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Electronic promoters and semiconductor oxidation: Alkali metals on Si(111) surfaces

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We examine the effect of thin (1–2 monolayers) overlayers of the low-electronegativity metals Cs and Na upon the oxidation of Si(111) surfaces. Synchrotron-radiation photoemission studies of oxygen chemisorption as a function of overlayer thickness and oxygen exposure indicate large oxidation-promotion effects and the formation of Si oxide phases where high Si oxidation states dominate. Comparison with promotion effects induced by transition-metal and noble-metal overlayers forces, for alkali metals, a reevaluation of the microscopic mechanisms proposed to explain overlayer-induced oxidation promotion.

Many metal overlayers on semiconductor surfaces give rise to oxidation-promotion effects upon exposure to atomic or molecular oxidizing species.[1-9] Most mechanisms proposed to explain oxidation promotion for silicon[1-9] are based on one or more of the following aspects: disruption of the semiconductor surface,[4] "metallization" of the surface,[5,10] disruption of the Si sp^3 hybridization,[3-5] and formation of low-stability interface alloys[3,5] with substantial catalytic activity for dissociating molecular species.[5,6]

To clarify the relative importance of these mechanisms, we have conducted a study of the oxidation of Si(111) surfaces in the presence of Cs and Na overlayers. These metals represent important test cases since they do not appear to give rise to substantial surface disruption or interdiffusion,[11-15] and they exhibit a well-defined transition from a nonmetallic to a metallic state at coverages on the order of 0.5 monolayers (ML).[12-16] Furthermore, a number of stimulating pioneering studies have shown that coadsorption of Cs and oxygen on metals[17] and GaAs (Ref. 6) may enhance the oxidation kinetics.

In the case of both Cs and Na overlayers we observe a strong oxidation-promotion effect that is not related to the formation of low-stability silicidelike phases at the interface, nor to the metallization[15] of the silicon surface, so that electrostatic overlayer-oxygen interactions mediated by the substrate should be examined to explain catalytic promotion.[18]

All experiments were performed at room temperature following the methodology described in Refs. 8, 9, 19, and 20, at the Synchrotron Radiation Center of the University of Wisconsin-Madison. Most of our data for Cs have been obtained at saturation coverage[12-15] (~1 monolayer). For Na, we have selected the monolayer coverage range for consistency. The results are summarized in angular-integrated energy distribution curves (EDC's) in Figs. 1–3. The results for the Si $2p$ core emission in Fig. 2 are shown after subtraction of a smooth secondary background, correction for substrate band bending, and (approximate) normalization to the main emission feature, in order to emphasize line-shape changes.

Results for the valence-band emission from the Si(111)-Cs system are shown in Fig. 1. The bottommost spectrum is representative of the clean-Si(111)-surface emission, while spectra displaced upward show the effect of the deposition of one monolayer of Cs followed by sequential exposure to oxygen. The valence-band emission for Si(111)-Cs before oxidation is in good agreement with the results of Tochihara and co-workers,[14] with a sharp emission feature at about 1 eV and the shallow $5p$ core levels between 10 and 15 eV. Correspondingly, the Si(111)-Cs system shows no interdiffusion, a strongly polar chemisorption bond that lowers the semiconductor surface work function, and, near saturation coverage, a "tailing" of valence states up to E_F (Fig. 1) and metalliclike plasmon loss features.[12-14,20]

Exposures as low as 0.25 L (1 L $=10^{-6}$ Torr sec) in Fig. 1 suppress the emission from the 1-eV feature—which is related to localized Cs-Si bonding states[20]—and give rise to a broad, structured oxide-related emission band centered about 6 eV below E_F. Emission from the shallow Cs $5p$ core states does not appear attenuated upon oxidation, while a definite broadening of the $5p$ line shape progressively takes place. Further oxygen exposure yields little change of the valence-band emission. At oxygen exposures up to 100 L a further decrease of the semiconductor-derived emission within 4 eV of E_F is observed, but the valence band remains dominated by the 6-eV oxide emission band and by the Cs $5p$ core states.

