Real-Time Study of Oxygen Reaction on Si(100)

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The reaction of oxygen Si(100) surfaces from 700 to 950 °C has been studied in real time with about 10-μs resolution, by use of pulsed molecular-beam reactive scattering. The oxygen reaction probability is roughly proportional to the normal component of the incident velocity of the O_2 molecule. An intermediate step between the initial adsorption of oxygen and the desorption of SiO was observed.

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A key to the understanding of reactions of gas molecules with solid surfaces is the unraveling of the chemical kinetics of the interaction. Molecular-beam–surface scattering has been shown to be a very useful probe.[1] The important quantity is the impulse-function response $R(t)$ which gives the time evolution of the reaction product for a δ-function reactant pulse impinging on the sample. With it, the evolution of the reaction product can be determined by a simple convolution with the incident reactant waveform. The conventional approach[2] is to use a square-wave–modulated (typically ~200 Hz) molecular beam to impinge on the sample. The amplitude and phase of the reaction-product signal are measured at different modulation frequencies. An amplitude-phase locus plot of the Fourier transform of $R(t)$ for the reaction is then obtained after the appropriate data analysis. In this paper we report a new approach. By use of very short pulses of molecules, in combination with time-resolved mass spectrometry, the surface kinetics can be studied in *real time* with a resolution in the tens of microseconds. This compares favorably with the time resolution in other real-time surface-reaction studies, by use of electron-energy-loss spectroscopy[3] (~10 ms) or photoemission[4] (~1 s). With this time resolution, we can work in a temperature range well above that required for stable adsorption. The advantage of this technique has been pointed out theoretically by Chang and Weinberg.[5] We applied our technique to study the initial reaction of oxygen on Si(100) surfaces from 700 to 950 °C, a temperature range of technological interest, to illustrate its capability.

A pulsed valve (Newport BV-100, 0.5-mm nozzle diameter), synchronized with a 200-Hz 17-μs full width at half maximum (FWHM) shutter-function rotating slot, was used to produce narrow supersonic pulses of oxygen at the sample at a rate close to 1 pulse per second. The use of these very sharp pulses is crucial for good time resolution. By measurement of the time of flight and the pulse shapes of the oxygen beam at two miniature ion gauges, it was estimated that for pure O_2 pulses the translational energy was about 0.1 eV and the temperature was about 9 ± 1 K. After collimating the beam with a skimmer and an aperture, the beam diameter was about 3 mm and the computed incident oxygen-*flux* waveform was about 40-μs FWHM at the sample. In this experiment, the sample temperature was high enough and the pulse repetition rate was sufficiently low that all the adsorbed oxygen from each pulse was removed before the arrival of the next pulse. The typical dose was 10^2 to 10^3 pulses with about 10^9 molecules/pulse. Since the oxygen coverage was always much less than a monolayer, we do not expect any appreciable adsorbate-adsorbate interaction. With three stages of differential pumping, the vacuum in the reaction chamber was maintained at about 1×10^{-10} Torr. Only SiO was detected as the reaction product. The product SiO number density was monitored through a 1.6-mm-diameter aperture by a liquid-nitrogen-shrouded, differentially pumped quadrupole mass spectrometer located at right angles to the beam direction. The distance between the sample and the ionizing volume was about 4 cm. The signal was detected by pulse counting and recorded by a multichannel scaler with a time resolution of 2 μs. Our Si samples were *n*-type, 10-Ω-cm Si(100) wafers cleaned by the usual Ar^+ sputtering and annealing cycles. *In situ* Auger analysis showed that the Si(*LVV*) to C(*KLL*) ratio was at least 250 and the low-energy electron diffraction gave sharp 2×1 spots. All these samples were direct-current heated. Sample temperatures were monitored by an infrared pyrometer. We estimated that there may be an error of ± 20 K due to nonuniform heating of the sample. Thermal etching due to prolonged heating was closely monitored. Samples showing visual signs of roughening or with diffuse LEED spots were replaced.

