si 2*p* binding energies for the Si²⁺ and Si³⁺ species by 0.14 and 0.23 eV, respectively. This change demonstrates the sensitivity of the Si 2*p* binding energies beyond the chemical shift.
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Due to the technological importance of Si oxides in semiconductor device applications, the oxidation of Si surfaces has been a topic of vigorous investigations.¹ Nevertheless, many fundamental issues of the initial oxygen adsorption on Si surfaces have remained unsolved.¹ One of the most important issues of the ongoing discussion is the determination of stable adsorption sites of atomic or molecular oxygen adsorbates.^{1–8} Furthermore, although the initial adsorption of oxygen was known to reach a certain saturation after a dose of 10–1000 L O₂, the structural and chemical evolution of the outermost Si layers have not been clarified during the initial adsorption.¹ Especially, this initial adsorption stage on the Si(001) surface has recently been characterized as the oxidation of the first Si layer within the “layer by layer” oxidation process.² This makes it an urgent task to investigate the detailed structure and chemistry of the two-dimensional oxidation of the first layer of the Si(001) surface.

Among various experimental probes, core-level photoemission has played a crucial role in elucidating structures and chemistry of the SiO₂/Si interfaces^{9–11} by resolving out the Si 2*p* components for the suboxide (Si¹⁺, Si²⁺, and Si³⁺) species. However, very few Si 2*p* photoemission studies are available for the initial oxygen adsorption, which is partly due to the limited resolution and sensitivity to the low density of oxygen. An early Si 2*p* study¹² suggested the presence of a high oxidation species (Si²⁺) for the oxygen coverages larger than ~0.8 ML. This result, however, was far from being unambiguous for the monolayer regime and an objection was subsequently given,³ which left this important issue as an open question. This issue is directly related to the problem of oxygen adsorption sites and the stoichiometry of the outermost Si layers. Moreover, recently the orthodox interpretation of the Si 2*p* core-level shifts by suboxides

has been challenged for model adsorbate systems,¹³ on which discussion is underway.¹⁴

In this paper, we report a high-resolution highly surface-sensitive Si 2*p* investigation of the initial oxidation on the Si(001) surface. The presence and evolution of the highly oxidized Si²⁺ and Si³⁺ species are clarified for submonolayer oxygen coverages. Furthermore, annealings above 530 K induced a drastic change of the Si 2*p* core-level shifts of the Si²⁺ and Si³⁺ species. These results provide insights into the initial oxygen adsorption mechanism and into the interpretation of Si 2*p* core-level shifts for suboxide species.

High-resolution photoemission measurements were performed on the photoemission beam line (BL-33) at the Max-I synchrotron radiation facility in Lund, Sweden.¹⁵ The total energy resolution was ~60 meV at a photon energy (*hν*) of 130 eV. Si 2*p* spectra were measured mostly with *hν*=130 eV at a grazing emission angle (*θ_e*=60°) and at 120 K for optimal surface sensitivity and resolution.¹⁶ Oxygen gas of 3.5–15 L was dosed onto a well-cleaned Si(001)*c*(4×2) surface at 120 K. This corresponds to oxygen coverages of 0.1~0.5 ML judged by a simple Si 2*p* intensity analysis^{9,10} and by careful O 2*p* studies.^{3,12} The fact that we indeed probe the submonolayer coverage range is corroborated by observing the Si 2*p* component from unaffected Si surface dimers and the dangling-bond surface states in valence band spectra.

Figure 1 shows the high-resolution Si 2*p* spectra taken for (a) clean Si(001)*c*(4×2), (b) oxygen adsorption on Si(001)*c*(4×2) at 120 K, and (c) a standard thermal oxide formed at ~875 K. In Fig. 1(c), one can identify from the raw spectrum itself the distinctive Si 2*p* components for the suboxides (Si¹⁺~Si³⁺) and for SiO₂ (Si⁴⁺).^{9,10} This spectrum was fitted by a standard curve fitting procedure with