Results for the valence-band emission from Si-Na are not shown here due to space limitations, but they are qualitatively similar to those of Fig. 1. Very little is known of Si-Na interfaces,[20] and we will draw on Si-K results[11-16]

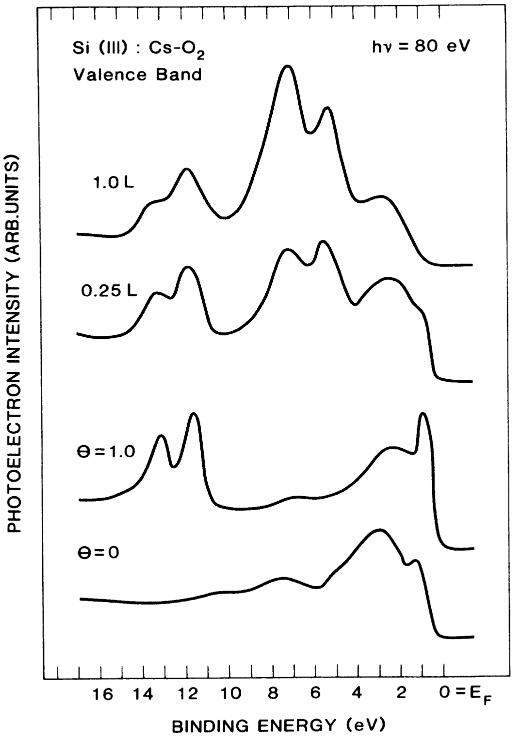

FIG. 1. Valence-band emission from the Si(111)-Cs interface as a function of oxygen exposure. The bottommost spectrum shows the clean Si(111) emission. Spectra displaced upward show the effect of monolayer Cs deposition followed by sequential oxygen exposure.

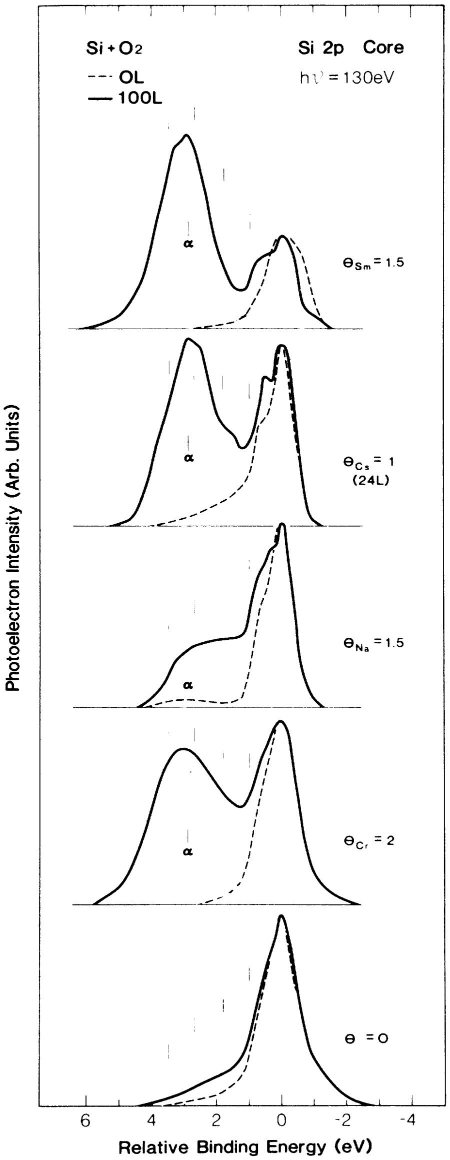

FIG. 2. Si 2*p* core emission before (dashed line) and after (solid line) exposure to 100 L (24 L for Cs) of oxygen. We show results for the free Si surface (bottommost EDC) while spectra displaced upward show the effect of Cr, Na, Cs, and Sm overlayers on Si oxidation. The vertical bars mark the position of Si 2*p* oxide features associated by Hollinger and Himpsel (Ref. 21) with Si atoms coordinated with one, two, three, and four oxygen atoms. Vertical bar *α* marks the position of a Si 2*p* oxide feature identified by Riedel *et al.* (Ref. 22) during oxidation of amorphous silicon.

in discussing our data because of the electronic similarity of Na and K. A recent paper by Ciraci and Batra[15] discusses the Si(100)-K case, and a number of analogies are found with the Si(100)-Cs and Si(111)-Cs cases. Experimentally, we observe no interdiffusion at the interface, and a strongly polar chemisorption bond.[20]

In Fig. 2 we show the effect of oxygen exposure on the Si 2*p* line shape for a number of Si-metal systems. Spectra for Sm (1.5 ML), Cs (1 ML), Na (1.5 ML), and Cr (2 ML) overlayers on Si(111) are shown before (dashed line) and after (solid line) exposure to 100 L of oxygen (24 L for Cs). For comparison we also show (bottommost spectrum) results for the oxidation of the free Si(111) surface. The overlayers included in Fig. 2 are those which exhibit the largest oxidation-promotion activity observed to date[1-9] on Si. We have chosen comparable metal coverages for all overlayers, although for Sm and Cr we have selected slightly larger values in order to exceed the critical coverage for oxidation promotion [about 2.5 Å for Sm (Ref. 9) and 1.5 Å for Cr (Ref. 8)]. Below this coverage the two overlayers exhibit little catalytic activity.[8,9] The vertical bars in Fig. 2 at 0.9, 1.8, 2.6, and 3.5 eV mark the position of the chemically shifted Si 2*p* contributions observed by Hollinger and Himpsel[21] during Si(111) oxidation, and associated by these authors with Si atoms bonded to 1, 2, 3, and 4 oxygen atoms, respectively. Vertical bar *α* marks the position of the dominant Si 2*p* oxide feature observed by Riedel, Turowski, Magaritondo, and Quaresina,[22] during oxidation of amorphous silicon.

