

Metastable Molecular Precursor for the Dissociative Adsorption of Oxygen on Si(111)

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The initial adsorption of oxygen on Si(111) surfaces proceeds via a molecular intermediate which is a precursor to the stable dissociated adsorption state. This metastable precursor can only be observed under certain conditions; its conversion to the stable state depends on temperature, probe, surface structure, impurities, and oxygen coverage. The precursor is likely to be a peroxy-bridge configuration whereas the stable dissociated oxygen species forms short-bridge bonds between adjacent Si atoms.

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The analysis of the initial stages of oxygen adsorption on silicon is one of the most widely studied and most lively discussed topics in surface science. This interest was prompted by the technological importance of SiO₂ films grown on silicon and the unique properties of the Si-SiO₂ interface. Moreover, this adsorption system has emerged as a test and model system for our microscopic understanding of oxygen adsorption on semiconductor surfaces. In spite of numerous investigations with a variety of analytical methods, most of the fundamental questions related to this system remained unanswered. This is particularly true for the key point, the bonding geometry, for which several different models have been proposed. These may be broadly classified into atomic (dissociated)¹⁻¹⁰ and molecular^{2,3,9-13} adsorbate configurations. The central issues are still the distinction between different geometric and electronic structures as well as the question of the number of and nature of oxygen states under certain, well-defined conditions.

In this Letter we show for the first time that, at least in the low-coverage regime, a *metastable molecular* state precedes the dissociated (atomic) stable adsorption state(s). Under certain conditions this molecular state is sufficiently long lived to be observable in a normal surface experiment. Its decay time strongly depends on temperature, surface structure, impurities, and probing technique. Our results (1) prove the existence of a molecular oxygen adsorbate on silicon, (2) allow a clear distinction between molecular and dissociated oxygen states, and (3) present the observation of a reaction intermediate since the molecular state forms the immediate precursor to dissociation. This latter result is of great practical interest for a better microscopic understanding of the dissociation mechanism¹⁴ and can be utilized for explaining, for instance, the adsorption kinetics.¹⁵

The experiments were performed in a modified VG ESCALAB I apparatus equipped with capabilities for x-ray and polarized-uv photoelectron spectroscopy (XPS, UPS), low-energy electron diffraction (LEED), and quadrupole mass spectrometry. The (111)-oriented Si samples (10×10×2 mm³, *n* type) were

polished, and then cleaned *in situ* by sputtering and annealing. The best samples in terms of stability of the molecular precursor showed absolutely no impurities (e.g., metal atoms or carbon) with XPS and exhibited a very sharp (7×7) LEED pattern. The crystals could be cooled to 150 K and were exposed to oxygen through a beam doser consisting of a capillary array in front of the Si surface.⁶ This doser made it possible to reproduce oxygen doses very accurately (1%) without detectable traces of impurities (< 0.1%) and without excitation of gas molecules by a hot filament or ion pump.

The existence of the metastable precursor, and its subsequent decay, are best illustrated by the XPS results shown in Fig. 1. On the left-hand side, original O 1s core spectra of oxygen adsorbed by an exposure of 2.5 L [1 L (langmuir) = 10⁻⁶ Torr sec] on a (7×7)-reconstructed Si surface at 150 K are displayed.

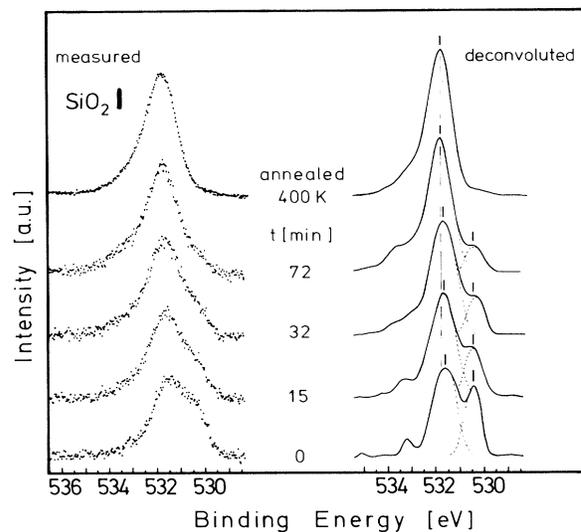


FIG. 1. Original (left) and deconvoluted (right) XPS O 1s spectra of (7×7) Si(111) exposed to 2.5 L O₂ at 150 K. Recording was started at time *t* (minutes) after adsorption, or after mild annealing. The energy position of SiO₂ is indicated (Ref. 16). Energies are referred to the Fermi level.