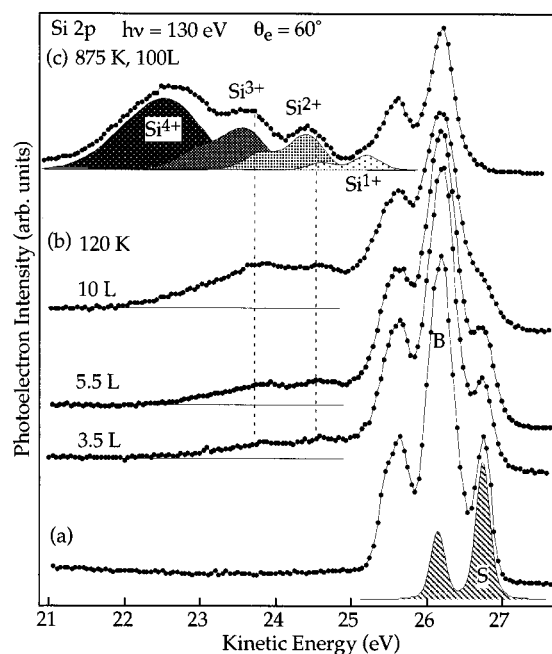


FIG. 1. Si 2*p* photoelectron spectra for (a) the clean Si(001)*c*(4×2) surface, (b) the Si(001) surface exposed to 3.5, 5.5, and 10 L of O₂ at 120 K, and (c) the Si(001) surface exposed to 100 L of O₂ at 875 K. All spectra were taken with a photon energy (*hν*) of 130 eV at a grazing emission angle (*θ_e*) of 60° from surfaces held at 120 K. The decompositions by standard curve fitting analyses are shown for the oxygen-related components (Si¹⁺–Si⁴⁺) in (c) and for the up-dimer atom component (*S*) in (a). The solid and dashed lines in (b) indicate the background levels and the peak positions of the two prominent structures at high binding energies, respectively.

spin-orbit split Voigt functions for quantitative analyses.^{16,17} For clarity reasons, only the oxygen-related components are shown in Fig. 1(c). The intensity distributions, core-level shifts, and other line-shape parameters are in good agreement with the previous reports.^{9–11,18} The accurately determined core-level shifts were 1.00, 1.81, 2.63, and 3.60 eV for Si¹⁺–Si⁴⁺, respectively. The similar analysis for the clean Si(001)*c*(4×2) surface is also consistent with the previous report¹⁶ [Fig. 1(a)], for which only the up-dimer atom component *S* of the Si surface dimers¹⁶ is shown.

From the spectra for oxygen adsorption at 120 K [Fig. 1(b)], two distinctive peaks are clearly identified, which correspond to the suboxide species Si²⁺ and Si³⁺ (dashed lines), even for the lowest oxygen dose of 3.5 L (~0.1 ML). The spectral weight of the Si³⁺ component is almost the same as that of Si²⁺. The presence of the Si¹⁺ and Si⁴⁺ components is not so evident from these raw spectra, but it will be made clear by the curve fittings. Another straightforward yet unexpected observation is that the binding energies of the Si²⁺ and Si³⁺ components are smaller than those for the thermal oxide by ~0.2 eV. The origin of these anomalous shifts will be discussed below. It should be noted at this point that this difference is not large enough to question their identification as the Si²⁺ and Si³⁺ components.

More detailed information on these spectra can be obtained by curve fitting as shown in Figs. 2(a) and 2(b). From these decompositions, it is evident that there are three

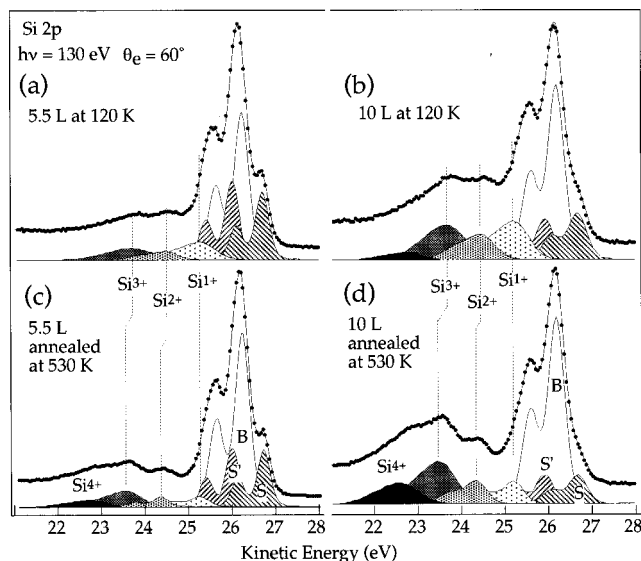


FIG. 2. Decompositions of (a), (b) two Si 2*p* photoelectron spectra shown in Fig. 1(b) and (c), (d) the corresponding spectra after annealing at 530 K. The results of the fitting overlap the experimental data. Each surface component is indicated by different hatching. Gaussian widths for the bulk (*B*) and the two clean surface components (*S* and *S'*) are 0.38 ± 0.02 and 0.38 ± 0.03 eV, respectively. See Fig. 3 for the details of the line shape parameters.

