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Thermal growth of SiO_2-Si interfaces on a Si(111)7×7 surface modified by cesium

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We have used photoemission spectroscopy to study the Cs-promoted formation of SiO_2-Si interfaces on the Si(111)7×7 surface. A large enhancement of the oxidation rate was observed at room temperature with monolayer Cs coverage, and by annealing the initially substoichiometric oxide at moderate temperature it was transformed into SiO_2; meanwhile the Cs was completely desorbed. Comparison with previous results from Si(100)2×1 indicates that differences in dangling-bond density are not of major importance for the initial oxidation, but, probably because of the more closed structure of Si(111) atomic planes, the oxide layer obtained after annealing was thinner and less stoichiometric than on Si(100)2×1. The results also suggest that Cs stays on top of the oxide, and is preferentially bonded to Si. The catalytic efficiency decreased rapidly as the Cs coverage was reduced, thereby demonstrating the strongly nonlocal nature of the catalytic mechanism.

I. INTRODUCTION

It has been known for about a decade that alkali-metal overlayers may promote the oxidation of semiconductor surfaces,[1] and recently there has been a renewed interest in this field. In addition to the remarkable enhancement at room temperature of the oxidation of III-V semiconductors[2] as well as silicon,[3,4] it has also been found that Cs,[4] Na,[4] and K (Refs. 5 and 6) are removable by flash annealing at moderate temperatures. The growth of SiO_2 on silicon surfaces has been achieved at lower temperature than with other processes,[7] which limits the diffusion of dopants and could provide oxides more resistant to radiation damage. Aside from being potentially important in device technology, such processes also provide insight into the fundamental mechanisms of catalysis. A number of mechanisms have been proposed as important in catalytic oxidation, e.g., enhanced sticking of O_2, dissociation of molecular oxygen, and increased reactivity through weakening of substrate backbonds.[8] The thermal desorption of alkali metals is in contrast to the behavior of several noble, transition, and rare-earth metals, which also promote the oxidation of semiconductors, but form bulk compounds with the substrate and become included in the oxide films.[9-11] With the exception of lithium, the alkali metals do not interdiffuse or form bulk compounds with the substrate. The electronic and structural properties of alkali metals adsorbed on semiconductors has been the subject of several studies, experimental[12-14] as well as theoretical.[15-17] Except for the work of Ref. 3, which included a room-temperature study of Cs-promoted oxidation of the Si(111)2×1 surface, all studies so far of silicon oxidation using alkali metals have been limited to the (100)2×1 surface. Although Si(111)7×7 is the most-studied silicon surface, and therefore well suited as a test case for surface reactions, no oxidation studies using alkali metals have been carried out on this surface. In particular, the fact that the (111)7×7 face is more stable and has a lower density of dangling bonds could allow us to study the relative importance of these factors in the promotion mechanism at room temperature as well as during the thermal growth of SiO_2.

In this paper, we therefore present the results of an investigation of the oxidation of cesiated Si(111)7×7 surfaces by means of valence-band and core-level photoemission spectroscopy (PES). In particular we have monitored the growth of oxide during increased oxygen exposures, and studied the catalytic efficiency of Cs at submonolayer coverage as compared to full monolayers. Our study includes measurements after room-temperature oxidation, as well as after thermal flash annealing and Cs desorption. It is the first study of alkali-metal-promoted oxidation of the Si(111)7×7 surface, and also the first study of a Si(111) surface involving thermal annealing. Comparing with results from the Si(100)2×1 surface[4] we found one remarkable difference in that the oxide film obtained after annealing is considerably thinner on the (111)7×7 than on the (100)2×1 surface, using the same Cs coverage and O_2 exposure. This is in strong contrast to the results of room-temperature oxidation, which were very similar for the two surfaces.

II. EXPERIMENTAL DETAILS

The photoemission experiments were performed in an ultrahigh-vacuum (UHV) chamber at a pressure of better than 5×10^{-11} Torr. Synchrotron radiation, dispersed by a 3-m toroidal grating monochromator, was provided by the 1-GeV storage ring at the Synchrotron Radiation Center of the University of Wisconsin–Madison. The energy distribution of the photoelectrons was analyzed by an angle-integrating double-pass cylindrical mirror analyzer (CMA). The overall energy resolution was estimated to be $\simeq 0.5$ eV in the photon energy range employed. The silicon sample was cleaned *in situ* by thermal annealing. Cesium was deposited on the silicon surface from a carefully outgassed SAES getter source.