The spectrum at the bottom was taken immediately after dosing; the next three spectra were recorded starting after the times indicated in the figure, whereas the spectrum at the top was obtained after annealing of the crystal to 400 K. With the improved resolution of our XPS spectrometer (total instrumental resolution without monochromator, 0.75 eV FWHM) one can clearly distinguish a major O 1s peak at 531.6 eV and a shoulder at 530.5 eV. This shoulder rapidly decreases with time and disappears after annealing. Annealing employed to accelerate the decay of the shoulder led to the same results as otherwise obtained after sufficiently long elapsed times. We also show deconvoluted spectra on the right-hand side of Fig. 1 which were obtained by deconvolution of the known (measured) instrumental function from the original spectra by a modified Jansson-van Cittert method.¹⁵ These spectra contain information exclusively due to the adsorbate without experimental broadening contributions and demonstrate more clearly the occurrence of a second, metastable adsorbate state and its conversion into a stable species. As will be discussed below, the major peak at 531.6 eV represents a dissociated (atomic) oxygen state (stable species), whereas the peak at 530.5 eV can be attributed to a molecular peroxy species. The small peak at 533.5 eV for $t=0$ (Fig. 1) is likely to be a satellite of the molecular species; for higher coverages or temperatures other structures which are due to silicon oxides appear in this energy range.^{15,16} We emphasize that the total amount of adsorbed oxygen stays constant upon the decay of the metastable species which means that *all* precursor molecules are converted to dissociated oxygen.

The results of a quantitative evaluation of the precursor decay under different conditions are shown in Fig. 2, which is a semilogarithmic plot of relative precursor intensity (referred to total oxygen intensity) versus time. Within experimental accuracy all equivalent data points lie on straight lines, indicating exponential decay of the precursor. A very important

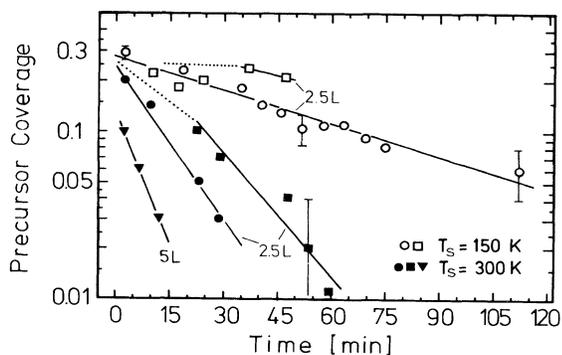


FIG. 2. Semilogarithmic plot of relative precursor intensity (referred to total oxygen coverage) versus time. Dotted lines represent intervals with the x-ray source turned off.

finding is the influence of substrate temperature and x-ray irradiation dose on the conversion rate. The precursor decays much more rapidly at room temperature (full circles, half-time 10 min) than at 150 K (open circles, half-time 45 min). These and similar data obtained at 400 K¹⁵ can be utilized to derive its thermal activation energy which is 0.2–0.3 eV, with account taken of the influence of x-ray irradiation which is also shown in Fig. 1. Without x-ray irradiation (dotted lines) the decay process is markedly retarded, proving that besides thermal activation electronic processes can also stimulate the dissociation reaction. We note that uv photons did not increase the decay rate, indicating that two- (or more-) hole final states created by an Auger decay of the O 1s core hole are more effective for the dissociation reaction than one-hole final states. A similar behavior has been found for desorption processes of molecular adsorbates.¹⁷

Surface structure (e.g., steps) and impurities also play a major role for the lifetime of the precursor. The longest lifetime could be obtained with a (7×7)-reconstructed, entirely clean Si(111) surface showing a very sharp LEED pattern. The decay was considerably faster, with increasing decay rates in this order, for (1) a sputtered and mildly annealed surface with no long-range order, (2) a quenched (1×1), Ni-stabilized surface,⁶ and (3) a totally disordered Si surface obtained by sputtering without annealing. For the (1×1) Ni surface the precursor was hardly detectable even at low temperatures (150 K) and for small amounts of Ni impurity atoms (≈ 0.01 monolayers). Less than 0.05 monolayer of C impurities did not influence the relative amount of precursor while enhanced C contamination caused some reduction. For exposures higher than 2.5 L O₂ the relative fraction of the precursor, observed immediately after dosing, decreased and the decay rate increased markedly; for doses higher than 5 L even the absolute precursor coverage decreased. For instance, about 10 L at room temperature, or 100 L at 150 K, were sufficient for suppression of the precursor.

