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Thermal and photochemical oxidation of Si(111): Doping effect and the reaction mechanism

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It has been proposed that a "harpooning"-like silicon-to-O_2 electron-transfer process to form an O_2^--like precursor is the crucial first step in the oxidation of Si(111). Here we use δ doping of silicon with boron to reduce the electron population of the silicon-surface adatom dangling bonds. We find that indeed the extent of oxidation and the amount of the O_2^--like species on the surface are greatly reduced by the doping. Moreover, we find an analogous suppression of the photo-oxidation process. The latter result indicates that the photodissociation of the same O_2^--like precursor is involved in the photoenhancement of the oxidation process.

Recent scanning-tunneling-microscopy studies have shown that reactions on semiconductor surfaces can be very site selective.[1-9] Furthermore, scanning tunneling spectroscopy has revealed a close relationship between the local electronic structure of a particular site and its chemical reactivity.[9,10] In general, the reactivity of semiconductor surfaces at not too high temperatures appears to be determined by electronic factors. In a recent study of the initial stages of the oxidation of the Si(111)-(7×7) surface[9] we have suggested that the observed preference of the reaction for corner-adatom sites and the faulted half of the Si(111)-7×7 unit cell primarily reflects differences in the occupancy of the corresponding dangling bonds. The loosely bound electrons in these dangling-bond surface states can be transferred to the $2\pi^*$ affinity level of incident O_2 molecules in a process akin to the "harpooning" process of gas-phase reactions.[11] In this way, O_2^--like molecular precursors are formed at the Si surface whose dissociation leads to the oxidation of the surface.[12] Comparison between ultraviolet photoemission spectra and density-of-states calculations for various possible structures[13] shows that the molecular precursor does not involve a bridge configuration[12] but rather an O_2^--like species interacting with a *single* dangling-bond site.

In this study we test these ideas on the mechanism of the thermal oxidation reaction and also investigate the mechanism of the photoinduced oxidation. As has been shown in studies of the reactivity of metal surfaces, the local reactivity can be altered as a result of coadsorption. Here we apply a similar approach in which we use the "surface" doping of silicon by boron in order to modify the occupancy of the adatom dangling-bond states. In earlier work[14,15] it was shown that adsorption of decaborane on Si(111)-7×7 followed by annealing to ~1000 °C leads to the restructuring of the surface. The top layer is now composed of a $(\sqrt{3}\times\sqrt{3})$ arrangement of Si adatoms while the B atoms form a δ layer in the third atomic plane. These B atoms are located directly below the Si adatoms and through a charge-transfer process remove electrons from the adatom dangling bonds.[14,15] The same δ-doped structure was also found to form through thermal segregation from heavily bulk-doped samples.[16,17] Comparison of the oxidation behavior of the undoped and δ-doped surfaces brings insight into the mechanism of both the thermal and photo-oxidation reactions.

The experiments were performed in an ultrahigh-vacuum (UHV) system with a base pressure of 7×10^{-11} torr. The experimental system was equipped for x-ray photoemission spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy, low-energy electron diffraction (LEED), low energy He^+-ion scattering spectroscopy (ISS), and thermal desorption spectroscopy. The UPS spectra were obtained using He II (40.8 eV) radiation; the binding energy refers to the valence-band maximum of the clean Si(111)-7×7 surface. The silicon sample was an *n* type, phosphorus-doped 10-Ω cm crystal. The sample was mounted on a liquid-nitrogen-cooled sample holder and the sample heating was Ohmic. The temperature was measured both by a Chromel-Alumel thermocouple cemented to the back of the crystal, and by a pyrometer. The clean Si(111)-7×7 reconstructed surface was prepared by 6 h annealing of the native oxide covered sample at 950 K, followed by desorption of the oxide film in ~60 sec annealing at 1250 K. The above treatment was followed by a short flash to 1300 K. The surface so prepared showed a sharp 7×7 LEED pattern and a UPS spectrum with intense, well-resolved adatom and rest-atom surface states. The B:Si(111)-$\sqrt{3}\times\sqrt{3}$ boron-doped surface was prepared by adsorbing 5 langmuir ($1\ \mathrm{L}=10^{-6}$ torr sec) decaborane-14 ($B_{10}H_{14}$) at 100 K and subsequently annealing to 1100 K. Such treatment results in a B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface with a sharp LEED pattern and on which ISS shows only silicon surface atoms. The ultraviolet (UV) light source used in this study was a Hamamatsu L879 deuterium lamp with a MgF_2 window, with spectral distribution of 115–400 nm. The lamp was mounted inside the UHV system 5 cm away from the crystal.

