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Multiple-bonding configurations for oxygen on silicon surfaces

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Using high-resolution core-level spectroscopy we show that up to four different oxidation states of silicon coexist even at monolayer oxygen coverage. This observation precludes current models with a single adsorption geometry. Below 0.2 monolayer coverage, a single oxidation state is seen but the (100) surface has an oxygen-bonding geometry different from the (111) surface evidenced by different valence states and work-function changes.

The chemisorption of oxygen on silicon surfaces has been intensely studied over many years.[1-13] The appeal of the oxygen-silicon system lies in the unique properties of Si-SiO_2 interfaces and of SiO_2 thin films which make silicon such a useful material for semiconductor devices. Surprisingly, the chemistry of oxygen adsorption on silicon is far from being understood. Many different bonding geometries have been proposed which might be classified into atomic[4] and molecular[2,3,5] adsorption models. Most of the discussion has been concentrated on distinguishing between these two classes[2,7,11-15] and on finding evidence for a single atomic[4,13] or molecular[5,12] configuration.

In this Rapid Communication we show that such an approach is inappropriate since several different bonding geometries coexist even at monolayer coverage where the bulk of previous experiments[2-11] has been performed. Using high-resolution core-level spectroscopy we identify up to four different oxidation states of Si surface atoms which could correspond to even more bonding geometries. A single oxidation state is found only a very low coverage ($\lesssim 0.2$ layer of oxidized Si atoms). Even under such conditions the bonding geometries appear to depend on the crystallographic orientation as evidenced in different valence states and opposite work function changes for Si(100) vs Si(111)-(7×7). The same four oxidation states are seen for many different preparation conditions. This observation allows us to simplify the current picture for the oxygen chemisorption on Si by considering only the four oxidation states of tetravalent silicon and not many different bonding geometries.

Using synchrotron radiation from Tantalus I and a 3-m toroidal grating monochromator combined with an ellipsoidal mirror spectrometer[16] we have taken angle-integrated (1.8 sr) Si $2p$ core-level spectra with high energy resolution (~ 0.2eV) and surface sensitivity (~ 5.4-Å escape depth[17] at $h\nu = 120$ eV). Special care was taken to obtain a quantiative estimate for the secondary electron background by taking spectra at different photon energies (112 and 120 eV) in the same kinetic energy range (see Fig. 1). After background subtraction the spectra were spin-orbit decomposed using an intensity ratio of Si $2p_{3/2}$/Si $2p_{1/2} = 0.52$ and a splitting of 0.61 eV (see Refs. 17 and 18). The splitting is an atomic quantity and not affected by oxygen adsorption. The intensity ratio is influenced by final-state effects[19] but any change in the density of final states induced by oxygen is smoothed out by a lifetime broadening of several eV. After spin-orbit decomposition, some structure remains at about 1.5 eV below the Si $2p_{3/2}$ level for clean Si surfaces (see Fig. 2) which could be due to bulk or surface-energy losses. The data-processing procedure shown in Fig. 1 reveals chemically shifted core-level features which are not discernible in the raw data.

Figure 2 shows multiple Si $2p_{3/2}$ core-level shifts for oxygen adsorbed on three different Si surfaces [annealed Si(100)-(2×1) and Si(111)-(7×7) and cleaved Si(111)-(2×1)]. The exposures (in L, 1 L $=10^6$ Torr sec) range within the initial "fast adsorption" regime which ends at about 1000 L.[20,21] The oxygen coverage has been estimated from the intensity of chemically shifted core levels[22] and from the intensity of oxygen valence states. The number of chemically affected surface atoms scales with the intensity of O $2p$ valence states with a scatter of about ±0.15 monolayers. Four discrete core-level shifts are observed (-0.9, -1.8, -2.6, and -3.5 eV) for the oxygen-exposed Si(111)-(7×7) surface; only three states dominate the (100)-(2×1) and (111)-(2×1) surfaces with shifts at -1, -1.8, -2.6 eV. After annealing to 700 °C four states are detected for both (111) and (100) surfaces (not shown) with shifts at -1.0, -1.8, -2.7, and -3.5 eV. The similarity

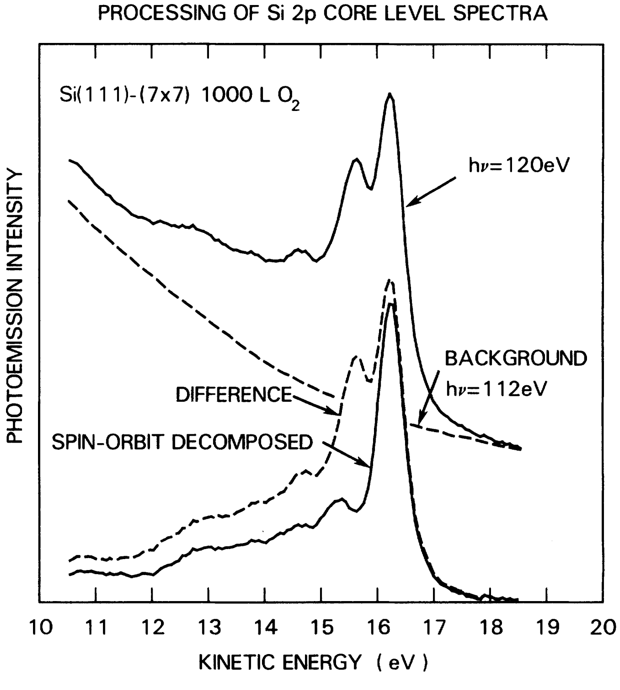

FIG. 1. Subtraction of the secondary electron background and spin-orbit decomposition for the Si $2p$ core level.