The pressure stayed below 1×10^{-10} Torr during the Cs deposition. Oxygen exposures ranging from 0.25 to 64 L (1 L = 1 langmuir = 1×10^{-6} Torr sec) were made using research-grade oxygen (99.99%). The Cs evaporations as well as the O_2 exposures were all made at room temperature. The sample temperature during annealing was measured by an optical pyrometer.

III. RESULTS AND DISCUSSION

Figure 1 shows Si 2*p* and Cs 4*d* core-level spectra recorded during a complete oxidation cycle, including complete Cs removal by annealing at 750 °C. The Si 2*p* chemical shifts, corresponding to different oxidation states of Si,[18] are indicated by vertical bars. The deposition of a Cs monolayer (ML) reduced the Si 2*p* intensity to less than a third of the original intensity. After exposure to 64 L of O_2, incomplete oxides with silicon bonded to one, two, and predominantly three oxygen atoms were formed. There is no indication that any significant amount of SiO_2 (silicon bonded to four oxygen atoms) is present. The annealing increased the oxidation stage, and SiO_2 was clearly formed, although the Si 2*p* chemical shift was somewhat smaller than the shift corresponding to Si bonded to four oxygen atoms. This, however, is generally the case in Si 2*p* spectra from thinner SiO_2 films. It is well known from earlier studies of Si oxidation that the chemical shift of Si 2*p* increases with oxide thickness, and reaches a limiting value of $\simeq 4.3$ eV for SiO_2 films thicker than $\simeq 50$ Å.[19] This change is presumably related to bond-angle strain rather than stoichiometry.

Turning to the Cs 4*d* spectra one should notice the extended tail in the clean Cs overlayer spectrum. Tochihara *et al.*[13] assigned this tail to extrinsic plasmon excitations in the Cs overlayer. The 64 L O_2 exposure removed this tail, indicating charge transfer from Cs, although the associated chemical shift was negligible. After a brief annealing at 700 °C some Cs was still present on the surface, but 750 °C for just a few seconds was found sufficient for complete Cs removal. We have observed that the temperatures needed to desorb Cs from Si surfaces are not much affected by whether the surfaces are oxidized or not. This is in striking contrast to what was reported in the case of oxygen and cesium coadsorption on tungsten.[20] In that case much higher temperatures were required to desorb the cesium, apparently due to a strong cesium–oxygen bonding. Together with the absence of significant chemical shifts of the Cs 4*d* levels upon oxidation, the desorption behavior in the present case indicates that oxygen interacts more strongly with the Si substrate than with the Cs overlayer. Considering this, the conclusion that formation of bulk alkali-metal oxides is an important step in the promoted oxidation of Si, drawn recently in a study of potassium on Si(100)2×1,[6] seems somewhat questionable. Although bulk cesium oxides form as thick Cs films are exposed to oxygen, the behavior of Cs monolayers depends on the substrate and is generally different from that of a thick film.[21] The large enhancement of the Si oxidation rate caused by a monolayer of Cs is apparently not associated with formation of strong cesium–oxygen bonds. Moreover, the ease with which Cs is removed by thermal desorption strongly suggests that it stays on top while SiO_2 is formed at the Cs-Si interface. If Cs atoms were being trapped underneath the SiO_2 layer, their desorption would be limited by the diffusion through the oxide, and also at higher temperatures Cs removal would be slow. The absence of damping of the Cs 4*d* emission after oxygen exposure [see Fig. 1(b)] is another clear indication that most of the adsorbed oxygen goes underneath the cesium layer, i.e, to the Cs-Si interface.