If we focus now on the results for Cs and Na overlayers, we note that the unoxidized Si 2*p* spectra (dashed line) show high-binding-energy features. A broad tail extends from 1.2 to 3.0 eV in the case of Cs overlayers, while a well-resolved feature is observed between 2 and 3.5 eV for

Na overlayers. We associate these features with $2p$ emission channels that involve collective excitations.[14,20] Upon oxidation, Fig. 2 shows that both Cs and Na overlayers exhibit oxidation promotion activity, that the magnitude of the promotion effect is larger for Cs than for Na, and that the reaction products involve several nonequivalent oxidation states for silicon, with high oxidation states being predominant. The nature of the reaction products appears similar to that observed in the presence of Sm and Cr overlayers, and consistent with what could be expected for a disordered, substoichiometric SiO_2 surface phase.[22]

Several microscopic mechanisms have been proposed to explain overlayer-induced silicon oxidation promotion. Most models[2-5] propose that the formation of interface reaction products breaks the sp^3 configuration of the silicon substrate so that the Si atoms at the interface would be in an amorphous metallic environment with "disrupted bonds"[2] and they could easily be oxidized.[2] Abbati *et al.*[5] explain the lack of adsorption saturation effects by proposing a self-sustaining mechanism in which a flow of Si atoms is established through a silicon-metal intermixed layer located between the growing oxide and the Si substrate. This layer would make Si atoms with "broken"[5] sp^3 configuration and "weaker" Si—Si bonds available for oxidation. The incoming oxygen would then react preferentially with Si and displace the metal from Si so that the metal would become available for intermixing with the substrate and produce further Si disruption.[5] Cros[3] points out that the increased density of states at E_F in the intermixed silicon-metal interface species would ease the breaking of the oxygen molecule and the creation of atomic oxygen excited states.[3]

In our view one of the experimental observations that most strongly supports the "reactive interface" picture[2-5] of oxidation promotion is the evidence of a critical coverage for oxidation promotion due to Cr and Sm overlayers.[8,9] Both overlayers show substantial catalytic activity *only* for metal coverages above a critical threshold coverage that corresponds to the onset of Si-metal interdiffusion and to the formation of silicidelike interface species. The results in Fig. 2, however, provide definitive evidence against the general applicability of this microscopic picture. Both Cs and Na overlayers are found to give rise to large oxidation promotion effects, although they do not intermix with silicon, they do not form silicidelike surface species, and they do not break the sp^3 hybridization of the Si surface atoms.

An alternative mechanism could involve the "metallization" of the Si surface[10,15] without disruption of the Si surface and breaking of the Si sp^3 hybridization. Okuno, Ito, Iwami, and Hiraki[10] had proposed that "tailing" of the metal wave function into the semiconductor may "screen" the Coulomb interaction and reduce the stability of the semiconductor covalent bonding. Although this picture was rather qualitative,[10] calculations by Ciraci and Batra[15] show that toward saturation coverage for K overlayers on Si(100) the adatom-substrate distance becomes smaller and results in an effective core screening[15] in agreement with work-function data. We sought to investigate this second microscopic picture by studying in Fig. 3 the evolution of the characteristic overlayer-induced collective excitations as a function of oxygen exposure. Upon deposition of Na on the Si(111) surface, well-defined loss features are observed on the high binding energy side of the Si $2p$ and Na $2p$ core lines. Such "interface plasmons"[20] are a direct manifestation of the overlayer-induced metallization[15] of the surface. Upon oxidation, the results of Figs. 2 and 3 indicate that Na-induced oxidation promotion effects are encountered in a wide range of oxygen exposures, although the characteristic metallic surface loss features disappears in the early chemisorption stage.

