Local catalytic effect of cesium on the oxidation of silicon

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We have studied the catalytic effect of adsorbed cesium on the initial sticking coefficient s_0 of oxygen on Si(100) at room temperature. Two different kinds of cesium sites were observed. s_0 was found to increase linearly with the coverage of each kind of cesium site. The data show that the effect of cesium is local, but s_0 does not correlate with the Cs dipole moment. An oxygen-cesium bond is formed in the reaction and cesium is passivated in this process, leading to an exponential decrease of the sticking coefficient with the oxygen coverage.

The catalytic effect of alkali-metal atoms in the oxidation of silicon has been under intense study recently.[1-6] The oxidation of silicon is a necessary procedure in silicon device fabrication. This processing step often proceeds at temperatures above 900 °C. Much effort has been focused on finding a means to lower the processing temperature to avoid unintended effects such as dopant diffusion. Transition metals, for example, have been found to promote the oxidation of silicon even at room temperature by dislodging Si atoms from the substrate to form a silicon-metal intermix layer,[7] but these materials also cause defects in the oxide.[8] In contrast, alkali metals, which also promote silicon oxidation, can easily be removed by thermal desorption at moderate temperatures of about 700 °C. Besides this potential application in semiconductor technology, alkali-metal-promoted oxidation of silicon has attracted much interest from a more fundamental point of view in understanding catalytic processes.

Nøskov, Holloway, and Lang,[9] and Lang, Holloway, and Nøskov[10] have suggested that the catalytic effect of alkali-metal atoms is due to the local electric-dipole field (local work function) of the alkali-metal adsorbate. The local potential increases the molecular adsorption energy, the filling of the antibonding molecular level ($2\pi^*$ for O_2), and, thereby, the dissociation rate. According to the local character of this mechanism, the promotion should be strictly proportional to the number of alkali-metal atoms present at the surface, at least in the low-coverage regime.

An alternative approach is given by Franciosi et al.[11] and similarly by Hellsing.[12] Here it is suggested that the dissociation rate of O_2 is enhanced by lowering the macroscopic work function (a nonlocal quantity) through the dipole layer produced by the alkali metal. As the work function is lowered, the oxygen $2\pi^*$ level is shifted into the region of the dangling-bond band, and charge transfer from this band into the antibonding molecular level takes place as the O_2 molecule approaches the surface. In this case, no simple linearity between catalytic action and Cs coverage is expected.

Experimentally, Ortega and co-workers[1,2] used Auger-electron spectroscopy (AES) to determine the amount of silicon oxide formed as a function of Cs coverage. The Si surface was dosed with up to 200 L (1 L $=10^{-6}$ Torr s) of O_2 and annealed to remove the Cs. They reported a linear relation between the amount of SiO_2 formed and the Cs coverage, therefore favoring the local catalytic interaction picture. In contrast, Starnberg and co-workers[3,4] observed in their photoemission study that after a large dosage with oxygen and thermal annealing, the amount of SiO_2 formed is nonlinear with the Cs precoverage. They concluded that the catalytic effect is nonlocal in nature.

Both theory and experiment are hence equally divided. However, the theoretical models all agreed that the initial dissociation of O_2 largely determines the oxidation rate. Any enhancement is associated with an increase of the sticking, and hence, dissociation probability of O_2. In our experiment, instead of measuring the amount of oxide formed after a large oxygen dosage to estimate the catalytic effect of Cs, we performed a direct measurement of the absolute value of the sticking coefficient s_0 of oxygen on a cesiated Si(100) surface. This more fundamental quantity of the oxidation process is compared to the Cs coverage and to the work-function change as measured by photoemission. This combined study unambiguously determined that Cs-atom promoted oxidation is local in nature. However, surprisingly, the sticking coefficient does not correlate with the dipole moment per Cs atom.

The sticking coefficient of oxygen was measured by the beam-reflectivity method of King and Wells[13] using a pulsed supersonic oxygen beam in an ultra-high vacuum chamber. The apparatus is similar to the one reported earlier[14] except for an additional stage of differential pumping to reduce the effusive background, so that the lower limit of measurable s_0 is about 0.03. The energy of the oxygen molecules was varied by seeding the oxygen with helium or xenon. Measurements were made with the oxygen beam at normal incidence. Each gas pulse has about 10^{12} oxygen molecules spread over a beam diameter of about 4 mm. About 10 pulses were used for initial sticking coefficient measurements so that the surface coverage was always in the dilute coverage limit. The silicon samples were 0.1-Ω cm, n-type, 16-mm-diam Si(100) disks. The sample surfaces were cleaned by prolonged heating at about 600 °C by a heater filament at the backside of the sample, and short flashes to 1000 °C to remove the surface oxide until in situ x-ray photoemission (XPS) measurements showed no trace of contaminations, and low-energy electron diffraction (LEED) showed a $p(2\times1)$ reconstruction. Cesium was deposited by a carefully outgassed SAES getter. The Cs coverage was measured by