In Fig. 1 we show UPS spectra of the clean Si(111)-7×7 surface, after 0.2 L and 0.4 L O_2 exposure at 95 K and after 10 sec annealings at increasing temperatures up to 450 K. The clean surface spectrum shows the characteristic S_1 and S_2 surface states due to adatom and rest-atom dangling bonds, respectively.[18] After 0.2 and 0.4 L oxygen exposure at 95 K the S_1 state is preferentially quenched and a peak at ~3.8 eV is observed along with other peaks at 7.5 eV and between 9 and 14 eV below E_F. A continuous monitoring of the oxygen uptake using the

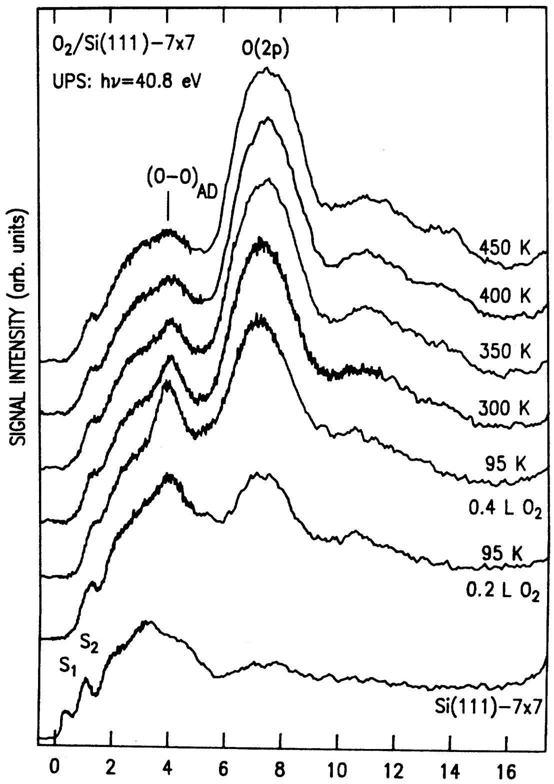

FIG. 1. Ultraviolet photoemission spectra of clean and O_2-exposed Si(111)-7×7 surfaces as a function of O_2-exposure and annealing temperature.

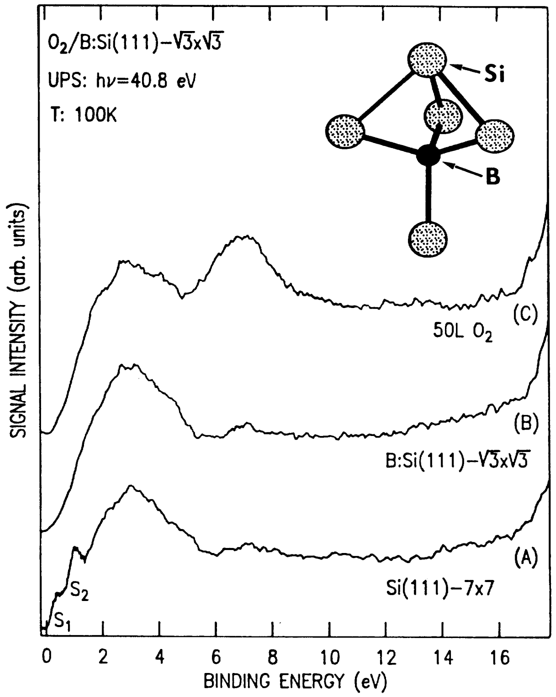

FIG. 2. Ultraviolet photoemission spectra of clean Si(111)-7×7 (curve *A*), boron doped B:Si(111)-$\sqrt{3}\times\sqrt{3}$ (curve *B*), and oxygen-exposed B:Si(111)-$\sqrt{3}\times\sqrt{3}$ (curve *C*) surfaces. Inset shows the local structure of the Si adatoms sites on the B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface.