Since SiO was the only reaction product, the overall reaction was $Si(s) + O_2(g) \rightarrow 2SiO(g)$. Figure 1 shows the data obtained at 950 °C and 45° angle of incidence. Curve *a* is the incident oxygen-flux waveform with about 40-μs FWHM at the sample, computed by our assuming the measured values of beam temperature and translational energy. Curve *b* is the SiO signal. To obtain the impulse-function response $R(t)$, we have to correct for the transit time of the SiO molecules between the sample and the detector, and the width of the incident O_2 pulse, using the standard Fourier-transform deconvolution technique.[2,6] We assume that the velocity distribution of the SiO molecules is a Maxwell-Boltzmann distribution with

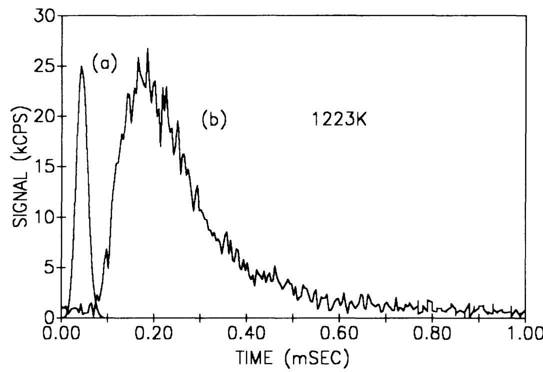

FIG. 1. Comparison between curve a, computed incident O_2 flux, and curve b, product SiO waveforms at 950 °C. The time origin is arbitrary. The scale in kilocycles per second refers to curve b.

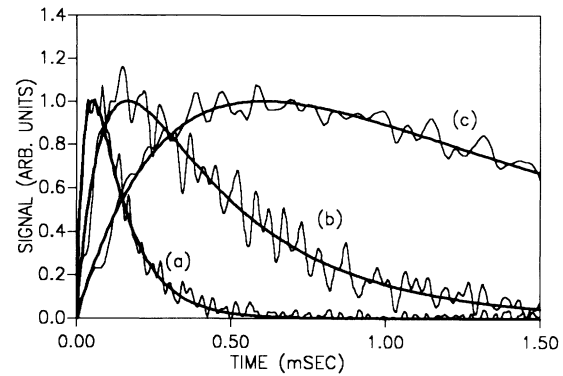

FIG. 2. Impulse-function response for the production of SiO in the O_2/Si(100) reaction at (curve a) 950 °C, (curve b) 900 °C, and (curve c) 850 °C. The relative y scales among the curves are arbitrary.

the sample temperature. At 950 °C, the broadening of the SiO-product waveform due to the transit time is about 60 μs. The advantage of our using sharp incident pulses and a short sample-to-detector distance is that the above corrections are significant only in the submillisecond regime. Figure 2 shows $R(t)$ for the production of SiO (or equivalently the SiO waveform for a δ-function O_2 pulse applied at time 0) at (curve a) 950 °C, (curve b) 900 °C, and (curve c) 850 °C. It shows for the first time by a real-time technique that there is an induction time for the peak production of SiO. The whole reaction is strongly temperature dependent. We found that $R(t)$ fits very well to the difference of two exponential functions as shown by the solid lines in Fig. 2:

$$R(t) \propto \exp(-k_2 t) - \exp(-k_1 t), \tag{1}$$

with $k_2 < k_1$. k_2 is mostly determined by the falling edge of the waveform. Figure 3 shows the Arrhenius plots for k_1 and k_2, yielding the respective temperature dependencies

$$\begin{aligned} k_1 &= 6\times 10^{14} \exp[-(2.5\text{ eV})/k_B T]\text{ s}^{-1}, \\ k_2 &= 8.1\times 10^{16} \exp[-(3.0\text{ eV})/k_B T]\text{ s}^{-1}. \end{aligned} \tag{2}$$