the magnitude of the XPS Cs $3d$ spectrum. The work-function change was measured by *in situ* ultraviolet photoemission (UPS) using the He I photons for excitation. Similar to other reports,[15] we found that the Cs coverage reached a self-limiting value which we shall define as one monolayer (ML) for convenience although the exact amount is still a subject of controversy. We note that the quality of the sample suffered in the course of the experiment as judged by the increasing background in the LEED pattern from the clean surface, presumably due to the creation of defects during high-temperature flashes. In this case, further deposition of Cs at room temperature was possible. Hence, all data reported here were collected from well-ordered samples where the self-limiting value for the Cs coverage was detected. The $p(2 \times 1)$ LEED pattern was observed throughout the Cs deposition.

We found strong evidence that the catalytic effect of the Cs atoms is local. Figure 1 shows that the sticking coefficient s_0 is linear with the Cs coverage except for the change of slope at about 0.2–0.3 ML. This linear behavior holds for all three different energies of the oxygen beam: 34, 86, and 390 meV. The sticking of oxygen on the clean silicon (100) surface has a strong activated adsorption behavior as we have previously observed on the Si(100) (Ref. 16) and Si(111) (Ref. 17) surfaces at higher temperatures. s_0 is below 0.03 at 34 meV, but reaches 0.16 at 390 meV, showing the presence of an activation energy barrier. s_0 increases linearly with the Cs coverage until about 0.3 ML, at which point the rate of increase with the Cs coverage changes. This strongly suggests that the additional Cs atoms occupy different sites. Hints of such changes in adsorption site have been observed during Cs adsorption on Si(100) by Ortega *et al.* [1] and by Papageorgopoulos and Kamaratos[6] using Auger spectroscopy, and by Holtom and Gundry[18] who observed extra LEED spots. Recently Abukawa and Kono[15] reported that their photoelectron diffraction data is consistent with Cs atoms occupying both the pedestal sites along the silicon dimer rows on the (100) surface, and the cave sites between the dimer rows. The sequence in the

occupation of these sites has not been established. Hence we cannot identify which cesium and/or site combination gives the more effective catalytic action. The sticking coefficient of oxygen reaches about 0.77 at 0.9-ML Cs coverage at 34-meV kinetic energy. This is a very large enhancement in s_0 when compared to less than 0.03 at zero Cs coverage. Enhancement factors at higher oxygen kinetic energies are smaller because s_0 on the clean silicon surface is larger. s_0 at high Cs coverage is practically unity. The lack of strong energy dependence of s_0 at high Cs coverages indicates the much smaller activation energy barrier for the adsorption of oxygen on the cesiated surface.

We found no simple correlation between the work-function change $\Delta\phi$ with the sticking coefficient of oxygen on these cesiated silicon surfaces. Figure 2 shows s_0 as a function of $\Delta\phi$. s_0 rises rapidly with further increases in Cs coverage even when the work function reaches its lowest value at about 0.5 ML Cs. The linear relation between s_0 and the Cs coverage, coupled with the lack of correlation with the work-function change, clearly implies that the catalytic effect of the Cs results from a local interaction.

Our photoemission data supports the suggestion[2,5] that oxygen forms bonds with both silicon and Cs on the cesiated Si(100) surface at room temperature. The XPS O $1s$ spectrum is a superposition of two peaks, consistent with the observations by Michel *et al.*[2] and Schaefer *et al.*[5] The Cs core levels, however, do not show detectable chemical shifts between the adsorption on silicon, and the bonding to oxygen. The O $2p$ spectrum also shows two distinct peaks. Figure 3 shows a comparison between the differences of the UPS spectra obtained before and after 5000 pulses of oxygen for (a) a Si(100) surface with 0.7 ML of Cs, and (b) a clean Si(100) surface. The UPS difference spectrum in case (a) shows two peaks at about 5 and 6.5 eV below the Fermi level while the silicon case (b) shows only the 6.5-eV feature. This is indicative of another type of oxygen bond on the cesiated surface. The likely explanation is that the O_2 molecule dissociates at
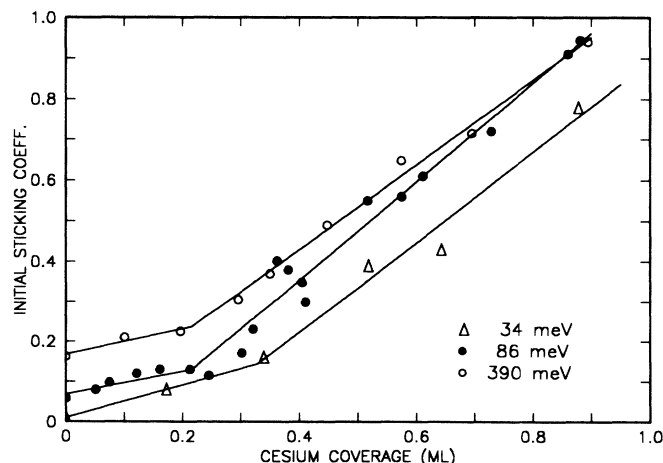