We emphasize that the short lifetime at room temperature and the influence of x-rays or high-energy electrons, defects, more open surface structures, impurities, and higher doses of oxygen are the reasons that the precursor was not detected or identified as a metastable state in previous investigations. Some of the discrepancies in the literature may be explained by the occurrence and time dependence of this metastable adsorbate species.

In Fig. 3 selected UPS spectra are compared. The spectra in the middle represent a mixed layer of precursor (30%–40%) and stable state (60%–70%), and the spectra at the top, the latter state only. The comparison of clean and stable-state spectra shows that the structures labeled 7–9 are predominantly due to the stable state. The major part of the Si-derived valence

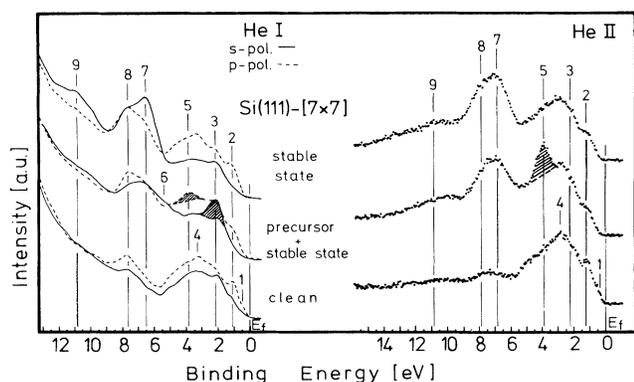


FIG. 3. He I ($h\nu = 21.2$ eV, polarized) and He II (40.8 eV) spectra of three different surface layers for normal emission. Adsorbate preparation for the top and middle spectra are the same as for the top and bottom spectra of Fig. 1. Hatched peaks indicate the precursor.

band between 0 and 6 eV is hardly affected by the presence of the stable species apart from some overall attenuation. The precursor state, on the other hand, has minor influence on the spectra in the energy range above 6 eV but results in two prominent (hatched) peaks labeled 3 and 5 for He I and one peak (5) for He II, respectively.

So far we have concentrated on the conditions under which the precursor can be observed. We now turn to the characterization of the low-coverage states. The stable state can unambiguously be described as dissociative, most probably as oxygen atoms in a short bridge between two Si atoms in the first and second layer as has been suggested earlier^{2,5} [Fig. 4(c) or 4(d)]. Convincing arguments for this model can be derived from high-resolution electron-energy-loss (HREELS) data,² core photoemission spectra,^{1,15} or high-resolution Auger spectra.^{6,15} It is further corroborated by comparing various calculations⁷⁻¹⁰ with our UPS spectra of Fig. 3. The calculations for dissociated O adsorbates are compatible with peaks above 6 eV, as our peaks 7-9, but not with peaks 3 and 5. However, the fact that the major oxygen-derived structure is split into two peaks (labeled 7 and 8 in Fig. 3) clearly excludes the on-top position [Fig. 4(f)] and the unlikely long-bridge model [Fig. 4(e)], but supports the short-bridge model [Figs. 4(c) and 4(d)].^{8,9} Moreover, the observed relative positions of peaks 7-9 and, in particular, their dependence on uv polarization (Fig. 3) agree very well with calculations for the short-bridge configuration. Because of symmetry selection rules for our experimental geometry p_z , a_1 , or σ states are expected to be predominantly observable for p polarization and to be quenched for s polarization, whereas the opposite is expected for $p_{x,y}$, b , or π states. With account taken of some tilt of the symmetry axis in the local C_{2v} adsorbate symmetry [see Figs. 4(c) and 4(d)], the results

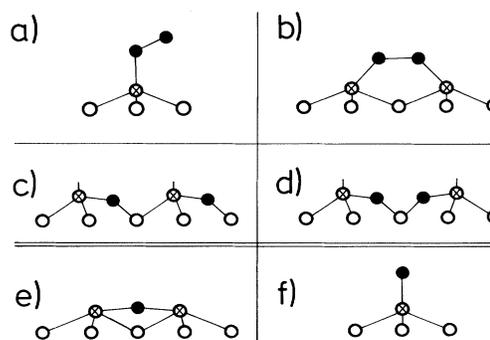


FIG. 4. Selected models for adsorbed oxygen on Si: (a) Peroxy radical and (b) peroxy bridge represent conceivable configurations of the molecular precursor. (c), (d) Very likely and (e), (f) rather unlikely representations of the stable dissociated state. Full circles, oxygen atoms; open circles with (without) crosses, Si atoms in the first (second) layer.

