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Atomic versus molecular reactivity at the gas-solid interface: The adsorption and reaction of atomic oxygen on the Si(100) surface

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The reaction of atomic oxygen with the Si(100) surface has been examined by employing supersonic beam techniques. Atomic oxygen adsorbs with unit probability on the clean Si(100) surface. The rate of oxidation decreases rapidly with increasing coverage up to ~3–4 monolayers, followed by a regime that exhibits a weaker dependence on coverage. At surface temperatures above ~1000 K, atomic oxygen reacts with the substrate to produce SiO(g). The kinetics of this reaction depends on the nature of the gas-phase reactant: A single stable surface intermediate is formed from O(g), whereas two intermediates are implicated from $O_2(g)$.

Gas-surface reactions play important if not dominant roles in numerous physical phenomena of technological interest, which include heterogeneous catalysis, epitaxial growth, and corrosion. By far the great majority of fundamental examinations of gas-surface reactivity has involved the interaction between stable gas-phase molecules and solid surfaces.[1] In particular, the scientific literature is virtually devoid of quantitative, unambiguous comparisons of atomic versus molecular reactivity on solid surfaces (e.g., via molecular-beam techniques). In view of the increasing use of technologies based on exploiting the reactivity of atoms and radical species, a better understanding of the gas-surface chemistry is clearly desirable.

We have employed supersonic molecular-beam techniques to examine in detail the reaction between both atomic and molecular oxygen and the Si(100) surface. We shall emphasize here the reaction of atomic oxygen. Although the oxidation of silicon surfaces has attracted a great deal of interest from both technological and fundamental points of view,[2] the reactions of *atomic* oxygen remain largely poorly understood and unexplored.[1(a),3–5] We shall consider here both the initial stages of "passive" oxidation, i.e., formation of an amorphous $SiO_2(s)$ overlayer, and "active" oxidation, i.e., volatilization of the substrate to form SiO(g). It is possible that the surface intermediates involved in these two major reaction channels may be different, and, consequently, the rate of their formation may depend strongly on the nature (i.e., atomic versus molecular) of the gas-phase reactant. Thus, it is of interest to compare and contrast the behavior of atomic and molecular oxygen in regard to these two major reaction pathways.

The experiments were conducted in a molecular beam apparatus which contains facilities for x-ray photoelectron spectroscopy (XPS), low-energy ion-scattering spectroscopy (ISS), and mass spectrometry.[6] The Si(100) crystal, which is heated by a combination of radiative and direct resistive heating, is mounted on a rotatable liquid-nitrogen-cooled sample holder. The supersonic oxygen atom beam is generated by a radio-frequency glow discharge, essentially identical to that described previously.[7] Once formed, the beam passes through two intermediate differential pumping stages before striking the sample. In the first intermediate chamber the beam passes through a 10-cm-long, 3-kV/cm deflection field, which removes any ions present in the beam.

Mass spectrometric analysis of the direct beam is provided by a differentially pumped quadrupole, which is situated 110 cm downstream of the beam nozzle. Typically, the level of dissociation achieved in the beam was 40–70 %, with corresponding fluxes of atomic oxygen impinging on the sample of 0.01–1.0 $\mathrm{ML\,s^{-1}}$ [1 monolayer $(\mathrm{ML}) \equiv 6.8\times10^{14}$ $\mathrm{atoms\,cm^{-2}}$]. Since our nozzle discharge conditions (e.g., stagnation pressure, rf power, seeding gas) were bracketed by those employed by Sibener *et al.*,[7] we expect the beam to be composed of primarily ground-state oxygen atoms (^3P) and molecules. In particular, Sibener *et al.*[7] were unable to detect excited O(^1D) atoms in a beam composed of O_2-Ar mixtures, whereas production of O(^1D) was observed in O_2-He mixtures. However, even the O_2-He mixtures were composed primarily of ground state O(^3P) atoms (mole fraction >0.9).[7]

We have examined the kinetics of the adsorption of atomic oxygen on the Si(100) surface by employing XPS. From the measured coverage-exposure relationships [i.e., $\theta(\epsilon)$] we have derived the probability of adsorption of atomic oxygen (i.e., $S \equiv d\theta/d\epsilon$) as a function of coverage, substrate temperature, and average beam (translational) energy. These derived adsorption probabilities are shown in Fig. 1, where, for comparison, corresponding values for molecular oxygen derived from the data of D'Evelyn *et al.*[6] are also shown. Before discussing these results in detail, one important point must be made from Fig. 1. In particular, for all coverages, the reaction probability of atomic oxygen is much greater than that of molecular oxygen. This fact permitted us to essentially ignore the presence of nondissociated molecular oxygen in the beam of atomic oxygen, which greatly simplified the analysis.