FIG. 1. Initial sticking coefficient of oxygen as a function of Cs coverage at three different oxygen energies: 34, 86, and 390 meV.
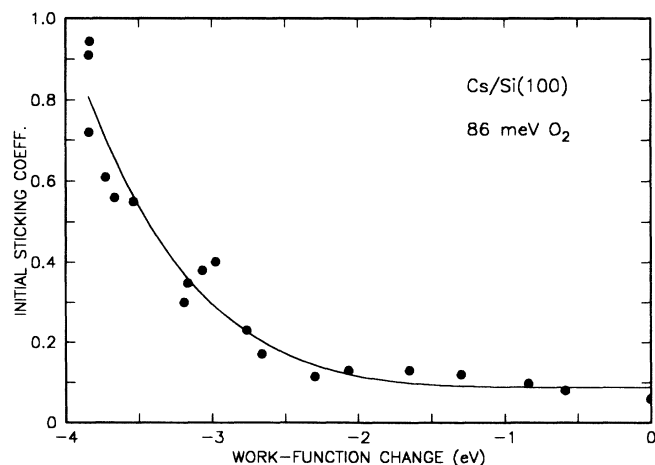

FIG. 2. Initial sticking coefficient of 86-meV oxygen as a function of the work-function change induced by the Cs deposition. The solid line is a guide for the eye.
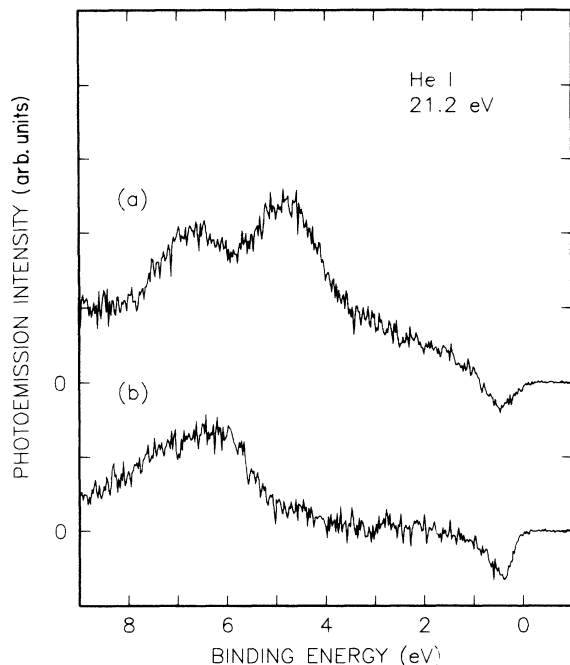
FIG. 3. Difference spectra obtained by subtracting the UPS spectra after 5000 pulses of oxygen by the spectra before oxygen dosing; for (a) Si(100) with 0.7 ML of Cs, (b) clean Si(100).

the Cs site, with one oxygen atom bonded to Cs, and one to a neighboring silicon atom. That oxygen bonds to Cs is further evidenced by the following oxygen dosing experiment.

There is strong experimental indication that the adsorption of oxygen passivates the Cs atom from further catalytic action. Figure 4 shows the variation of the sticking coefficient s with the total number of oxygen pulses for 0.4-, 0.65-, and 1-ML Cs coverages and oxygen beam energy of 86 meV. The sticking coefficient of oxygen decreases exponentially with increasing oxygen dosage, and
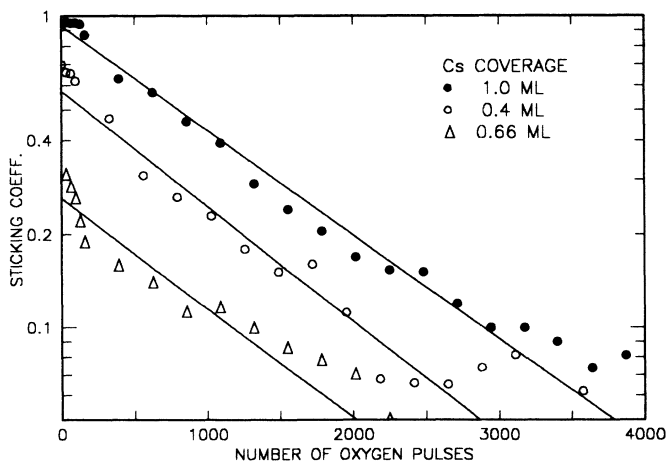

