

Electronic properties of O₂ on Cs or Na overlayers adsorbed on Si(100) 2 × 1 from room temperature to 650 °C

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Valence-band and core-level photoemission spectroscopy experiments using synchrotron radiation were performed at various temperatures to study the effect of oxygen on cesium or sodium overlayers adsorbed on a Si(100)2×1 surface. At room temperature, a large enhancement of the silicon oxidation was observed with formation of high oxidation states such as Si³⁺. Thermal annealing to low temperatures resulted in the formation of a SiO₂-Si interface with subsequent complete desorption of the alkali metal.

In recent years, there has been a growing interest in the study of the electronic properties of alkali-metal adsorption on metal surfaces¹⁻⁴ combined with new theoretical approaches using full-potential linearized augmented-plane-wave (FLAPW) calculations⁵ for transition metals. Similar works have been reported for alkali-metal adsorption on semiconductors by theoreticians⁶⁻⁸ as well as experimentalists.⁹ Intensive efforts have also been devoted to the coadsorption of oxygen with alkali metals on metal surfaces.^{1,4,10} However, despite the promising results obtained so far in the pioneer work on GaAs,¹¹ it is only recently that comparable work has been performed on semiconductors where cesium and sodium were shown to dramatically enhance the oxidation rate of silicon^{12,13} by several orders of magnitude, and of indium phosphide¹⁴ by up to 10¹³. The oxidation of semiconductors is important in device technology. High oxygen exposures [10³-10⁶ L (1 L = one langmuir = 10⁻⁶ Torr sec)] combined with temperatures on the order of 1000 °C are necessary to oxidize silicon (see Ref. 15, and references therein) while oxygen exposures between 10⁹-10¹³ L are required for III-V compound semiconductors.¹⁶ These difficulties have redirected the effort to look for catalysts such as noble, transition, and rare-earth metals,¹⁷ which also promote the oxidation of semiconductors as is done by alkali metals.

In this Rapid Communication we present, as a function of increasing temperature, the electronic properties of the Si(100) 2×1 surface covered with Cs or Na overlayers at room temperature, followed by molecular oxygen exposures. Valence-band and core-level photoemission spectroscopy was performed using synchrotron radiation. For the first time, we show that the room-temperature catalytic oxidation was combined with the subsequent total thermal desorption of the catalyst at moderate temperatures, resulting in the formation of a clean SiO₂-Si interface.

The experiments were carried out at the new 1-GeV storage ring at the University of Wisconsin-Madison. The

light was dispersed by a Grasshopper Mark II monochromator. The experimental chamber was equipped with a double-pass cylindrical-mirror analyzer (CMA) with a co-axial electron gun for Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) optics. The overall resolution (electrons+photons), which was 0.3 eV in the valence band, was estimated at 0.9 eV in the Si 2*p* core-level region. The pressure was 3×10⁻¹¹ Torr. The Si(100) single crystal was cleaned by cycles of ion bombardment and thermal annealing at 1000 °C and checked for cleanliness by AES while LEED showed the expected 2×1 reconstruction. Pure cesium or sodium was deposited on the silicon surface by the use of carefully outgassed chromate sources. The pressure did not increase by more than 2×10⁻¹¹ Torr for cesium and 5×10⁻¹¹ Torr for sodium during the time necessary to deposit one monolayer.¹²

Figures 1(a) and 1(b) display the behavior of Si 2*p* and Cs 4*d* core levels for the O₂/Cs/Si(100)2×1 system at various temperatures from room temperature to 650 °C. When one monolayer of cesium deposited on Si(100) is exposed to molecular oxygen at room temperature, a new structure appeared to grow at 2.6-eV higher binding energy from the Si 2*p* core level. It is related to silicon atoms bonded to three oxygen atoms,¹⁵ Si³⁺. When the temperature was raised to 650 °C, the chemical shift is increased to 3.9-eV higher binding energy relative to the Si 2*p* core level. It corresponds to the formation of silicon dioxide¹⁵ SiO₂ on the silicon surface. If we follow the corresponding behavior of the Cs 4*d* core level [Fig. 1(b)], one can observe that oxygen exposures change the shape and the intensity ratio between the 4*d*_{5/2} and 4*d*_{7/2} spin-orbit-split components. This could be related to the disappearance, in the presence of oxygen, of the plasmon satellite¹⁸ as a consequence of the charge transfer from cesium to oxygen. We will discuss this point in detail elsewhere.¹⁹ With increasing temperatures, the Cs 4*d* core-level intensity [Fig. 1(b)] decreased and cesium was completely removed from