oxygen-induced components, Si¹⁺, Si²⁺, and Si³⁺. The bulk component *B* shows a subtle but distinctive asymmetry at the high binding energy side, which leads to another component *S'*. This component is due to the second layer Si atoms of the clean surface,^{16,17} and it shows a gradual intensity decrease upon increasing the oxygen dose in a similar fashion as *S*. In the spectrum for the 10 L dose [Fig. 2(b)], the SiO₂ component (Si⁴⁺) is barely observed. We have performed similar curve fittings for the Si 2*p* spectra of the Si(001) surfaces with six different O₂ doses, which are summarized in Fig. 3 (see the solid lines and the closed symbols). For all coverages the Si²⁺ and Si³⁺ components have more than half of the intensity of Si¹⁺ and all suboxide components grow in a roughly linear way as function of the oxygen coverage. The binding energies of the Si¹⁺–Si⁴⁺ components are also constant as function of the oxygen coverage (see Fig. 3).

As shown clearly in Figs. 1–3, the Si surface atoms in high oxidation states, Si²⁺ and Si³⁺, appear from the lowest dose investigated, ~0.1 ML. That is, there is a significant portion of Si surface atoms doubly and even triply bonded to oxygen adsorbates for the initial adsorption at a temperature as low as 120 K. Si 2*p* spectra in a wider temperature range indicate an increase of the amount of multiply bonded Si atoms at higher temperatures.¹⁹ This unambiguously indicates that the agglomeration of oxygen adsorbates to form multiply bonded Si surface atoms is a fundamental process of the initial oxidation of the Si(001) surface. Although very important, a reliable quantification of different oxidation states is prohibited by the uncertainties due to the photoelectron diffraction effect¹¹ and due to the possible difference in the Si 2*p* cross sections of different oxidation states.^{9,10}

An early Si 2*p* study for the room-temperature oxygen adsorption¹² suggested the existence of Si¹⁺ and Si²⁺ species

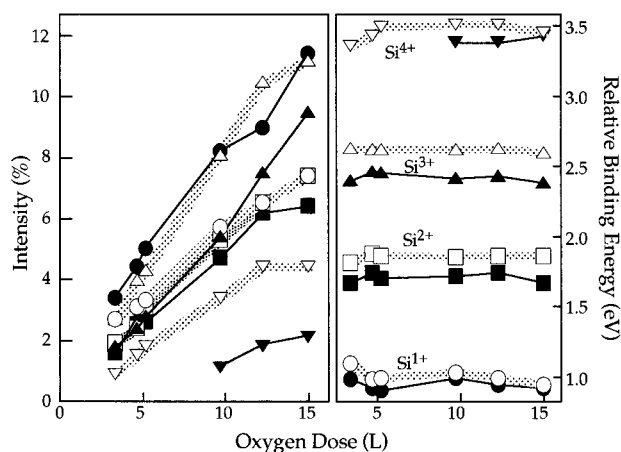


FIG. 3. Si $2p$ binding energies (relative to the bulk component B) and intensities (percentages of the total integrated intensities) of the Si^{1+} (\circ , \bullet), Si^{2+} (\square , \blacksquare), Si^{3+} (\triangle , \blacktriangle), and Si^{4+} (∇ , \blacktriangledown) components obtained for the $\text{Si}(001)$ surfaces exposed to O_2 at 120 K (solid symbols and solid lines) and for the surfaces after subsequent annealings at 875 K (open symbols and gray lines). Average values for the relative Si $2p$ binding energies of Si^{1+} , Si^{2+} , Si^{3+} , and Si^{4+} are 0.94 ± 0.04 (1.00 ± 0.05) eV, 1.71 ± 0.03 (1.85 ± 0.02) eV, 2.42 ± 0.03 (2.65 ± 0.01) eV, and 3.40 ± 0.03 (3.40 ± 0.06) eV, respectively, for the as-exposed (annealed) surfaces.