FIG. 4. Semilogarithmic plot of the sticking coefficient of 86-meV oxygen as a function of oxygen dosage in units of pulses, for three different Cs coverages: 0.4, 0.66, and 1.0 ML.

has about the same rate in all the three cases with small deviations at low oxygen doses. The data is more scattered at low s values (< 0.1). This exponential behavior is a strong evidence for the local passivation of the Cs site by the formation of the O-Cs bond. It can be explained qualitatively if the interaction that leads to the adsorption of oxygen is local. In the zero oxygen coverage limit, the sticking coefficient s_0 is given by

$$s_0 = \Theta_{Cs}s_1 + (1 - \Theta_{Cs})s_2 ,\qquad (1)$$

where s_1 is the sticking coefficient at the Cs site, s_2 is the sticking coefficient at the silicon site, and Θ_{Cs} is the Cs coverage. There are two limiting cases for the distribution of oxygen on the surface. First we assume that the distribution is completely random. Then the sticking coefficient, when the oxygen coverage on the surface is Θ_{O_2}, is given by

$$s(\Theta_{O_2}) = s_0(1 - \Theta_{O_2}) .\qquad (2)$$

Using the relation that $\Theta_{O_2} = n_0^{-1} J \int s\, dN$, where N is the number of oxygen pulses, J is the dose per unit area per pulse, and n_0 is the number of sites per unit area; s is related to N by

$$s = s_0 \exp(-n_0^{-1} s_0 J N) .\qquad (3)$$

This result predicts the exponential dependence of s on N with a "decay constant" which is inversely proportional to s_0, and not independent of s_0 as depicted by Fig. 4. The other limit, where oxygen selectively reacts with the Cs sites first and blocks these sites from further catalytic action, gives a better description of our data. In this case,

$$s(\Theta_{O_2}) = s_1(\Theta_{Cs} - \Theta_{O_2}) + s_2(1 - \Theta_{Cs}) .\qquad (4)$$

s is related to N by

$$s = s_0 \exp(-n_0^{-1} s_1 J N) .\qquad (5)$$

Equation (5) gives a constant "decay constant" which is independent of s_0 as long as $\Theta_{O_2} < \Theta_{Cs}$. Oxygen would be distributed to the silicon sites when all the Cs sites are passivated. This results in deviations from Eq. (5) at small values of s, as observed experimentally.

The overall oxygen uptake Θ_{O_2} depends on how s varies with the oxygen dosage. For example, Eq. (3) gives $\Theta_{O_2} = 1 - \exp(-n_0^{-1} s_0 D)$, where $D (= JN)$ is the total oxygen dosage, while Eq. (5) leads to $\Theta_{O_2} = s_0 s_1^{-1} \times [1 - \exp(-n_0^{-1} s_1 D)]$. In both cases, the oxygen uptake is not linear with s_0 or Θ_{Cs}. A detailed knowledge of $s(\Theta_{O_2})$ is necessary to deduce the relation between the catalytic efficiency and the Cs coverage. In general, the oxygen uptake after large oxygen exposures as in Refs. 1–6 does not provide the information on initial adsorption without a detailed analysis. Hence our measurement of the initial sticking coefficient is a more definitive way to assess the local character of the catalytic effect.

Our data clearly show that the catalytic effect of Cs is local as suggested by the electric-dipole models of Refs. 9 and 10. However, the correlation of the sticking coefficient with the dipole moments of the Cs atoms is not strong. The initial sticking coefficient remains linear with the Cs coverage even after the minimum work function is

reached. In this region ($\Theta_{Cs} > 0.5$), the averaged dipole moment per Cs atom is actually decreasing with increasing coverage, but the catalytic effect per Cs atom does not decrease. That Cs is also oxidized suggests an important role played by the Cs $6s$ electrons in the catalytic reaction, and not just by the dipole moment of the Cs atoms. Recent experiments[19,20] have shown the importance of covalent bonding in the adsorption of alkali-metal atoms on tungsten and silicon, meaning that the Cs still retains a portion of the $6s$ electrons. The dipole moment of the Cs atom alone does not adequately describe the catalytic action at the Cs site. Our experiment points to the importance of the Cs valence electrons in the catalytic reaction.

In summary, we have shown experimental evidence that the catalytic effect of Cs atoms on the Si(100) surface is best described as "local." Two adsorption sites with different catalytic effectiveness have been seen. The Cs atom lowers the activation energy for the adsorption of oxygen so that the sticking coefficient can practically reach unity at high Cs coverages. Cesium dissociates the oxygen molecule to form both Cs-oxygen and silicon-oxygen bonds. The reacted Cs is passivated and is no longer effective as a catalyst. Our experiment shows that the effect of the dipole moment of Cs is only part of the mechanism for the catalytic effect.

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