

Alkali-metal-promoted oxidation of the Si(100)2 × 1 surface: Coverage dependence and nonlocality

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We have studied the effect of alkali-metal (Na,Rb,Cs) coverages in the monolayer range on the oxidation of the Si(100)2 × 1 surface by core-level photoemission spectroscopy using synchrotron radiation. By comparing oxide thicknesses obtained using various coverages of Na and Cs, we find that coverages in excess of ≈ 0.5 monolayer are required to enhance significantly the oxidation of silicon. The existence of such a threshold demonstrates that the mechanism for alkali-metal-promoted oxidation is essentially nonlocal in nature, in strong contrast to the conclusions drawn in a recent Auger-electron-spectroscopy study. We also observe that the thickness of oxides grown with Na increases (by about 50%) upon annealing, while those grown with Cs do not change appreciably. Using Rb, we obtain intermediate results. In all cases, annealing results in higher-oxidation states. We also report spectral changes with time, which are to some extent analogous to those associated with annealing of the sample.

I. INTRODUCTION

The oxidation of silicon surfaces is of enormous importance in semiconductor device technology, and consequently there is much interest in novel oxidation processes. In recent years much attention has been paid to the remarkable enhancement of Si oxidation at room temperature caused by overlayers of noble, transition, and rare-earth metals.¹⁻⁷ These metals do not, however, result in pure SiO₂ films. Instead, they form reaction products that cannot be separated from the oxide. However, an alternative is offered by the alkali metals. These have been found to promote the oxidation of both III-V compound semiconductors^{8,9} and silicon.¹⁰⁻¹⁹ In contrast to other metal catalysts,¹⁻⁷ alkali metals can be desorbed from the silicon surface by annealing at moderate temperatures, leading to the formation of SiO₂-Si interfaces.¹¹⁻¹⁹ With the exception of Li, they do not interdiffuse or form bulk compounds with the substrate. The growth of SiO₂ on silicon surfaces has in this way been achieved at lower temperature than with other processes,²⁰ limiting the dopant diffusion and other detrimental effects of high temperatures.

Besides potential applications in device technology, alkali-metal-promoted oxidation also may contribute to the fundamental understanding of catalysis. A number of mechanisms have been proposed as important for promoted oxidation, i.e., increase of the oxygen sticking coefficient, dissociation of molecular oxygen, backbond

weakening,^{9,11-13} transfer of electrons to antibonding O₂ orbitals,¹⁰ or oxidation via decomposition of alkali-metal oxides.¹⁶⁻¹⁸ The electronic and structural properties of alkali metals adsorbed on silicon surfaces has been the subject of several studies, experimental²¹⁻²⁷ as well as theoretical.²⁸⁻³⁰ These studies have clearly demonstrated the layer-by-layer growth of alkali metals on silicon surfaces.

There has been considerable controversy regarding the mechanism of alkali-metal-promoted oxidation of silicon, in particular whether it is local or not in nature. The essential steps needed for the oxidation are (i) sticking of O₂, (ii) dissociation of the oxygen molecule, and (iii) formation of Si—O bonds. In case the sticking is dissociative in nature, the two first steps may be considered as a single one. There are, however, indications that molecular oxygen is present on the surface.³¹ Also, in oxidation studies of thick K and Cs films, oxides containing O₂ species were observed.^{17,32} The third step, however, may be further divided into Si backbond weakening, transfer of oxygen from alkali-metal to the silicon substrate, etc., so the number of steps is to some extent a matter of definition. We will use the three steps given above as a framework for our discussion of the promoted oxidation.

Regardless of whether the dissociation of O₂ takes place immediately as the molecule impinges on the surface or later, the dissociation step is often considered to be the most crucial one in the oxidation process, largely determining the oxidation rate. It has been suggested

that local electrostatic forces in the vicinity of alkali-metal atoms are responsible for the dissociation.¹⁸ Under such presumptions the promotional effect would be strictly proportional to the number of alkali-metal atoms present on the surface, at least for low coverages. At higher coverages nonlinear effects would be expected as the active areas associated with each alkali-metal atom begin to overlap. A completely opposite view would be the dissociation of O₂ caused by charge transfer into antibonding molecular orbitals due to completely nonlocal alkali-metal-induced changes of the surface electronic structure.¹⁰ A model very much like that was quite successfully used to explain the strongly enhanced (by a factor of $\approx 10^4$) oxidation rate of evaporated carbon films observed when K was deposited prior to oxygen exposure.³³ In that model the charge transfer to antibonding molecular orbitals was facilitated through the decreased work function and the associated increase in density of states at the Fermi level E_F . In a semiconductor like Si the situation is similar, but complications arise because of the band gap. However, the model may still be relevant after some modification. Between the opposite viewpoints mentioned above is a range of possibilities involving various degrees of locality.