k_B is the Boltzmann's constant. We attempted to determine the physical significance of k_1 and k_2 by studying the formation of SiO with NO beams under identical conditions. NO reacts with Si at high temperatures to form SiO and silicon nitride.[7] Figure 4 shows the comparison of the SiO impulse-function responses for O_2 and NO on Si(100) at 825 °C. The induction time of the SiO peak is practically 300 μs shorter for the NO case. The NO dosage was kept low to avoid any complication from the accumulation of silicon nitride on the surface, which might change the SiO desorption kinetics. By fitting with Eq. (1), as shown by the solid curves in Fig. 4, we found that they have the same k_2 value (7.5×10^2 s^{-1}) to within 20%, while k_1 for NO (8×10^4 s^{-1}) is much larger than that for O_2 (7×10^3 s^{-1}). Since the desorption of SiO is the common step in both reactions, k_2 is most likely related to the desorption of SiO from a Si(100) surface.

Our data are consistent with the following reaction model.[8] The O_2 molecule first reacts with the Si(100) surface to form a nonvolatile intermediate oxide I. We cannot address this step since it has a time scale not resolvable in our experiment, and we do not have structural or chemical state information on I. There are a large number of reports on the chemisorption step in the literature.[9] However, none of the data were obtained in the same temperature range and with the same time resolution. We postulate that the intermediate compound I is then transformed at a rate k_1 to form an SiO desorption precursor SiO(a) which subsequently desorbs with a rate k_2. Let $F(t)$ be the flux of the oxygen pulse

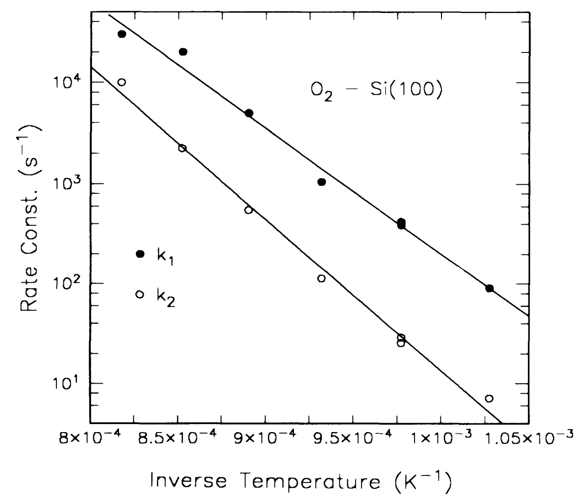

FIG. 3. Arrhenius plot of the two reaction rates k_1 and k_2.

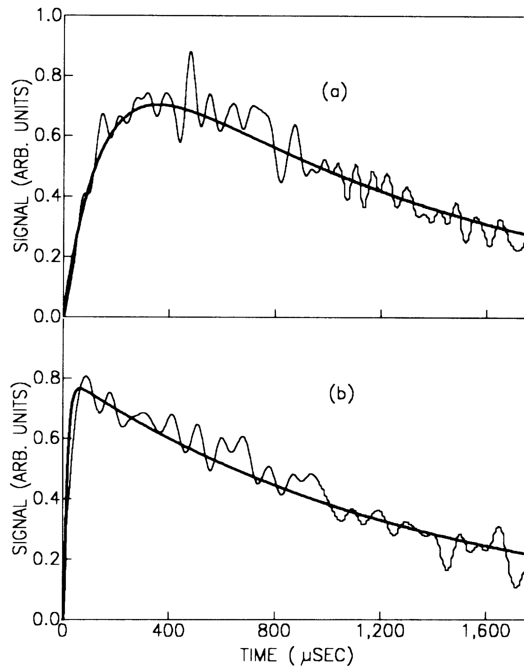

FIG. 4. Comparison between the transfer functions for the production of SiO by our reacting Si(100) with (a) O_2 and (b) NO at 825 °C.

in atoms/s, s_0 be the sticking coefficient, and $[I]$ and $[SiO(a)]$ be the amount (in units of oxygen atoms) of the intermediate compound I and $SiO(a)$ on the surface, respectively. The reaction is governed by the following equations:

$$d[I]/dt = s_0 F(t) - k_1[I],$$
$$d[SiO(a)]/dt = k_1[I] - k_2[SiO(a)]. \quad (3)$$

$R(t)$ for the production of SiO in this model, obtained by our calculating the term $k_2[SiO(a)]$ for $F(t)=\delta(t)$, is

$$s_0 k_1 k_2 (k_1 - k_2)^{-1}[\exp(-k_2 t) - \exp(-k_1 t)],$$

which is consistent with Eq. (1). k_2 also has a large preexponential factor which is typical for a desorption process.[10] In the NO oxidation experiment, the different value of k_1 measured suggests a different reaction pathway to form $SiO(a)$ but the rate of desorption of $SiO(a)$ is still the same.