at >0.8 ML but only Si^{1+} at lower coverages. However, a subsequent Si $2p$ study pointed out the apparent ambiguity of this suggestion for coverages below 1 ML and provided an alternative interpretation of the high binding energy structure as satellite contributions.³ The latter concluded a unique Si^{1+} configuration at ≤ 1 ML.³ From the present high-resolution study, it is now obvious that the Si^{2+} and even Si^{3+} species are formed at the submonolayer coverages. Due to the significant improvement of the energy resolution and the surface sensitivity in the present work, we can also clearly rule out the satellite interpretation:³ one cannot find any structures at the binding energies of the Si^{2+} and Si^{3+} components for the clean surface in contrast to these previous studies.

From Fig. 3, it is also clear that the average oxidation state is almost constant in the coverage range studied here: the intensity ratios of Si^{1+} – Si^{4+} (in percentages of the integrated intensities of them all) are quite uniform for different coverages, which are averaged as $43.4 \pm 5.6\%$, $25.0 \pm 2.5\%$, $28.5 \pm 2.9\%$, and $3.2 \pm 3.5\%$, respectively, for the as-exposed surfaces. This finding contradicts the idea of a gradual increase of the oxidation state with an increase of the oxygen coverage, which assumes a homogeneous adsorption.^{1,20} Recently, the initial oxidation was shown to occur in a layer-by-layer fashion on $\text{Si}(001)$.² The present result, then, suggests that the oxidation within the first layer is not laterally uniform but occurs as a random formation of microscopic patches of adsorbate complexes with a similar stoichiometry. This is generally consistent with the recent microscopy investigations.^{2,21}

In contrast to the present conclusion, most of recent theoretical investigations have concentrated on the singly bonded Si for the initial oxygen adsorption on $\text{Si}(001)$.^{4,5,22} A recent calculation has indicated that the active agglomera-

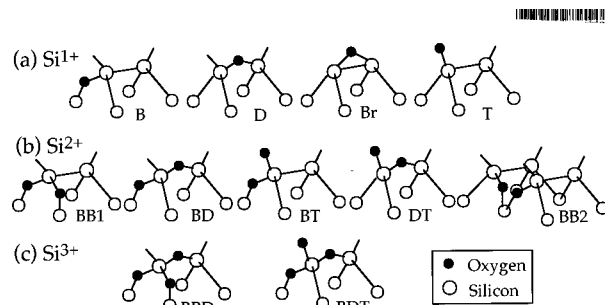


FIG. 4. Schematic illustration of the possible structures of adsorbate complexes of the (a) Si^{1+} , (b) Si^{2+} , and (c) Si^{3+} species for the oxygen adsorption on the Si dimers of the $\text{Si}(001)$ surface. B , D , and T mean the oxygen insertion into the back bonds, dimer bonds, and the dangling bonds, respectively.

tion in forming the Si^{3+} species occurs only at high temperatures for the initial oxidation of $\text{Si}(001)$.²³ This is obviously not true in view of the present results. Figure 4 shows the possible structures of the Si^{1+} – Si^{3+} species for the adsorption on the Si dimers of $\text{Si}(001)$. Since the initial oxidation is shown to occur in a layer-by-layer fashion, the oxygen insertion between the second and the third layer is not considered. Among various adsorption sites, the on-top site [denoted as T in Fig. 4(a)] is shown to be energetically unfavorable,⁵ which can simply be understood from the number of O–Si bonds. We can then suggest the favorable structures as those without the T -site occupation, i.e., $BB1$, BD , and $BB2$ (BBD), respectively, for the Si^{2+} (Si^{3+}) species. For the very initial stage, a rather preferential adsorption on C -type defect sites was indicated,²³ which may lead to structures not shown in Fig. 4. However it can be noted that the typical density of C -type defects is not enough to cover the whole surface with adsorbate complexes in a uniform stoichiometry as indicated in Fig. 3. Even in the case that the adsorption on the defect sites cannot be neglected, the structures discussed here can be good starting points of theoretical considerations.