As may be seen in Fig. 1(a), the initial (zero-coverage) probability of adsorption of atomic oxygen on the Si(100)

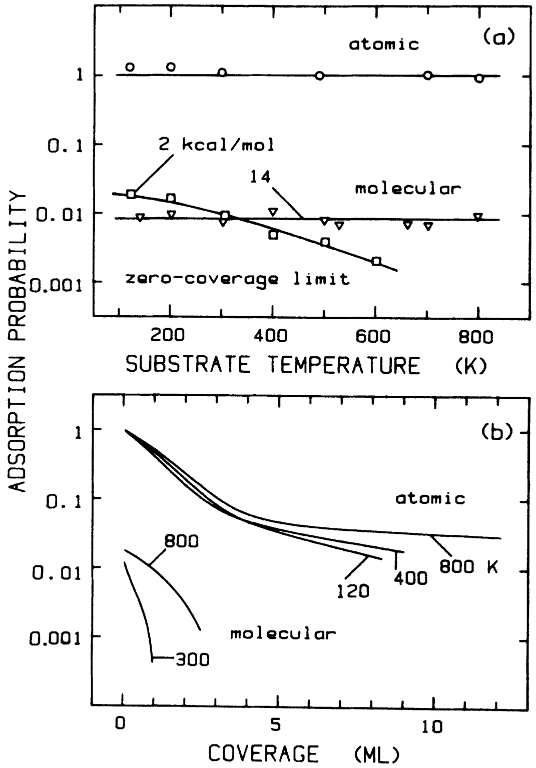

FIG. 1. Probability of adsorption of atomic and molecular oxygen on the Si(100) surface. (a) Adsorption probabilities at zero-coverage as a function of substrate temperature. Incident mean translational energies were 4 kcal mol^{-1} for O(g), and as indicated for $O_2(g)$. Incident angle in both cases was 75° from normal. (b) Adsorption probability vs oxygen coverage. Substrate temperatures are as indicated. Mean translational energies were 5 kcal mol^{-1} for $O_2(g)$, and 16 kcal mol^{-1} for O(g).

surface is essentially unity, i.e., 1.0±0.2, independent of substrate temperature ($T_s = 120-800$ K). An additional set of experiments indicates that the initial probability of adsorption is also insensitive to incident mean translational energy ($\langle E_{tr} \rangle = 4-16$ kcal mol^{-1}) and angle of incidence (23°–73° from normal). These observations are consistent with facile, "direct" adsorption of atomic oxygen. In contrast, the initial probability of adsorption of molecular oxygen on the Si(100) surface depends in a complex fashion on both average beam energy and substrate temperature, and varies between approximately 0.002 and 0.04.[6] Surface defects, such as atomic steps, have been suspected to play a role in the dissociative adsorption of O_2 on clean Si,[8] however no such behavior was found here for atomic oxygen. For example, the adsorption probabilities for atomic oxygen given in Figs. 1(a) and 1(b) were found to be essentially unaffected by sample history and sample-to-sample variations in surface perfection.

The coverage of oxygen obviously has a strong effect on the adsorption probabilities of atomic and molecular oxygen, as may be seen in Fig. 1(b). In particular, for atomic oxygen, the adsorption probability decreases rapidly with increasing coverage up to approximately 3–4 ML, followed by a much slower stage of adsorption above this coverage, which displays a weaker dependence on coverage. The "fast" stage of adsorption is described reasonably well by first-order Langmuirian kinetics [$S(\theta)=(1-\theta/\theta_s)$, $\theta_s \simeq 3-4$ ML], whereas the "slow" stage can be described by direct logarithmic kinetics [$S(\theta) \propto e^{-\alpha\theta}$].[9] Saturation of the fast stage of adsorption at 3–4 ML is consistent with the structure of the Si(100)-(2×1) surface. In particular, if we consider potential sites for bridging atomic oxygen, i.e., Si—O—Si, the following sites are roughly equally accessible, and equivalent to a surface concentration of 3.5 ML: insertion into the Si—Si dimer bond in the first layer [$\frac{1}{2}$ ML of O(a)]; between the first and second layers (2 ML); between the second and third layers not adjacent to the first-layer dimer (1 ML). Molecular oxygen shows a similar dependence on coverage, i.e., two stages of adsorption, however for O_2 the transition between the fast and slow stages of adsorption occurs near 1 ML (at $T_s = 300$ K). Concerning the effect of substrate temperature, for atomic oxygen the dependence is weak in the relatively fast stage of adsorption, whereas above 3–4 ML the rate of oxidation clearly increases with increasing substrate temperature.