O(1*s*)-XPS intensity or by the UPS intensity at 7.5 eV indicated a nearly constant sticking coefficient of ~0.4 at 95 K up to near saturation coverage. Under these conditions the work function of the surface increased by 1.4 eV. The 3.8 eV peak in the spectra of the oxygen exposed surface has been ascribed to an adsorbed O_2^--like species.[9,12] Upon annealing this peak disappears, accompanied by a parallel increase in the intensities of the O(2*p*) oxygen features at 7.5 eV and between 9–14 eV. These results, combined with previous scanning tunneling microscope[9] and photoemission data[9,12] suggest that the oxygen adsorbs with high sticking probability (s_0~0.4 at 100 K) initially at adatom sites in a negatively charged (O_2^--like) molecular precursor state. Some dissociative adsorption was also observed even at low temperatures. The molecularly adsorbed oxygen dissociates upon mild annealing. UPS spectra of analogous oxygen adsorption experiments on the B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface are shown in Fig. 2. A comparison of the UPS spectra of the clean Si(111)-7×7 (curve *A*) and B:Si(111)-$\sqrt{3}\times\sqrt{3}$ (curve *B*) surfaces shows that the boron-doped surface has no occupied surface states, because of charge-transfer to subsurface B atoms which occupy substitutional sites right below the Si adatom sites as discussed before.[14,16,17] After large oxygen exposure such a surface shows very little oxidation (see curve *C* and also Fig. 4) and no adsorbed O_2^--like species (3.8 eV UPS peak) can be observed on this boron-doped surface. Since the structure of the Si adatoms on

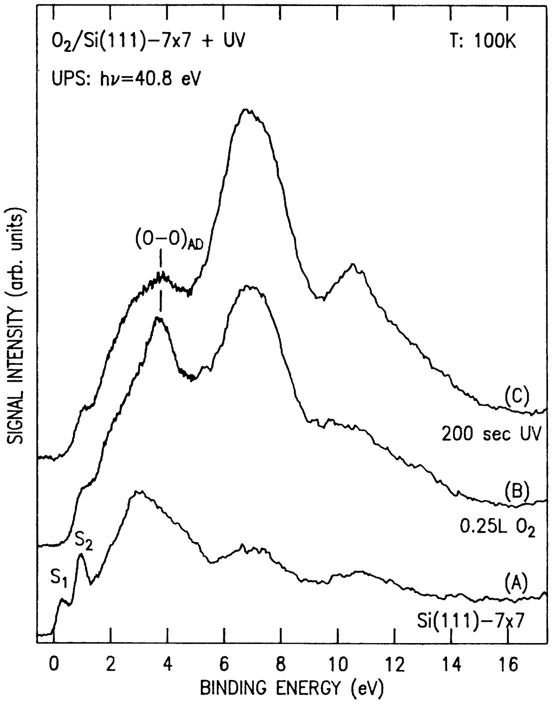

FIG. 3. Photodissociation of adsorbed oxygen. Ultraviolet photoemission spectra of clean Si(111)-7×7 (curve *A*), after 0.25 L O_2 exposure at 100 K (curve *B*), and after a 200 sec UV exposure of the oxygen-exposed surface (curve *C*).

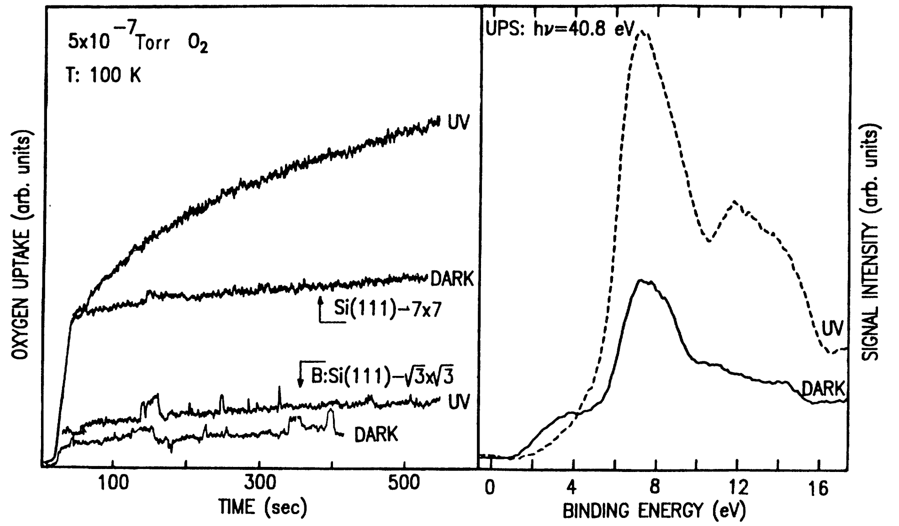

FIG. 4. Left panel: Oxygen uptake, measured by O(1*s*) XPS, of the clean Si(111)-7×7 and B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surfaces in the dark and under UV exposure at 100 K. The O_2 pressure was 5×10^{-7} torr. Right panel: Ultraviolet photoemission spectra of the Si(111) surface after oxygen exposure in the dark and under UV illumination.