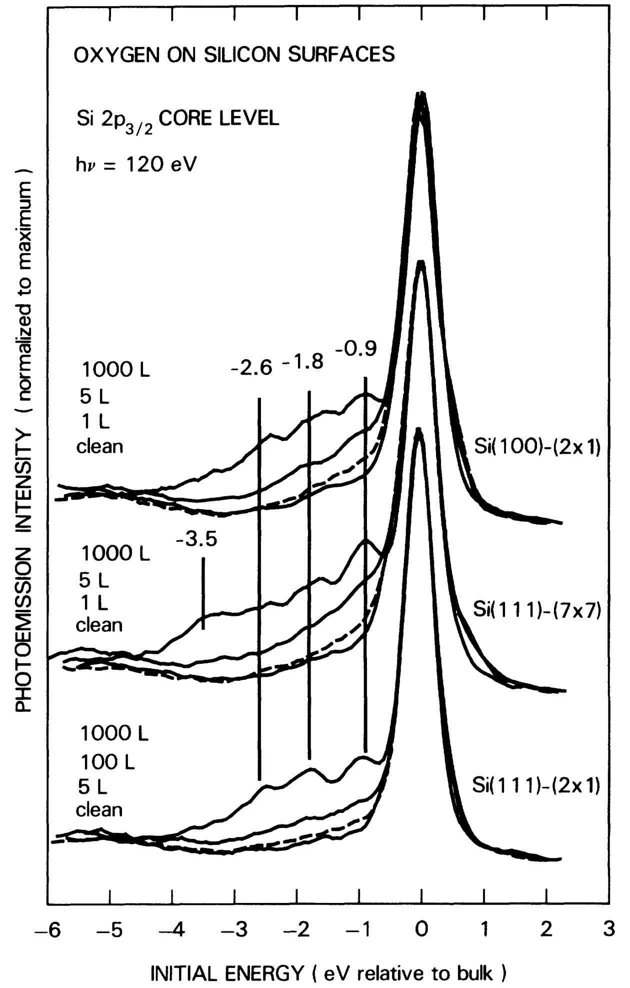

FIG. 2. Multiple core-level shifts for oxygen adsorption in the monolayer range at three different Si surfaces. The spectra have been decomposed as shown in Fig. 1. Pressures are equal to 10^{-8}, 5×10^{-8}, 10^{-6}, and 10^{-5} Torr for 1, 5, 100, and 1000 L, respectively.

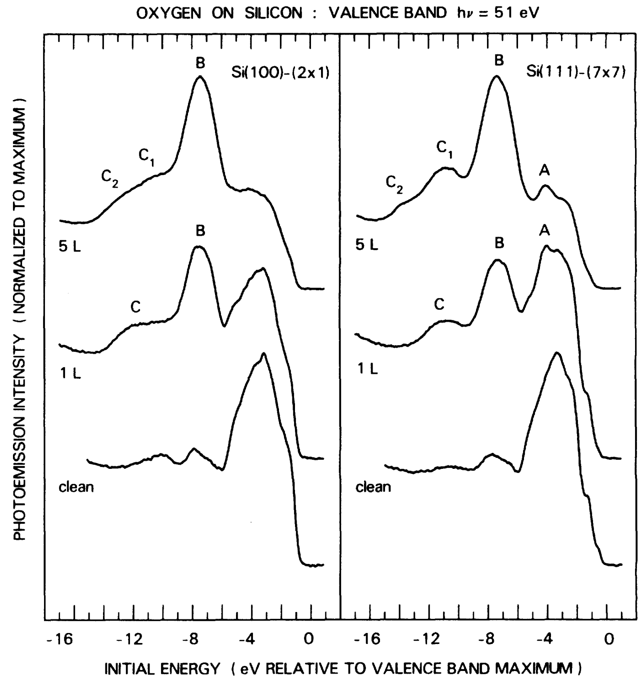

FIG. 3. Valence spectra for clean and oxygen-exposed Si(111) and Si(100) surfaces. At 1-L exposure (~0.2 layers) a single core-level shift of −1 eV exists for both surfaces (see Fig. 2) but the valence states exhibit an extra feature at $E_F-3.8$ eV for Si(111)-(7×7) which is absent for Si(100)-(2×1). The splitting of structure C into C_1, C_2 in the spectra at 5-L exposure is characteristic of multiple oxidation states.