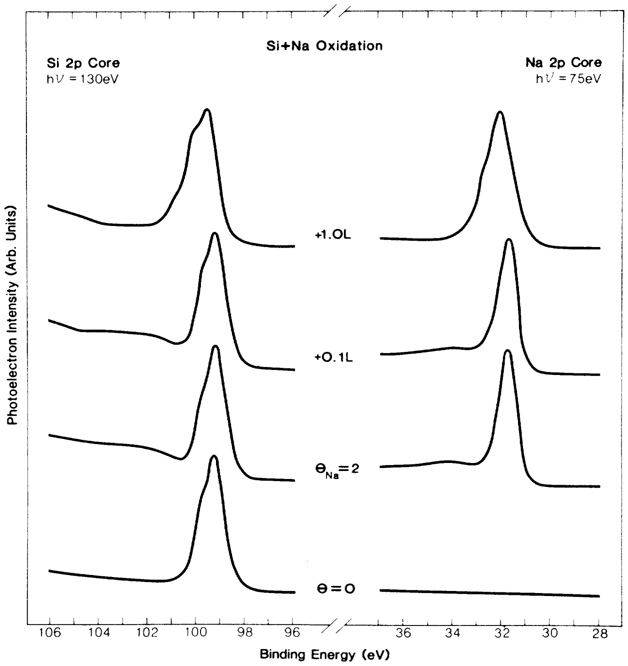

FIG. 3. Emission from the Si $2p$ and Na $2p$ core levels from a 1.5-ML Na overlayer on Si(111). The bottommost spectra show the situation before Na deposition. Spectra displaced upward show the effect of Na deposition and of the following exposure to 0.1 and 1.0 L of oxygen. Collective loss features visible on the high binding energy side of the core lines reflect the overlayer-induced metallization of the semiconductor surface. These characteristic loss features are suppressed in the early stages of oxygen chemisorption (topmost spectrum).

Another aspect of alkali-metal chemisorption, namely, the establishment of a substantial surface dipole, may instead play a role in explaining oxidation promotion effects induced by alkali metals. The chemisorption of alkali metals induces a modification of the electrostatic potential in the surface region:[18] The alkali valence electrons are polarized[15,18] toward the substrate surface leading to a dipole layer which raises the electron levels of the metallized silicon surface relative to the vacuum level. The rigid shift of the Fermi level yields the measured reduction of the work function. If a molecular species is absorbed ***within*** the surface dipole layer, the energy shift of the molecular level is less pronounced than that of the substrate levels. This may result in a relative shift to higher binding energies of the molecular levels relative to E_F, charge transfer to molecular antibonding orbitals, and formation of atomic oxygen that can react with Si atoms in the interface region. This mechanism was verified by Wimmer, Fu, and Freeman[18] for K and CO coadsorption on Ni, and its extension to the Si-O_2 case is only tentative and based on the following points: (1) Alkali-metal chemisorption does induce a metallization of the Si surface and (2) establishes a surface dipole layer as shown by the decrease in work function. (3) A quantitative analysis of the variation of Cs, Na, and Si core-level emission intensity with oxygen chemisorption indicates that oxides are nucleated *below* the alkali-metal monolayer.[20,23] This can be seen, for example, in Fig. 1, where the emergence of the oxide band and the corresponding attenuation of the Si valence-band emission are not accompanied by detectable attenuation of the Cs 5*p* emission. In contrast, for a number of noble- and transition-metal overlayers on Si (Refs. 1, 4, and 8), it appears that Si oxide species nucleate on top of the silicidelike metallic surface layer.[24] (4) The model is consistent with the reduced activity of Na overlayers relative to Cs overlayers in promoting oxidation: Because of the higher electronegativity of Na relative to Cs the chemisorption-induced surface dipole is expected to be reduced in the case of Na. Furthermore, the reduced Na radius relative to Cs would make the location of chemisorbed molecular species within the surface dipole layer less likely for Na overlayers than for Cs overlayers.[25]

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[23] Early results for Cs and O coadsorption on metals (Ref. 17) and Si(100) surfaces were interpreted as suggesting the formation of a Cs-O substrate double layer.

[24] Since the oxide layer is formed underneath the metal overlayer, one could argue that oxidation should slow down rapidly because of the decrease in the electric dipole field with increasing layer thickness, until no more oxidation activity could take place. It is likely, though, that the Cs-Si surface dipole field responsible for the initial oxidation promotion is replaced in the following stages by an equally effective Cs-O surface dipole, as demonstrated by the lack of major changes in the Cs 5*p* binding energy in Fig. 1. In this connection we have to emphasize that we have no data for exposures greater than 10^3 L, so that saturation may indeed take place at higher exposures, and that inhomogeneities in the thickness of the oxide layer may also play a role.

[25] We mention that Su *et al.* (Ref. 6) have proposed that dissociative chemisorption of O_2 *on top* of a Cs overlayer could explain Cs-induced oxidation promotion effects on GaAs(110). The relative importance of the surface dipole layer, surface metallization, and overlayer morphology in the case of GaAs is more difficult to assess in the absence of a theoretical background (Refs. 15, 16, and 18).