As a very plausible explanation of the formation of the Si^{2+} and Si^{3+} species, we suggest the active capture of molecular precursors by the Si surface atoms with a pre-adsorbed atomic oxygen. That is, the molecular precursors might be preferentially captured by the Si^{1+} species, which would lead to the dissociation of oxygen molecules on those sites. In fact, a recent scanning tunneling microscopy study²⁴ and *ab initio* calculation²⁵ have shown that, on the $\text{Si}(111)$ surface, the molecular precursors stay on the Si surface atoms with an oxygen adsorbate inserted into a back bond (similar to B in Fig. 4). This configuration can provide a natural pathway for the agglomeration of oxygen adsorbates to form the Si^{2+} and Si^{3+} species.

We then turn to the discussion of the anomalous core-level shifts of the Si^{2+} and Si^{3+} components. For this purpose, we investigated the change of the Si $2p$ line shapes by annealings at 400–1200 K following oxygen exposures at 120 K. Annealing below ~ 500 K induced little changes in the Si $2p$ line shapes. The Si $2p$ spectra and their decompositions after the annealing at 530 K are shown in Figs. 2(c) and 2(d). Upon the annealing, the oxygen-related components undergo drastic changes in binding energies as well as intensities. For all O_2 doses studied here, the same trend can

be observed (see Figs. 2 and 3): (i) the increases of the binding energies of the Si^{2+} and Si^{3+} components by 0.14 and 0.23 eV, respectively, (ii) the increases of intensities of the Si^{3+} and Si^{4+} components at the expense of that of Si^{1+} , and (iii) a sharpening of the Si^{1+} , Si^{2+} , and Si^{3+} components. This result indicates that the annealing above ~ 500 K enhances the agglomeration of adsorbates by a rearrangement of the adlayer configuration. That is, the adsorbate complexes formed at 120 K are *metastable*. Similar annealing-induced changes of the adsorbates were recently observed for the initial oxidation of Ge(001).²⁶

As far as the core-level shifts are concerned, further annealings to higher temperatures did not induce further changes and the Si 2*p* binding energies of the suboxides after the annealing at 530 K are already identical to those of the thermal oxides. The binding energy of Si^{4+} is still 0.2 eV smaller than that of the thermal oxide, which is explained by the well-known charging effect of SiO_2 layers.⁹ This charging effect, however, cannot explain the annealing-induced shifts of the $\text{Si}^{1+}\sim\text{Si}^{3+}$ components since (i) the charging due to SiO_2 layers is not possible in the submonolayer range, where no such layers are present, and (ii) the binding energies of the suboxide components are identical for the annealed spectra and for the thermal oxide irrespective of the large difference in the SiO_2 thickness. The invariance of the Si^{4+} binding energy before and after the annealing supports the former argument. Thus it can be concluded that *the anomalous core-level shifts of the Si^{2+} and Si^{3+} components are intrinsic properties of the metastable adsorbate complexes formed at 120 K*. It is suggested that the annealing-induced changes of the binding energies are due to

a certain change of the adlayer chemistry and structure. We note that this is a clear experimental demonstration of the sensitivity of the Si 2*p* binding energies of $\text{Si}^{1+}\sim\text{Si}^{4+}$ species beyond the chemical shifts without any uncertainties due to charging or other artifacts.

The possible origins for the annealing-induced shifts are structural changes of the metastable adsorbate complexes and/or changes in the second nearest-neighbor configuration. Although the latter effect has been poorly understood,⁹ a recent *ab initio* calculation of the Si 2*p* core-level shifts reported that a shift of ~ 0.2 eV for the Si^{4+} component is induced by the changes of Si-O bond angles and bond lengths.¹⁴ Thus it is plausible to attribute the observed shifts of the Si^{2+} and Si^{3+} components (0.1–0.2 eV) to such structural changes of the suboxide complexes induced by annealing. The metastable adsorbate complexes formed at 120 K (shown in Fig. 4) are, then, suggested to be strained in terms of the optimal Si-O bond angles and bond lengths, which are relaxed by annealing. The fact that this change needs a certain critical temperature (~ 500 K) supports the present argument of the strain relief by annealing. The structural effects on the Si 2*p* core-level shifts are not enough to make the orthodox interpretation ambiguous for each suboxide component in the case of the initial oxygen adsorption. It is not clear if this sort of structural deformation can also explain the previous observation of the large deviation of Si 2*p* core-level shifts for the model molecular adsorbates.^{13,14}

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