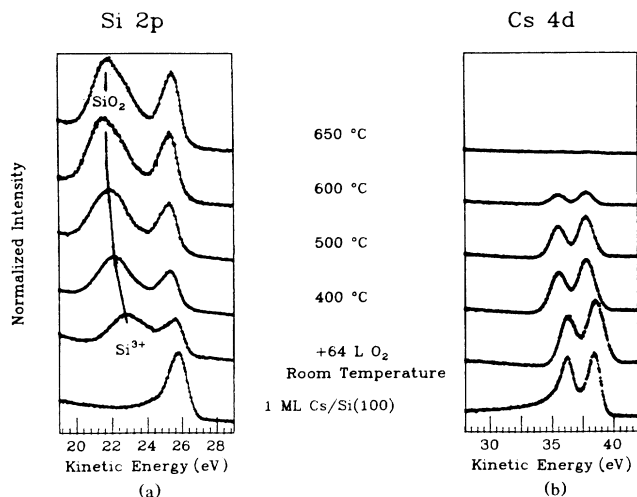


FIG. 1. (a) 64-L O₂/1 ML Cs/Si(100): Photoemission spectra showing the Si 2*p* core level for increasing temperatures with the use of an incident photon energy of 130 eV. The photoelectron intensity is normalized to the beam current. (b) 64-L O₂/1 ML Cs/Si(100): Photoemission spectra showing the Cs 4*d* core levels for increasing temperatures with the use of an incident photon energy of 120 eV. The photoelectron intensity is normalized to the beam current.

the surface at 650 °C. Figure 2 displays the intensity of the Cs 4*d* core levels versus temperature. Note that above 500 °C, the amount of cesium present on the surface decreases rapidly and linearly. Concurrently, the ratio of “2*p*” core-level intensities between SiO₂ and Si is seen to remain constant. The total desorption of cesium was reached at 650 °C while temperatures well above 1000 °C were necessary to remove it completely from transition metal surfaces.²⁰ Therefore, a clean (uncesiated) SiO₂-Si interface is formed at 650 °C (Ref. 12) which is a lower temperature than that necessary¹⁵ to form such an interface without cesium.

Figure 3 displays the valence band of the cesiated Si(100) 2×1 surface, and the oxygen-covered Cs/Si(100)2×1 surface from room temperature to 600 °C. The exposure of the cesium overlayer to 64-L oxygen results in the growth of peaks *A* and *B* which are related to oxygen 2*p* levels. The cesium 5*p* semicore levels are shifted to lower binding energy by 0.4 eV. One must note that much larger shifts have been reported^{4,10} for transition metal substrates. This implies a preferential reaction of oxygen with silicon rather than with cesium, as can be deduced from the large chemical shift of the Si 2*p* level [Fig. 1(a)]. This is in contrast with the behavior of cesiated transition-metal surfaces, where both substrate and adsorbate were markedly oxidized.^{4,10} When the temperature was raised, peak *A* disappeared while peak *B* is shifted upward to 7.4-eV binding energy above 550 °C, corresponding to the formation of SiO₂ as already observed on the Si 2*p* chemical shift. At 600 °C the shoulder between peak *B* and the Fermi level was related to emission from the silicon valence band. Peak *C* (11 eV) was also related to SiO₂ formation.¹⁵ From the Si 2*p* core-level intensities, it