In a recent study Ortega *et al.*¹⁸ favored the view that for the Cs/Si(100)2×1 system the oxidation enhancement is an effect localized to the vicinity of the alkali-metal atoms, while in our study of the Cs/Si(111)7×7 system,¹⁹ we concluded that the promotion effect is essentially non-local in nature. Although the surfaces were different, one would not expect any fundamental difference in the promotion mechanism, since the similarities in the oxidation behavior of the two surfaces are otherwise striking. Strict proportionality between oxide thickness and alkali-metal coverage has also been claimed by the same group in recent studies of promoted oxidation of Si(100)2×1 using potassium.^{15–17} It should, however, be noted that the most of those results were obtained with multilayer K coverages. This is actually a very different situation, since it involves formation of bulk K oxides, and, according to Si 2*p* spectra presented in Refs. 15–17, there is hardly any Si oxidation at all before annealing. Obviously, the K multilayers bond the oxygen so tightly that the substrate is not significantly attacked by reactive oxygen species. Upon annealing there is a reaction between the silicon surface and the bulk K oxides, leading to SiO₂ formation and K desorption. The proportionality between K coverage and the resulting oxide thickness is a rather trivial consequence of the highly effective transfer of oxygen from potassium oxides to the silicon substrate. The very different behavior at low coverages compared to multilayer or bulk properties is not peculiar to potassium. Similar effects were found by Woratschek *et al.*³² in a study of cesium oxidation. They also noted that the substrate strongly influenced the oxidation properties of thin Cs overlayers. In order to further the understanding of alkali-metal-promoted oxidation, one has to study in detail the action of thin (submonolayer to a few monolayers) alkali-metal overlayers since these are true promoters of room-temperature Si oxidation. Since the growth of SiO₂ using thicker overlayers seems to be mainly about the re-

action between bulk alkali-metal oxides and silicon,^{15–18} it is doubtful whether use of the term “promoted oxidation” is at all adequate in that case.

In this paper, we present results from core-level photoemission spectroscopy studies of the oxidation of Si(100)2×1 promoted by overlayers of Na and Cs. In particular, we focus on how the oxidation enhancement depends on the alkali-metal coverage in the monolayer range, and the relevance of this to the controversy over whether the effect is local or not. Our study includes measurements after room-temperature oxidation, as well as after thermal flash annealing and alkali-metal desorption. Special attention is also paid to how annealing affects the oxides grown with different alkali metals. Although the main emphasis still is on Na and Cs, we present in this context also results obtained using (for the first time) Rb overlayers.

II. EXPERIMENTAL DETAILS

The photoemission experiments were performed at the Synchrotron Radiation Center of the University of Wisconsin–Madison, using the University of Illinois “ERG” monochromator and the 3-m toroidal grating monochromator (TGM). The pressure in the ultra-high-vacuum (UHV) chamber was below 5×10^{-11} Torr during the measurements. The energy distribution of the photoelectrons was analyzed by an angle-integrating double-pass cylindrical mirror analyzer. The overall energy resolution was estimated to be ≈ 0.5 eV in the photon-energy range employed. The samples were cut from a silicon wafer exhibiting a mirrorlike (100) surface. They were initially cleaned *in situ* by careful out-gassing and subsequent annealing at 1000 °C for 10 min, a procedure known to produce high-quality (100)2×1 surfaces. During the experimental runs the samples were repeatedly cleaned by flashing to ≈ 1000 °C. The surface cleanliness was verified by the absence of any contamination-related structure in the photoelectron spectra. Na, Rb, and Cs were deposited on the silicon surface from thoroughly out-gassed SAES getter sources. Oxygen exposures ranging from 0.25 to 1024 L [1 langmuir (L) $\equiv 1 \times 10^{-6}$ Torr sec] were made using research-grade oxygen (99.99%). The alkali-metal evaporations as well as the O₂ exposures were all made at room temperature. The sample temperature during annealing was measured by an optical pyrometer.