To complete the description of the reaction, we also measured the sticking coefficient s_0 in Eq. (3). We found that s_0 of the O_2 molecule on the Si(100) surface depends strongly on the normal component $E_\perp$ of the O_2 beam translational energy E. $E_\perp$ was changed between 30 meV to 1 eV by our seeding the O_2 with Xe, He, and H_2 and by changing the angle of incidence. s_0 was measured by a combination of beam reflectivity and SiO-yield measurements. We used the beam-reflectivity

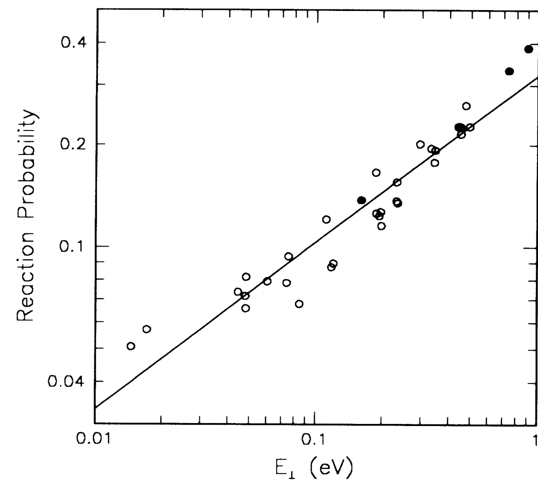

FIG. 5. Reaction probabilities of O_2 on Si(100) at 950 °C, as a function of the normal component of the translational energy. The best-fit line is $R \propto E_\perp^{0.49}$.

method reported by Rettner, DeLouise, and Auerbach[11] with the effusive correction. A residual-gas analyzer was used to measure the rise of the partial pressure of oxygen in the chamber from the unreacted portion of the individual O_2 pulse. A sputtered cleaned gold surface at the sample position was used to simulate the $s_0=0$ case. s_0 was measured by the difference in the unreacted O_2 signals between the sample and the gold. Since s_0 has to be determined by the difference between two large numbers, the method was not quite accurate for s_0 less than 0.1 in our experiment. For lower reaction probabilities (open circles in Fig. 5), we fixed the sample at 45° to both the beam and the mass spectrometer. The relative reaction probabilities were measured by the time-integrated SiO yields at different experimental conditions, while we used the beam-reflectivity measurements on gold described above to determine the total O_2 dose per pulse for normalization. Then the results were scaled to match the absolute reactivity at a high s_0 value determined by beam reflectivity. To observe the incident-angle dependence, we used the beam-reflectivity method with a H_2-seeded beam.[12] The data suggest a correlation with the normal component of the translational energy as shown by the solid circle data points (averaged over six runs) in Fig. 5. In general, s_0 varies roughly as $E_\perp^{0.5}$, or equivalently as the normal component of the incident velocity. s_0 reached about 0.4 for 1-eV O_2 at normal incidence at 950 °C. This result suggests the existence of an activation barrier as observed in other chemical systems.[11,13] The reaction probability is only weakly temperature dependent. s_0 was increased by 1.5 times between 550 and 950 °C.

Hence we have shown that the impulse-function response with resolution in the tens of microseconds can be determined with this technique. We have unambigu-

ously observed in real time the intermediate step between O_2 adsorption and the production of SiO. The fastest reaction rate which we have measured for the O_2/Si(100) system is 3×10^4 s^{-1} (k_1 at 950 °C). The future challenge will be to obtain accurate structural and bonding information with the same or better time resolution.

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