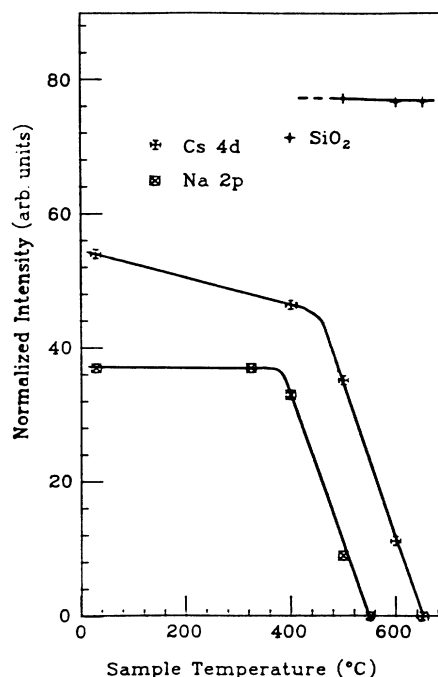


FIG. 2. The intensities of the Cs 4*d* and Na 2*p* core level vs temperature for the 64-L O₂/1 ML Cs or Na/Si(100) using incident photon energies of 120 and 82 eV, respectively, are displayed. Also shown is the ratio between the Si 2*p* core-level intensities for the SiO₂ and Si species, obtained with a photon energy of 130 eV.

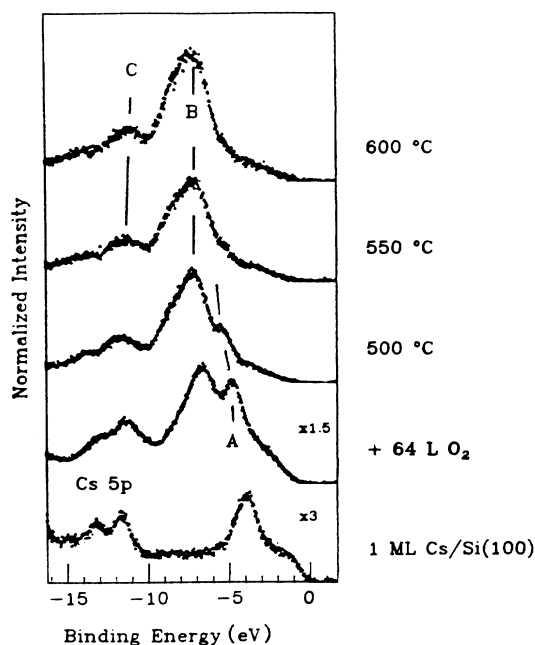


FIG. 3. The valence-band spectra for the 1-ML Cs/Si(100) and 64-L O₂/1 ML Cs/Si(100) systems at various temperatures are shown. An incident photon energy of 82 eV was used. The photoelectron intensity is normalized to the beam current.

is possible to estimate the thickness of the silicon dioxide as greater than 10 Å.¹⁵ One must note that the oxygen saturation exposure was not reached at 64 L.

Figures 4(a) and 4(b) show the behavior of Si 2*p* and Na 2*p* core levels of the 64-L O₂/1 ML Na/Si(100)2×1 system for various temperatures up to 550°C. The behavior of sodium was found to be similar to that observed for cesium. The exposure to oxygen of the sodium overlayer induced the growth of Si³⁺ as can be deduced from the 2.6-eV chemical-shift feature¹⁵ on Fig. 4(a). However, for the same conditions, the amount of Si³⁺ was lower with sodium than it was with cesium, as can easily be seen from the relative intensity of the Si³⁺ oxide peak on both systems [Figs. 1(a) and 4(a)]. When the temperature was raised to 550°C, the oxide chemical shift increased to higher binding energy by 3.9 eV from the Si 2*p* level, corresponding to the formation of SiO₂.¹⁵ The Fig. 4(b) exhibits the corresponding sequence of the Na 2*p* core level. In the presence of 64-L O₂, the full width at half maximum (FWHM) of the Na 2*p* core level doubled. With increasing temperatures, its intensity decreases rapidly and linearly from 400 to 550°C, where it reaches zero (Fig. 2). This indicates that sodium was entirely removed from the silicon surface at 550°C, and a clean (sodium free) SiO₂-Si interface was formed.