III. RESULTS

A. Na overlayers

Sodium was repeatedly deposited on the clean Si(100)2×1 surface. After every deposition the sample was exposed to 64 L of O₂ and subsequently annealed by flashing to 600 °C. Figure 1 shows Si 2*p* spectra obtained with varying Na coverage (a) after the O₂ exposures, and (b) after the flash annealings. The Si 2*p*_{1/2} component has been numerically subtracted to ensure that the chemical shifts associated with the Si oxidation are not confused by the Si 2*p* spin-orbit splitting. The Si 2*p* chemical shifts, corresponding to different oxidation states of

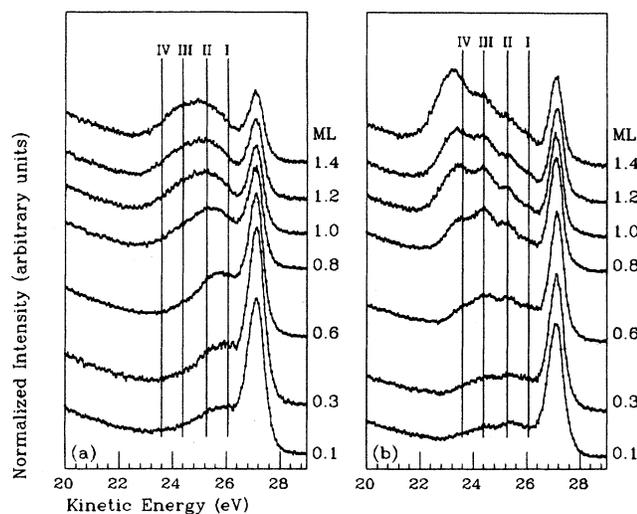


FIG. 1. $L O_2/Na/Si(100)2 \times 1$: Si $2p$ core-level spectra obtained with varying Na coverage (a) after 64 L O_2 exposure at room temperature, and (b) after 600°C flash annealing. The Si $2p_{1/2}$ component has been subtracted numerically. The different oxidation states (Si^+ , Si^{2+} , Si^{3+} , and Si^{4+}) are indicated by vertical bars (I, II, III, and IV, respectively). The photon energy was 130 eV.

Si^{34-36} are indicated by vertical bars. In accordance with our previous studies,^{11,12} nonstoichiometric oxides were already formed at room temperature, but the annealings, which also removed the Na by desorption, resulted in more stoichiometric oxides, mainly SiO_2 . It is also clear that the amount (and stoichiometry) of the oxides increased as the sodium coverage was increased, but in order to get more quantitative information a more detailed analysis of the data is required. As a measure of the amount of oxide produced, we will use the area under the Si $2p$ peaks corresponding to oxidized Si, divided by the height of the substrate Si $2p$ peak. Because of the overlap of oxide- and substrate-derived structures in the Si $2p$ spectra, the tails of the substrate peaks have to be extrapolated and subtracted from the oxide peaks in a somewhat subjective way. The extrapolation of the tails was assisted by extensive comparison with Si $2p$ spectra recorded prior to the oxidation. We are therefore confident that the errors introduced were kept reasonably small. The use of the height of the substrate peak, rather than the area, is justified by the absence of any significant changes of the width of this peak. It furthermore prevents the introduction of additional errors associated with the subjective decomposition of spectra. Figure 2 shows how the Si $2p$ oxide-to-substrate ratio depends on the Na deposition time. In order to relate the deposition time to the resulting Na coverage, the height of the substrate peak prior to O_2 exposure is also shown. The alkali-metal sources used have, in separate calibration runs, using Auger electron spectroscopy and core-level photoemission, been found to provide a nearly constant flow after an initial warming-up period. The nearly linear

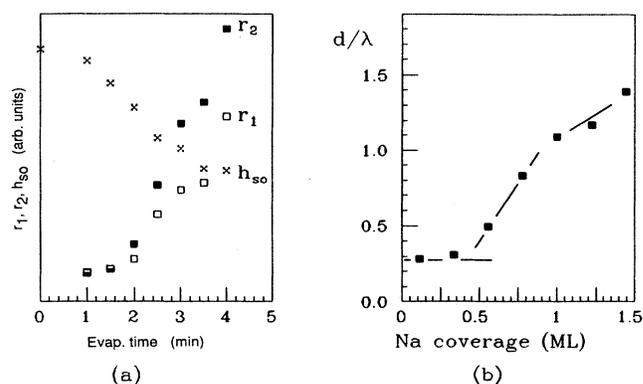


FIG. 2. $64 L O_2/Na/Si(100)2 \times 1$: (a) Si $2p$ oxide-to-substrate ratios vs evaporation time. r_1 and r_2 are ratios before and after annealing, respectively, h_{Si} is the height of the Si $2p$ peak immediately after Na evaporation. (b) r_2 data converted to oxide thickness vs Na coverage.