of the chemical shifts obtained in these different situations allows us to assign the four shifts to silicon atoms bonded to 1, 2, 3, and 4 oxygen atoms, respectively, analogous to a similar assignment proposed by Grunthaner *et al.*[23] for oxide films. Although these films were many layers thick and were grown at high temperature (1000 °C) the observed core-level shifts (−0.6, −1.5, −2.8, and −4.5 eV) are similar to ours and the differences could be explained by different second-nearest-neighbor geometries and by a change in extra atomic relaxation for SiO_4 units.[24] A decomposition into several discrete peaks has also been attempted for very high *in situ* oxygen exposures (10^6–10^{12} L) which yielded broadened chemically shifted core levels.[7] At lower oxygen exposures (~10^3 L, i.e., about 1.5 layer coverage[22]) a variety of core-level shifts has been reported[6-11] ranging from 0 to 2.7 eV depending on the exposure and annealing conditions. However, the discrete nature of four different shifts with only the intensity ratios depending on the preparation conditions has not been resolved.

In order to obtain a single bonding configuration we have lowered the oxygen coverage below a monolayer (Figs. 2 and 3). At 5-L exposure (~0.8 layer coverage[22]) one can still distinguish two oxidation states with core-level shifts of −1.0 and −1.9 eV for Si(111)-(7×7). For about 1-L exposure (~0.2 layer coverage) a single core-level shift of −1 eV prevails on the annealed Si(111)-(7×7) and Si(100)-(2×1) surfaces (dashed lines in Fig. 2). The cleaved Si(111)-(2×1) surface has a lower sticking coefficient and exhibits a wide range of core-level shifts down to our detection limit. The valence-band spectra in Fig. 3 demonstrate that even a common core-level shift of −1 eV at low coverage does not imply identical bonding geometries. For Si(111)-(7×7) an oxygen-induced feature (A) is observed at 3.8 eV below E_F which is absent for Si(100)-(2×1). This extra feature seems to be correlated with a work function increase (by up to 0.7 eV at 5-L exposure) on Si(111)-(7×7) which is in contrast to a negligible work function change on Si(100)-(2×1) (decrease by 0.02 eV at 5 L). For comparison, the effect of multiple oxidation states on the valence spectra is shown in Fig. 3 (top). The lowest valence feature (C) splits into C_1 and C_2 as soon at multiple oxidation states are seen.

A single oxidation state is observed only for $\lesssim 0.2$ layer coverage. The core-level shift corresponds to a silicon atom bonded to one oxygen atom. The present data show that different initial adsorption geometries exist on the (111) and (100) surfaces since different features are seen in their valence-band spectra. In the case of the (111)-(7×7) reconstructed surface the large work function increase favors a top site for the initial adsorption. Atomic or molecular oxygen adsorption states should produce different structures in the electron density of states probed in the valence-band spectra. According to the theoretical calculations,[13-15] the main O $2p$ band at −7.5 eV seen in Fig. 3 is characteristic of an atomic adsorption, whereas molecular adsorption should give states at lower binding energy (in the region of the band A). This suggests that even in the first step of the adsorption (0.2 monolayer coverage) the atomic species are predominant. To decide whether or not some molecular species exist as minority species requires analysis of high-resolution O $1s$ core-level data, temperature-dependent experiments, and calculations for different adsorption geometries such as those described in Ref. 11.

Our observations affect the current picture of oxygen adsorption on Si surfaces. Present thinking concentrates on finding one single adsorption geometry in the monolayer regime for each preparation condition (e.g., activated versus ground-state oxygen, annealing after exposure or not, different surface reconstructions). We simplify the picture of many preparation-dependent configurations by resolving only four oxidation states with preparation-dependent relative intensities. We show for the first time that, at a monolayer coverage, all four oxidation states can exist simultaneously and we explain their origin. Multiple oxidation states persist into the submonolayer regime. From the relative abundance of different oxidation states it appears that most of the oxygen molecules are dissociated and that Si–Si bonds have been broken to form oxidelike Si–O–Si chains before the first Si layer is completely oxidized. It is therefore demonstrated that at one monolayer coverage the adsorption of oxygen is mainly atomic[4,13] in agreement with a very recent vibrational-loss study[25] and cannot be described by a single molecular state[5,12] as proposed in earlier studies. The distribution of oxidation states provides a convenient description of the chemical environment of the Si atoms which complements vibrational loss and surface-extended x-ray-absorption fine-structre (SEXAFS) experiments where the Si–O bond strength and bond length are probed. Such a concept promises to be useful for other disordered chemisorption systems as well.

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[20] The oxygen pressure was measured with an ion gauge. During exposure the sample was not facing the gauge and the influence of excited oxygen is expected to be small. This is confirmed by comparing our spectra from oxygen-exposed Si(111)-(7×7) and Si(111)-(2×1) surfaces with those obtained by Su *et al.* (Ref. 10) after exposure to nonexcited oxygen.

[21] A more extensive account of this work including a wide range of exposure will be published.

[22] The intensity of chemcially shifted core levels I_s relative to the total core-level emission I_t has been converted into a coverage θ of oxidized Si atoms (in monolayers) using a continuum model:

$$\theta = l/d \ln[I_t/(I_t - I_s)]$$

with a mean free path $l = 5.4$ Å and a lattice plane spacing $d = 1.36$ Å.

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