The most interesting feature of the data displayed in Fig. 1(b) is the break in the kinetics observed for atomic oxygen at 3–4 ML. We have attempted a qualitative assessment of the configuration of the adlayer formed at 3–4 ML employing both XPS and ISS.[10]. Briefly, the ISS measurements suggest strongly that adsorption of atomic oxygen up to 3–4 ML is confined to the 2–3 topmost layers of the Si(100) substrate, whereas the XPS measurements are indicative of an adlayer composed of a mixture of oxidation states, Si^{+x}, where $x = 1-4$.[10,11] These results are consistent with the model suggested above for the structure of the adlayer at 3–4 ML, i.e., oxygen atoms occupying bridging positions in the 2–3 topmost layers of the Si(100) substrate. In regard to the oxidation kinetics, these results imply that oxidation above 3–4 ML is limited by transport of O (or possibly Si) across this oxide film.

Modulated molecular-beam reactive scattering techniques (MMBRS) have been applied to evaluate the kinetics of the reaction O(g)+Si(s)→SiO(g). Previous work[6,12] has identified the following reaction sequence for the reaction of molecular oxygen on the Si(100) surface:

$$O_2(g) \xrightarrow{S_{O_2}} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} \mathrm{SiO}(g)\ , \qquad (1)$$

i.e., the reaction pathway involves two intermediates, which are produced sequentially, with the further reaction of each intermediate following first-order kinetics. Note that the previous analysis,[6,12] which identified a "fast" and a "slow" step, could not unambiguously assign these two measured rate coefficients as to their order of occurrence, nor identify the intermediates I_1 and I_2. A Fourier analysis of the desorbing SiO(g) product waveforms, presented elsewhere,[10] indicates that the reaction of atomic oxygen follows a single-step, first-order process, involving a *single* intermediate. Thus, for atomic oxygen the reaction mechanism is given by

$$O(g) \xrightarrow{S_O} I' \xrightarrow{k'} \mathrm{SiO}(g)\ . \qquad (2)$$

The first-order rate coefficients derived from this analysis are plotted in Fig. 2. For comparison, the data derived for the molecular oxygen reaction are also shown. As may be seen, the rate coefficients k' for atomic oxygen are *identical*, within experimental uncertainty, to those found for the "slow" reaction step involving molecular oxygen.

The most reasonable interpretation of the results displayed in Fig. 2 is the following. The adsorption of atomic oxygen results directly in the formation of the intermediate designated I_2 in Eq. (1). Consequently, the rate coefficient measured for atomic oxygen, k', is identical to that measured for the slow, second step for molecular oxygen, i.e., k_2. A likely candidate for the intermediate I_2 is an adsorbed diatomiclike monoxide species or surface silanone complex, Si—(Si$=$O)—Si.[13,14] Thus, the rate coefficient measured here for atomic oxygen, which is equivalent to the slow step for molecular oxygen, represents the desorption rate coefficient for this adsorbed monoxide species.

Several factors may be involved in explaining the observed differences between the reactivity of the atomic and molecular species, i.e., for both "active" and "passive" oxidation. First of all, obviously for the atomic species no chemical bonds in the gas-phase reactant need to be broken. In the case of the molecular species, chemisorption can be expected to involve interactions between both the empty surface states of the substrate and the filled bonding orbitals of $O_2(g)$, and the filled surface states and the antibonding orbitals of $O_2(g)$. If such a transfer of electron density involves significant overlap of the appropriate orbitals then one might expect facile chemisorption. If, on the other hand, the overlap is poor, then chemisorption may occur with low probability, which could be ascribed to a configurational requirement.[15]

A second factor that may influence reactivity is the overall energetics of the reaction. The reaction of both atomic and molecular oxygen with the clean Si surface is exothermic. However, obviously for the atomic species the reaction is more exothermic (by approximately 59 kcal mol^{-1}). Thus, liberation of this energy upon the adsorption of atomic oxygen could be funneled into a particular reaction channel converting, for example, a metastable adsorbed species into a more thermodynamically stable species. Such a conversion of adsorbed species upon adsorption may not be possible for the molecular species. Obviously, the rate of dissipation of the heat of adsorption by the Si substrate will determine if such a conversion between adsorbed species can indeed occur.