Valence-band spectra were also measured, and found to be very similar to those obtained from the Si(100)2×1 surface.[8]

Of interest for technological purposes, in addition to the moderate temperature required, is the fact that, as in the case of our previous studies on Si(100)2×1,[4,5,8] flash annealing of only a few seconds duration is sufficient for the SiO_2 formation. This may allow for growth of SiO_2-Si interfaces with less defects, as recently demonstrated by Fogarassy *et al.*[22] for direct (without promoter) oxidation of silicon by thermal flashing.

In order to study the initial oxidation of monolayer cesiated Si(111)7×7 in more detail, we made stepwise O_2 exposures up to 16 L, starting at 0.25 L, and recorded the relevant spectra at each step. Figure 2 shows the development of Si 2*p* spectra at increasing oxygen exposure. The spectra are normalized so that the unshifted component is of constant height. As in Fig. 1 the shifts corresponding to different oxidation states of silicon are indicated by vertical bars. As could be expected there is no firm indication of SiO_2 formation, and furthermore

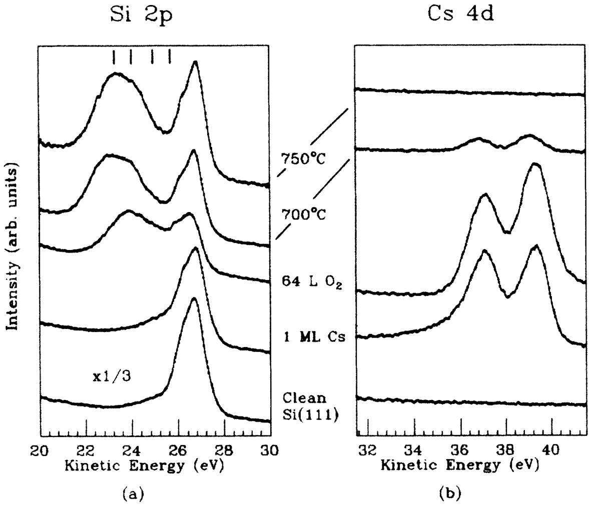

FIG. 1. Photoemission spectra showing (a) the Si 2*p*, and (b) the Cs 4*d* core levels for clean Si(111)7×7, after deposition of 1 ML (monolayer) of Cs, after exposure to 64 L of O_2, and after annealing at 700 and 750 °C, respectively. Photon energies were 130 eV in (a), and 120 eV in (b). The photoemission intensities are normalized to the beam current. The positions of Si 2*p* oxide features, associated with Si atoms bonded to one, two, three, and four oxygen atoms (Ref. 18), are indicated by vertical bars.

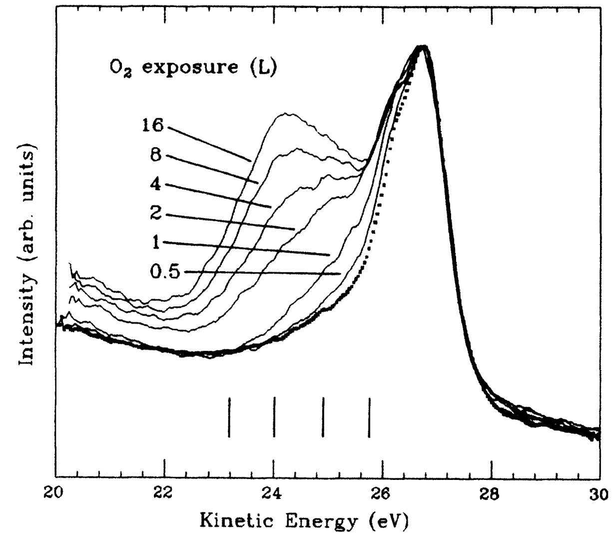

FIG. 2. Si 2p core-level spectra showing the growth of oxides on the cesiated (1-ML) Si(111)7×7 surface for oxygen exposures up to 16 L. The photon energy was 130 eV. The spectra are normalized to give substrate peaks of equal height. Vertical bars as in Fig. 1.