the B-doped surface is very similar to that of the adatoms on the undoped surface,[14,19] the absence of the molecular precursor and the suppression of the oxidation process are likely due to the depletion of the surface dangling-bond state. Specifically, the proposed harpooning-like charge-transfer process from the adatoms to the $2\pi^*$ level of incident O_2 molecules[9] would be suppressed. In earlier work[20] it has been argued that adatom oxidation may involve the adatom backbonds, not the dangling bonds. The residual reaction observed at the B-doped surface gives an upper bound to the contribution of the reaction channels directly involving the strained adatom backbonds.

We now turn to the photochemical oxidation of the Si(111)-7×7 and B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surfaces. First we show the effect of UV exposure on the molecularly adsorbed oxygen on Si(111)-7×7. Figure 3 shows UPS spectra of Si(111)-7×7 after oxygen adsorption and after UV exposure following the oxygen adsorption. The intense peak at 3.8 eV in spectrum (*B*) shows the presence of a significant amount of adsorbed O_2^--like precursor following 0.25-L-O_2 exposure at 100 K. Upon 200 sec UV exposure at 100 K the 3.8 eV peak practically disappears while the O(2*p*) peaks at 7.5 eV and between 9–15 eV increase in intensity. The transformation of the spectrum is identical to that observed as a result of thermal annealing (see Fig. 1) which leads to the dissociation of the molecular precursor. Thus, the photodissociation of the molecular precursor is implicated in the photoenhancement of the oxidation process. To observe significant photoenhancement a high O_2 sticking coefficient and long residence on the surface, i.e., O_2^- formation at low temperatures is needed. The photodissociation step involves the population of antibonding states, most likely of the $3\sigma^*$ level of the O_2^- species. Both intra-adsorbate and substrate-to-adsorbate photoinduced charge-transfer processes can be active under the wide-band excitation conditions utilized here.[21–24] In Fig. 4 we show the oxygen uptake in 5×10^{-7} torr O_2 on the Si(111)-7×7 at 100 K in the absence of illumination and under illumination. The uptake curve in the absence of illumination ("dark") shows that after the initial rapid adsorption of the first monolayer oxygen the curve reaches a plateau, and further adsorption takes place only at a very low rate (perhaps partly as a result of illumination by the UPS He lamp itself). Under UV illumination, however, there is oxygen uptake at a significant rate after the rapid adsorption of the first monolayer leading to oxidation far beyond the monolayer level. This is illustrated in Fig. 4, which also shows UPS spectra taken after the oxygen exposure with and without UV illumination. The latter spectrum shows a valence-band maximum at significantly lower energy, i.e., band-gap opening, which indeed indicates photochemical oxidation of the silicon extending beyond the surface layer. We now turn to the effect of B doping on the photo-oxidation. Oxygen uptake by the B:Si(111)-$\sqrt{3}\times\sqrt{3}$ surface, under identical conditions, is also plotted in Fig. 4. It is apparent that no significant oxygen adsorption takes place in the dark, and no significant enhancement of oxygen uptake is induced by UV illumination, which, as we saw in the case of the undoped surface, has a dramatic effect.

In conclusion, we have shown that by reducing the occupation of the surface dangling-bond states through boron δ doping, we can drastically reduce the reactivity of silicon towards oxygen. This effect is due to the elimination of a surface-to-O_2 charge-transfer process which leads to the generation of O_2^--like surface species. The thermal and photochemical dissociation of such precursors leads to surface oxidation. The results presented here provide further support to the notion that the observed site selectivity in the oxidation of Si(111)-7×7 reflects the local variations in the occupation of the S_1 surface state.[9] The doping effects we discussed here along with a previous report on the effect of B doping on the NH_3 dissociation by silicon[15] provide examples of short-range doping effects involving direct dopant-reaction site interactions.

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