As in the case of cesium, a plasmon satellite exists on Na/Si(100) near the Na 2*p* core level and is destroyed in the presence of oxygen by charge transfer from Na to O₂. This point will also be discussed elsewhere.¹⁹

Figure 5 displays the valence-band spectra for 1-ML Na/Si(100), for this system exposed to 64-L oxygen at room temperature, and then followed by annealing at various temperatures up to 550°C. The photon energy was 82

eV. Peaks *A* and *B* are related to oxygen 2*p* levels. However, at room temperature the spectrum at 64-L O₂/Na/Si(100) exhibits peak *B* less intense than peak *A* while the situation was reversed with cesium. Furthermore, on O₂/Cs/Si(100), peak *A* has a binding energy 5 eV instead of 5.75 eV for O₂/Na/Si(100) system. These differences are most likely related to the size of the cesium atom which is much larger than silicon, while sodium and silicon radii are about the same. Concurrently, a smaller amount of oxide (Si³⁺) was formed at room temperature with Na when compared to Cs [Figs. 4(a) and 1(a)]. On O₂/Cs/Si(100) system, oxygen migrated underneath the cesium as already reported on metallic substrates.^{4,10} A similar oxygen migration may also occur in the case of sodium although its smaller size allows Na atoms to come closer to the silicon surface, reducing the space for an oxygen atom. Therefore, the differences in the O 2*p* levels could also be related to a different environment for oxygen in the presence of Cs than of Na. With increasing temperatures, the O 2*p* levels were modified as follows: peak *A* disappeared, and peaks *B* and *C* arose at 7 and 11 eV at a temperature of 500°C, which corresponds to formation of SiO₂ (Ref. 15) (with ~4-eV gap) as already has been deduced from the Si 2*p* chemical shift [Fig. 4(a)]. As in the presence of cesium, the shoulder between *B* and the Fermi level (at 550°C) was related to emission from the silicon valence band. The thickness of SiO₂ was estimated to be 7–8 Å.

Although core-level photoemission spectroscopy has detection limits on the order of 0.1%, the rapid and linear

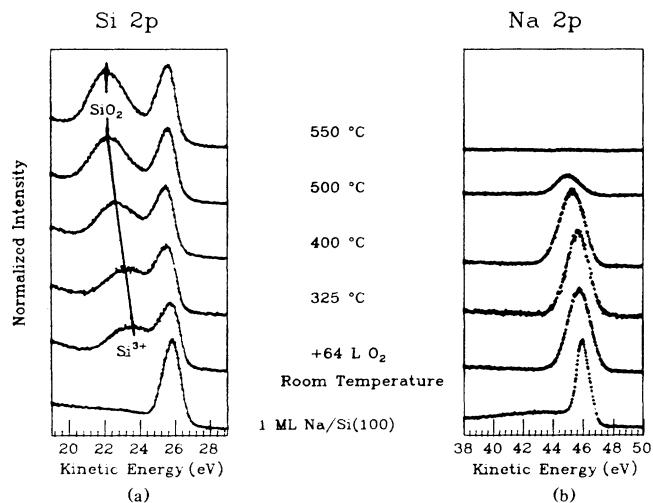


FIG. 4. (a) 64-L O₂/1.0 ML Na/Si(100): Photoemission spectra showing the Si 2*p* core level for increasing temperatures with the use of an incident photon energy of 130 eV. The photoelectron intensity is normalized to the beam current. (b) 64-L O₂/1 ML Na/Si(100): Photoemission spectra showing the Na 2*p* core levels with increasing temperature with the use of an incident photon energy of 82 eV. The photoelectron intensity is normalized to the beam current.