Possibly the most intriguing of the results reported here is the observation of different mechanisms for the active oxidation reaction. It is of interest to develop a microscopic understanding of this reaction. A possible scenario is depicted in Fig. 3. The (2×1) reconstructed Si(100) surface can be considered to consist of a topmost layer containing a single "dangling" bond, i.e., these bonds being almost free radical in character. A very like-

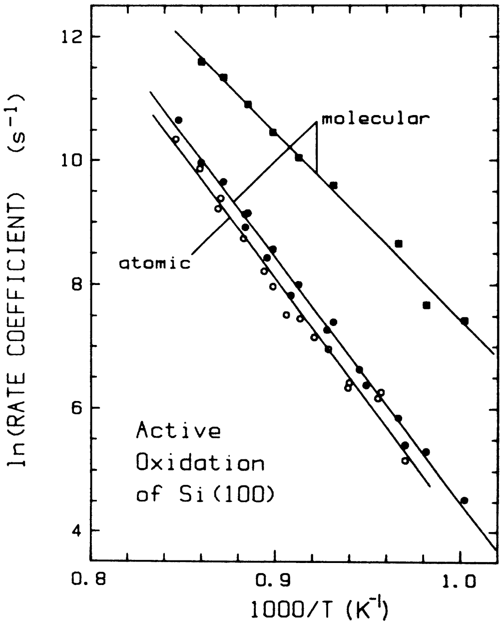

FIG. 2. Reaction rate coefficients for the formation of SiO(g) from the reaction of the Si(100) surface with atomic oxygen (open circles) and molecular oxygen [solid circles ("slow" step) and solid squares ("fast" step)].

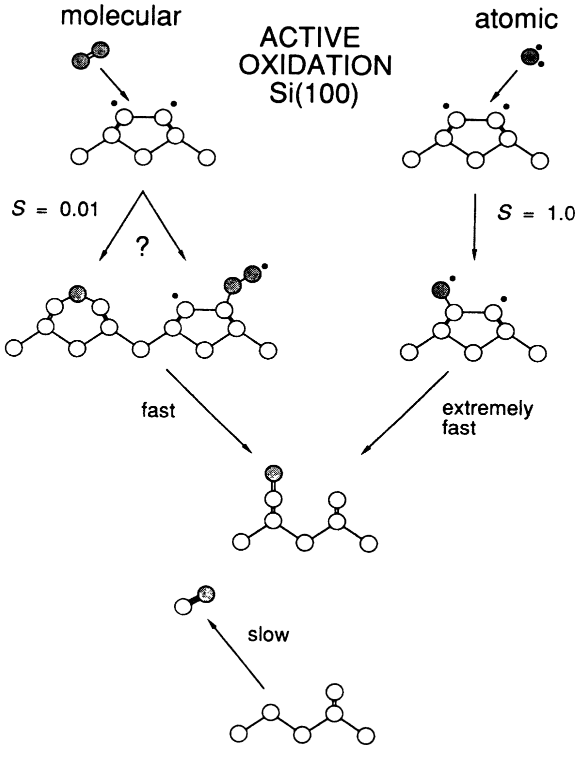

FIG. 3. Schematic representation of possible mechanisms for the "active" oxidation of the Si(100) surface, $O_x(g)+Si(s)\rightarrow SiO(g)$. Perspective is parallel to (100) surface, perpendicular to the surface dimer bond axis. Symmetric dimers are depicted for purely aesthetic reasons. The small solid circles represent partially filled molecular orbitals, i.e., dangling bonds. Only one of two possible bridging sites for O(a) is shown, i.e., oxygen atoms bridging between the first- and second-layer Si atoms is also a possibility.

ly initial interaction between ground-state (^3P) oxygen atoms and this surface is attachment to the dangling bond, forming a triplet diradical surface intermediate, ●O—Si—Si●. This species is probably metastable at best and decomposes extremely quickly ($\ll\mu$s) to form the monoxidelike adsorbed SiO(a) species. The release of the heat of adsorption of atomic oxygen no doubt facilitates this decomposition. It is of interest to note that gas-phase analogs of this reaction exist for the reaction of O(^3P) and halogenoethene molecules, C_2X_4, i.e., $O+C_2X_4 \rightarrow CX_2O+CX_2$,[16] in comparison to that depicted in Fig. 3, $O+L_2\text{Si-Si}L_2 \rightarrow L_2\text{Si}{=}O+L_2\text{Si}$, where L_2Si—SiL_2 is the surface dimer. Thus, in the case of atomic oxygen, our MMBRS measurements can only detect the rate of desorption of the monoxidelike SiO(a) species.