decrease of the Si $2p$ peak height (measured prior to O_2 exposures) seen over a wide range in Fig. 2 verifies that that is the case. There is, however, an apparent break in this linear behavior after 180 sec. We interpret this as due to completion of the first ordered overlayer and will refer to this as the monolayer (ML) coverage. This assignment is in good agreement with the calibration runs mentioned above. It is then straightforward to determine the Na coverage with high accuracy from 0 up to 1 ML, which is the range of importance here.

It should be noted that even without any Na on the surface, 64 L of O_2 results in a Si $2p$ oxide-to-substrate ratio comparable to that associated with 60 or even 90 s of Na deposition. Once this alkali-metal-independent oxidation is accounted for, it is obvious that there is an onset of the Na-promoted oxidation at ≈ 0.5 ML coverage. It should be noted that the Si $2p$ oxide-to-substrate ratio is not strictly proportional to the oxide thickness. We have therefore converted the annealed film ratios into thicknesses, making use of the rule that equal areas under the oxide and substrate peaks correspond to a thickness of $0.8\lambda_1$, where λ_1 is the photoelectron escape depth.¹⁶ These results are also shown in Fig. 2, and after the still evident onset of Na-promoted oxidation at ≈ 0.5 ML the oxide thickness grows fairly linearly with evaporation time, until at ≈ 1 ML Na coverage the growths slows down, reflecting a slower increase of the Na coverage due to the reduced sticking coefficient.

B. Cs Overlayers

Following the procedure used in our previous study of the $O_2/Cs/Si(111)7 \times 7$ system,¹⁹ we determined cesium coverages from height ratios of Cs $4d$ and Si $2p$ spectral peaks. At room temperature the saturation coverage is 1 ML, as previously characterized by Levine.³⁷ Figure 3 shows the Si $2p$ oxide-to-substrate ratio after 64 L of O_2 exposure and after annealing (650°C) as a function of initial Cs coverage. The data for the annealed oxide are also

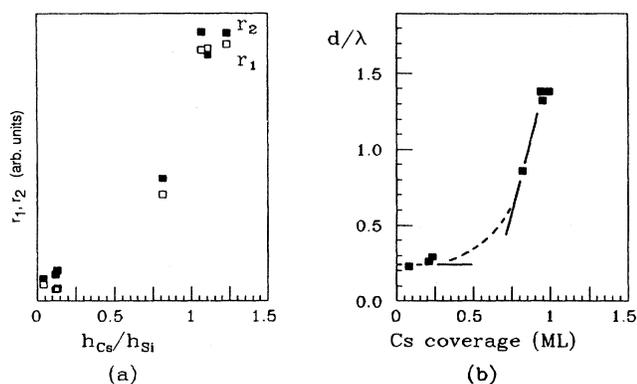


FIG. 3. 64 L O_2 /Cs/Si(100)2 \times 1: (a) Si 2*p* oxide-to-substrate ratios vs (Cs 4*d*)/(Si 2*p*) peak-height ratios. r_1 and r_2 are ratios before and after annealing, respectively. (b) r_2 data converted to oxide thickness vs Cs coverage.

shown after conversion to a thickness scale. In agreement with the results obtained on the Cs/Si(111)7 \times 7 surface¹⁹ and on the Na/Si(100)2 \times 1 system, the data indicate an onset of Cs-promoted oxidation at a Cs coverage \approx 0.5 ML.

C. Rb Overlayers

Figure 4(a) displays Si 2*p* spectra obtained at room temperature with 64 L of O_2 exposure for various Rb coverages. As in Fig. 1 the Si 2*p*_{1/2} component has been