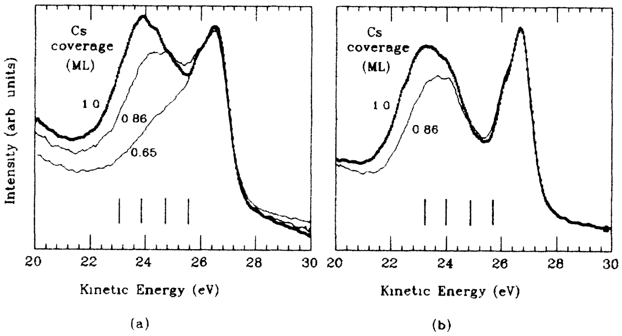

FIG. 3. Si 2p core-level spectra at 130 eV photon energy from the Si(111)7×7 surface exposed to 64 L of O_2 after Cs depositions of varying duration. Spectra in (a) were taken directly after oxygen exposure, those in (b) after annealing at 750 °C. The Cs coverages (1.0, 0.86±0.05, 0.65±0.08 ML) were determined from relative intensities of the Cs 4d and Si 2p core levels, and by using the fact that the saturation coverage is 1 ML at room temperature. Normalization and vertical bars are as in Fig. 2.

the oxidation stage corresponding to one oxygen atom per silicon atom seems almost absent at any exposure. As observed for Si(111)2×1 (Ref. 3) and Si(100)2×1,[23] the silicon apparently goes rapidly to a state where it is bonded to several oxygen atoms, and as the exposure is increased above 4 L most involved silicon atoms are bonded to three oxygen atoms. There seems to be some kind of onset between 1 and 2 L of O_2, after which oxidation occurs more readily. We also observed that the Cs 4d tail assigned to plasmon excitations[13] disappeared after 1–2 L of O_2 exposure indicating that the Cs top layer is stripped of its 6s conduction electrons at a much earlier stage than the top layer of thick Cs films.[21]

Finally, we studied how the oxidation depends on the amount of Cs on the surface. Figure 3 shows Si 2p spectra (a) directly after exposure to 64 L of O_2, and (b) after annealing at 750 °C, with varying Cs coverage prior to oxygen exposure. As before, different oxidation stages are indicated by vertical bars. It is clear that submonolayer cesium coverages resulted in smaller amounts of oxide, and also the average stage of oxidation was reduced, as is evident from the smaller chemical shifts. This finding applies to the annealed oxides as well. The valence-band spectra for submonolayer coverages showed lower intensities of all oxygen-related peaks. These results imply a general reduction of the oxygen trapping capability, leading to thinner and less stoichiometric oxide layers. It is interesting to note that the lowest Cs coverage reported in Fig. 3(a) was not, even using a lowest limit estimate, below half a monolayer. Yet the amount of oxide formed was just a tiny fraction of what was obtained using a full monolayer of Cs. This shows that there is a very rapid decrease in the catalytic activity at increasing Cs-Cs separations, and that isolated Cs atoms are not efficient promoters. The strongly nonlinear dependence on Cs coverage emphasizes the nonlocal nature of the catalytic mechanism. Also, if the deposited Cs had formed islands rather than spreading uniformly over the surface, one would expect a more proportional relationship between Cs coverage and catalytic action.

From these results and our previous studies,[3,4,8,23] it seems possible to describe the catalytic oxidation process at room temperature as consisting of the following steps. (i) The oxygen molecules stick to the cesiated surface, and (ii) they are dissociated. It is not fully clear where and how the dissociation takes place, or what role the substrate plays, but it has been suggested[3] that O_2 is dissociated within the surface dipole layer by charge transfer to antibonding molecular levels, as was calculated by Wimmer *et al.*[24] for K and CO coadsorption on Ni. Finally, (iii) the atomic oxygen start forming bonds with the topmost Si layer. An oxygen-related valence-band peak, which we, from comparison with the results of Hofer *et al.*,[25] associate with molecular oxygen, was observed to saturate approximately simultaneously with the onset of oxidation as seen in Si 2p spectra (see Fig. 2). The intensity of another peak, characteristic of atomic oxygen, continued to increase as further oxygen exposures were made. Provided that the assignment of valence-band peaks is correct this observation indicates that the onset is primarily associated with the dissociation step.