Two possibilities exist for the initial interaction between molecular oxygen and the Si(100)-(2×1) surface. First, recent work employing surface extended x-ray-absorption fine structure (SEXAFS),[17] suggests that the predominant species formed at 300 K from the adsorption of molecular oxygen on the Si(100) surface is a bridging atomic species, i.e., Si—O—Si. If we assume that the same holds true at 1000 K, then a probable two-step mechanism can be put forward. In particular, in the case of molecular oxygen our MMBRS measurements detect the relatively fast conversion from the bridging Si—O—Si species to the monoxidelike Si—(Si=O)—Si species, followed by the relatively slow desorption of the SiO(a) species. Second, it is possible that intermediate I_1 in Eq. (1) is an adsorbed *molecular* oxygen species, e.g., a peroxy radical[18] formed by attachment to a single dangling bond, or a peroxide bridge[19,20] formed by attachment to a pair of dangling bonds. In this case, the fast step detected by MMBRS would correspond to the dissociation of the peroxy species to form (presumably two) monoxidelike SiO(a).

Consideration of the second possibility must include a discussion of several experimental observations. For example, if a peroxy species were involved one would expect competition between its desorption and conversion to SiO(a). In particular, the reaction probability would be expected to be proportional to the ratio of rate coefficients: k_r/k_r+k_d, where k_r is the rate of conversion of the peroxy species to SiO(a), and k_d is the rate of desorption of the peroxy species. We have observed that the reaction probability of $O_2(g)$ is $\sim 10^{-2}-10^{-1}$, varying by less than a factor of 2 over the range 970–1150 K.[6,10] To be consistent with the lack of a temperature dependence we must have either $E_d \simeq E_r$ or $E_r \ll E_d$. The measured activation energy for the fast step involving $O_2(g)$ from Fig. 2 (i.e., E_r) is 60±2 kcal mol^{-1}, which implies that the binding energy of the molecularly bound O_2 (i.e., E_d) is ≥ 60 kcal mol^{-1}. This limiting value is remarkably close to the value estimated by Goddard *et al.*[18] for the binding energy of a peroxy radical species, namely 51–58 kcal mol^{-1}. Consequently, it would appear that our experimental results are also consistent with a reaction model involving a peroxy radical as an intermediate. Unfortunately, on the basis of our results, we cannot distinguish conclusively between these two mechanisms for the reaction of $O_2(g)$ on the Si(100) surface.

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[3] Recent experiments employing oxidants other than $O_2(g)$, such as $N_2O(g)$ (Refs. 4 and 5) are useful, however such studies provide little information concerning the reactivity of (ground-state) oxygen atoms, which we address in detail here. Likewise, photolysis of N_2O with 193-nm radiation (Ref. 5) produces excited ^1D atomic oxygen, which can also produce excited NO by further reaction with N_2O.

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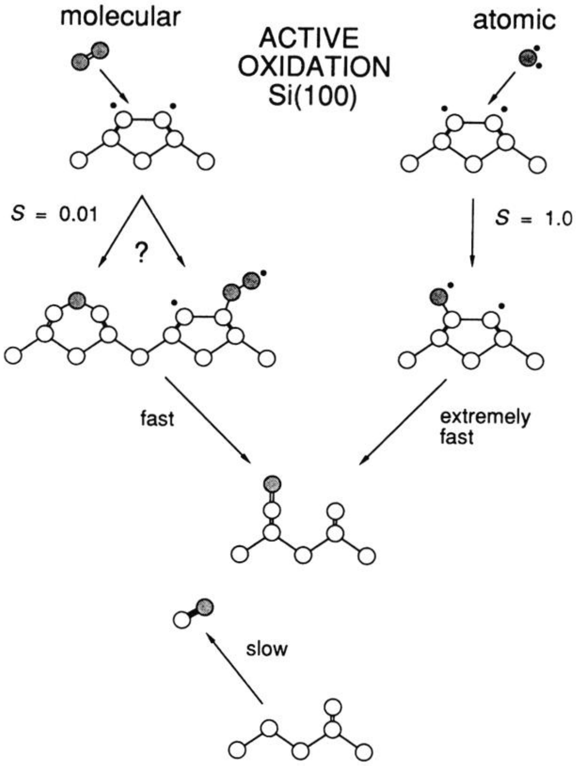

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