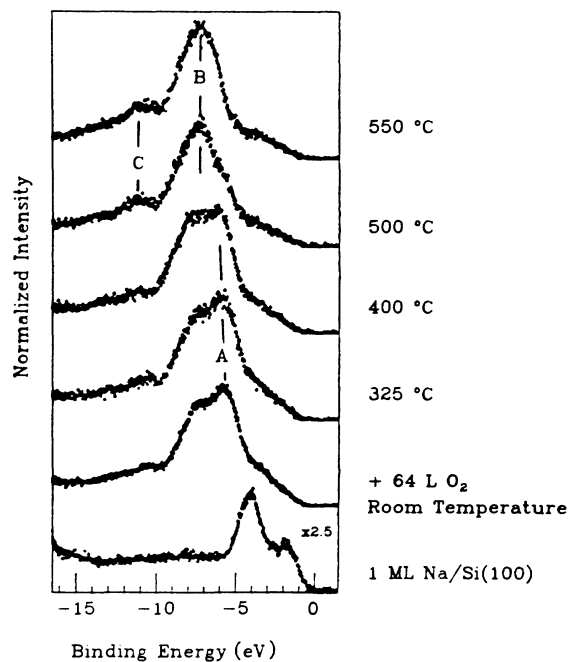


FIG. 5. The valence-band spectra for the 1-ML Na/Si(100) and 64-L O₂/1 ML Na/Si(100) systems at various temperatures are shown. An incident photon energy of 82 eV was used. The photoelectron intensity is normalized to the beam current.

decrease of Cs 4*d* and Na 2*p* core levels versus temperature suggests the complete removal of each of these alkali species by thermal desorption. If diffusion were occurring, the observed linear decrease would not be expected. Therefore, it is probable that no catalyst remains on the surface above the observed desorption temperatures.

In contrast with other metals or rare-earth metals,¹⁷ our results indicate that cesium and sodium showed no silicide formation. On Si(100), Cs and Na form a polarized bond which lowers the surface work function. With both alkalis, we found that “*s*” valence electron hybridized with “*p*” levels of the silicon substrate.^{19,21} A similar hybridization was also reported on transition metals involving “*d*” surface states in very good agreement with FLAPW calculations.^{3,5} The alkali metal weakens the back bonds of silicon which are therefore easily broken in the presence of oxygen, which is dissociated by the presence of cesium or sodium on the surface. Our results also indicate that a precursor oxygen molecular state exists prior to dissociation by alkali metals. This step is directly related to the onset of oxidation.¹⁹ Cs and Na also increase the oxygen sticking coefficient dramatically. All these factors contribute to the enhancement of silicon oxidation. In comparison with transition metals,²⁰ the rather low temperature of alkali desorption indicates that the bonding between Cs

or Na and silicon is rather weak.

Similar to Cs and Na the other alkali metals should play the same role of electronic promoter of Si oxidation. This has already been shown for Li and K, where potassium also desorbed at mild temperatures.²² However, in contrast with the other alkali metals, Li interdiffuses through the surface and therefore is not removable by thermal desorption.²³

In conclusion, we have shown that alkali metals enhance the oxidation of silicon by 4–6 orders of magnitude. Our results have revealed that in the presence of a sodium or cesium layer, oxygen preferentially reacts with the silicon substrate in contrast to metallic substrates,^{4,10} where both adsorbate and substrate react with oxygen. Finally, for the first time the catalytic oxidation of silicon was combined with the removal of catalyst at moderate annealing temperature.

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¹S. A. Lindgren and L. Wallden, *Phys. Rev. B* **22**, 5967 (1980); *Solid State Commun.* **28**, 282 (1978).

²L. Surnev, G. Blisnakov, and M. Kiskinova, *Solid State Commun.* **37**, 87 (1981).