We are now ready to compare the present results with those we previously obtained from the Si(100)2×1 surface.[8] In Fig. 4, Si 2p spectra from oxidized Si(111)7×7 and Si(100)2×1 surfaces, measured (a) before and (b) after annealing, are shown together. The spectra from the different surfaces have been normalized so that the unshifted Si 2p components are of equal height. The spectra measured before annealing are very similar, with the (111)7×7 surface only slightly less oxidized. The Si 2p spectrum measured at room temperature from the surface of cesiated Si(111)2×1 (Ref. 3) after O_2 exposure

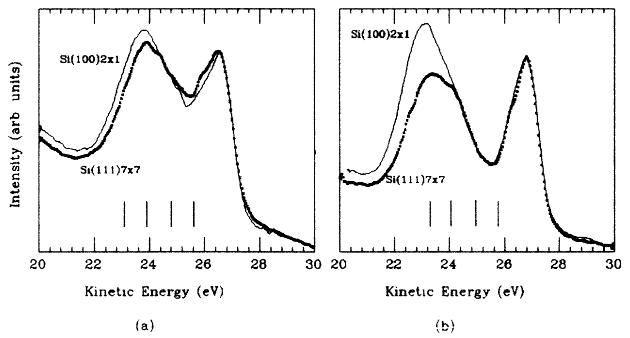

FIG. 4. Comparison of Si $2p$ core-level spectra at 130 eV photon energy from oxidized Si(100)2×1 (Ref. 2) and Si(111)7×7 surfaces. Spectra in (a) were taken directly after oxygen exposure, those in (b) after annealing at 750 °C. Normalization and vertical bars are as in Fig. 2.

is also very similar. After the desorption of the cesium, the resulting oxide film on Si(111)7×7 is somewhat less stoichiometric and significantly thinner than on Si(100)2×1. It seems very likely that the difference in oxide thickness after annealing can be associated with structural differences. The (111) atomic planes are harder to break up than the more open (100) planes, which have only two backbonds per Si atom. The similarity in behavior of the two surfaces during room-temperature oxidation shows that the top layers of both surfaces are equally susceptible to room-temperature oxidation. If the dangling-bond density was of major importance for the initial oxidation one would expect a more significant difference at this point. It is also likely that the reactivity of the top layers is increased by cesium-induced backbond weakening. The growing oxide layer may, however, counteract this mechanism by separating the cesium overlayer from the silicon substrate. It is also likely that the oxide layer may contribute to backbond weakening in a way similar to the Cs layer, although perhaps not as strongly. This could explain why annealing is needed to reach the highest oxidation stage. The slower reaction rate on Si(111)7×7 during annealing would also indicate that a considerable fraction of the trapped oxygen desorbs during the annealing. The lower stoichiometry of the oxide is a straightforward consequence of the reduced thickness. As intermediate oxidation states are characteristic of the oxide-silicon interface, leading to a less abrupt interface, they appear more important when the oxide layer is thin.

If the picture of the oxidation process given above is essentially correct, the growth of thicker oxide films could possibly be achieved at a temperature that allows for SiO_2 formation (as opposed to the room-temperature formation of lower oxides) simultaneously with continued oxygen adsorption. It is also likely that thicker Cs overlayers (sample cooling required) can trap and dissociate more oxygen, leading to a thicker SiO_2 film. Alkali-metal coverages in excess of one monolayer can increase the thickness of the resulting SiO_2 layer as has been demonstrated using sodium,[4] and lately verified using potassium.[6]

IV. CONCLUSIONS

In summary, we have demonstrated that 1 ML of Cs promotes the oxidation of Si(111)7×7 by increasing the sticking of O_2, by dissociation of the oxygen molecules, and most likely also by weakening the backbonds of the top Si layers so that initial oxidation takes place already at room temperature. The Cs stays on top and remains bonded preferentially to Si surface atoms. Annealing at moderate temperature desorbs the Cs completely and leads furthermore to the formation of a more stoichiometric oxide, although with less efficiency than on Si(100)2×1. This can probably be associated with the more closed structure of the Si(111) atomic planes. Significantly, there is no indication that the difference in dangling-bond density is relevant during the initial oxidation. Finally, we also found that the catalytic mechanism appears to be strongly nonlocal.

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