of Fig. 3 are fitted excellently by the short-bridge model: Peak 7 represents the nonbonding $2b_1$ orbital,¹⁸ or O_π band,⁸ respectively, and is most intense for s polarization, similar to peak 9 which can be attributed to a bonding $5b_2$ -type bond.¹⁸ Peak 8, on the other hand, has local a_1 character and should thus be dominant for p polarization.¹⁸

The same arguments can be applied to characterize the nature of the precursor state. Most calculations^{9,10} apparently agree that intense UPS structures close to the valence-band edge must be due to molecular adsorbate states (split π_g orbital of oxygen). Therefore our peaks 3 and 5 which are unambiguously correlated with the presence of the precursor clearly indicate its molecular nature. A molecular precursor is also consistent with the rather low O $1s$ binding energy of 530.5 eV which has also been found for molecular O_2 on Pt(111)¹⁹ and Ag.²⁰ This interpretation is further corroborated by the appearance of additional features in high-resolution Auger spectra,¹⁵ by a large work-function increase of up to 0.65 eV in the presence of the precursor¹⁵ as compared with 0.2 eV, at most, for the stable state, and, in particular, by the HREELS results of Ibach, Bruchmann, and Wagner.² These authors observed additional losses at 1230 cm^{-1} after adsorption at low temperatures which they attributed to molecular oxygen adsorbates. While they preferred the peroxy radical model [Fig. 4(a)] for this species, our results make it more likely that the peroxy bridge bond [Fig. 4(b)] is an adequate description for the precursor state, for three reasons. First, the close similarity between our XPS and UPS results for the precursor and those for molecular O_2 on Pt and Ag indicates a lying, bridge-bonded configuration since this has been proven at least for $O_2/\text{Pt}(111)$.¹⁹ Secondly, according

to the calculations of Goddard, Redondo, and McGill for the peroxy radical¹³ the peak with lowest binding energy (labeled 3) should have p_z and $p_{x,y}$ character, and the next one (peak 5) only $p_{x,y}$ character which is in contradiction to the polarization dependence of these peaks (see Fig. 3). Thirdly, in the case of a peroxy radical two O 1s peaks separated by 1.3 eV are expected, belonging to the two inequivalent oxygen atoms.²¹ However, the XPS spectra of Fig. 1 are not compatible with such a model: Assuming that the major peak at 531.6 eV contains a fraction of the precursor, which should be equally intense as the peak at 530.5 eV, would result in a ratio of 1:2 for atoms in the stable state relative to those in the precursor. This is in disagreement with the relative change of the UPS He II peaks 7 and 8 in Fig. 3 which show only a 50% increase of the stable state as expected for a peroxy-bridge model. A coincidence of two O 1s levels (the peak at 530.5 eV is rather narrow!) appears to be unlikely as a result of the inequivalence of the two O atoms in the peroxy radical.

The peroxy bridge also appears to be a rather plausible model for a metastable precursor which then converts to a short-bridge configuration (Fig. 4). The oxygen molecule first uses the dangling bonds of two silicon atoms in the first layer for adsorption [Fig. 4(b)] thereby weakening the intramolecular oxygen bond. Then thermal or electronic activation causes the oxygen atoms to flip from the peroxy molecule bond into backbonds between the involved Si atoms in the first layer and adjacent Si atoms in the second layer [Fig. 4(c) or 4(d)]. This picture would require dangling bonds to disappear upon precursor adsorption as a result of their being involved in the bond and to reappear upon conversion to the stable state which does not require them for bonding. In fact, such a behavior of the dangling bonds can be observed in the UPS spectra (peak 2 in Fig. 3) if one takes into account that the formation of the stable state causes some atomic rearrangement in the surface layer influencing the occupation of dangling bonds.

Finally, we note that the adsorption behavior of oxygen ("fast adsorption stage" followed by "slow sorption process"), which has been discussed since the first experiments were performed,⁵ and the temperature¹⁵ and time³ dependence of the adsorption kinetics can easily be understood by applying the present two-stage adsorption model.¹⁵ One main question concerning the lifetime of the precursor remains to be answered. We have discussed above that surface structure, impurities, and oxygen coverage strongly influence the lifetime of the precursor, indicating that local geometry and electronic structure (e.g., availability of dangling bonds) play a major role for its stability. Maybe only the (7×7) -reconstructed Si(111) surfaces make suitable adsorption sites available for sufficiently

long lifetimes. One can also speculate that some coadsorbed dissociated oxygen is necessary to stabilize the metastable precursor state.

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