³P. Soukiassian, R. Riwan, and Y. Borensztein, *Solid State Commun.* **44**, 1375 (1982); P. Soukiassian, R. Riwan, J. Lecante, E. Wimmer, S. R. Chubb, and A. J. Freeman, *Phys. Rev. B* **31**, 4911 (1985); P. Soukiassian, R. Riwan, J. Cousty, J. Lecante, and C. Guillot, *Surf. Sci.* **152/153**, 290 (1985); J. Cousty, R. Riwan, P. Soukiassian, and F. Mila, *J. Phys. C* **19**, 2883 (1986).

⁴P. Soukiassian, P. Roubin, J. Cousty, R. Riwan, and J. Lecante, *J. Phys. C* **18**, 4785 (1985).

⁵E. Wimmer, A. J. Freeman, J. R. Hiskes, and A. M. Karo, *Phys. Rev. B* **28**, 3074 (1983).

⁶S. Ciraci and I. P. Batra, *Phys. Rev. Lett.* **56**, 877 (1986).

⁷J. R. Northrup, *J. Vac. Sci. Technol. A* **4**, 1404 (1986).

⁸H. Ishida, N. Shima, and M. Tsukada, *Phys. Rev. B* **32**, 6246 (1985).

⁹T. Aruga, H. Tochihara, and Y. Murata, *Phys. Rev. Lett.* **53**, 3720 (1984); R. Avci, *J. Vac. Sci. Technol. A* **4**, 1400 (1986).

¹⁰P. Soukiassian, R. Riwan, Y. Borensztein, and J. Lecante, *J. Phys. C* **17**, 1761 (1984); P. Soukiassian, R. Riwan, and J. Lecante, *Surf. Sci.* **152/153**, 522 (1985); M. Kiskinova, G. Rangelov, and L. Surnev, *ibid.* **172**, 57 (1986).

¹¹W. E. Spicer, I. Lindau, C. Y. Su, P. W. Chye, and P. Pianet-

ta, *Appl. Phys. Lett.* **33**, 934 (1978).

¹²P. Soukiassian, T. M. Gentle, M. H. Bakshi, and Z. Hurych, *J. Appl. Phys.* **60**, 4339 (1986).

¹³A. Franciosi, P. Soukiassian, P. Philip, S. Chang, A. Wall, A. Raisanen, and N. Troullier, *Phys. Rev. B* **35**, 910 (1987).

¹⁴P. Soukiassian, M. H. Bakshi, and Z. Hurych, *J. Appl. Phys.* (to be published).

¹⁵G. Hollinger and F. J. Himpsel, *Phys. Rev. B* **28**, 3651 (1983); *Appl. Phys. Lett.* **44**, 93 (1984); M. Tabe, T. T. Chiang, I. Lindau, and W. E. Spicer, *Phys. Rev. B* **34**, 2706 (1986).

¹⁶G. Hughes and R. Ludeke, *J. Vac. Sci. Technol. B* **4**, 1109 (1986).

¹⁷J. Derrien and F. Ringeisen, *Surf. Sci. Lett.* **124**, 235 (1983); A. Franciosi, S. Chang, P. Philip, C. Caprile, and J. Joyce, *J. Vac. Sci. Technol. A* **3**, 933 (1985); F. U. Hillebrecht, M. Ronay, D. Rieger, and F. J. Himpsel, *Phys. Rev. B* **34**, 5377 (1986).

¹⁸H. Tochihara, M. Kubota, and Y. Murata, *Solid State Commun.* **57**, 437 (1986).

¹⁹M. H. Bakshi, P. Soukiassian, T. M. Gentle, A. S. Bommanavar, and Z. Hurych (unpublished).

²⁰J. L. Desplat and C. A. Papageorgopoulos, *Surf. Sci.* **92**, 97 (1980).

²¹P. Soukiassian, *Surf. Sci. Lett.* **172**, 6507 (1986).

²²P. Soukiassian, M. H. Bakshi, Z. Hurych, T. Kendelewicz, and I. Lindau, *Bull. Am. Phys. Soc.* **32**, 532 (1987).

²³T. M. Gentle, P. Soukiassian, and M. H. Bakshi (unpublished).