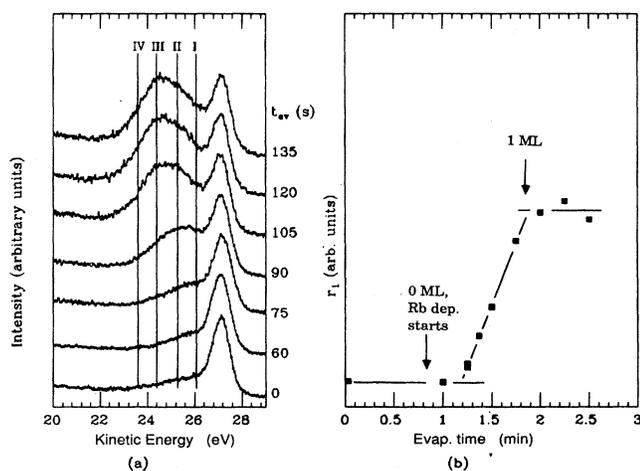


FIG. 4. 64 L O_2 /Rb/Si(100)2 \times 1: (a) Si 2*p* core-level spectra obtained at room temperature after 64 L O_2 exposures with varying Rb coverage. The Si 2*p*_{1/2} component has been subtracted numerically. The different oxidation states (Si⁺, Si²⁺, Si³⁺, and Si⁴⁺) are indicated as in Fig. 1. The photon energy was 130 eV. (b) Room-temperature Si 2*p* oxide-to-substrate ratio r_1 vs Rb evaporation time. The beginning of Rb deposition and the time when the 1-ML saturation coverage is reached are indicated by arrows.

numerically subtracted, and the oxidation-induced chemical shifts are indicated by vertical bars. Figure 4(b) shows the corresponding oxide-to-substrate ratios r_1 as a function of Rb evaporation time. Calibration runs using the Rb 3*d* and 4*s* levels showed that the evaporation started before 1 min had elapsed, and that, in analogy with Cs, a 1-ML saturation coverage was reached after \approx 2 min. Although our calibration data for the Rb source are less extensive than for the other sources, it is still clear that a threshold coverage of \approx 0.5 ML (or somewhat less) is required also for the onset of Rb-promoted oxidation. Similarly to Cs,^{11-14,19} Na,¹¹⁻¹⁴ and K,¹⁴⁻¹⁷ Rb is desorbed by rapid thermal annealing at moderate temperatures (below 650°C), leading to the formation of a SiO₂-Si interface free from rubidium.

D. Comparison of results with different alkali metals

We have also compared annealing-induced changes in the oxide-to-substrate ratios observed using Na, Rb, and Cs overlayers. The Si 2*p* spectra shown in Fig. 5 illustrate how strikingly different oxide films grown with Na and Cs, respectively, behave upon annealing. As in Figs. 1 and 4, the Si 2*p* component has been numerically removed. The oxygen exposure was 64 L in both cases, and the Na and Cs coverages were selected to give similar oxide-to-substrate ratios after the annealing. The annealing at 600°C increased the oxide-to-substrate ratio significantly for the Na-promoted oxide, while the Cs-promoted oxide became more stoichiometric without major changes in the oxide-to-substrate ratio. Very similar results were found for widely varying Na and Cs coverages. In Fig. 6 we have plotted the oxide-to-substrate ra-

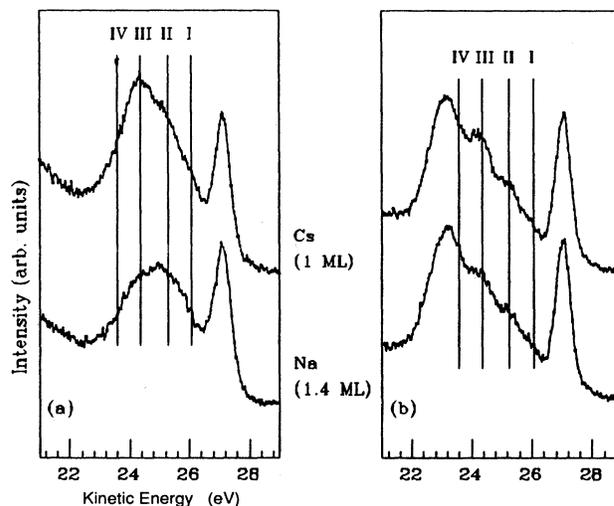


FIG. 5. 64 L O_2 /Cs/Si(100)2 \times 1 and 64 L O_2 /Na/Si(100)2 \times 1: Comparison of Si 2*p* core-level spectra from Si(100)2 \times 1 surfaces oxidized using Cs and Na, respectively, (a) before annealing and (b) after annealing. The Si 2*p*_{1/2} component has been subtracted numerically. The different oxidation states (Si⁺, Si²⁺, Si³⁺, and Si⁴⁺) are indicated as in Fig. 1. The photon energy was 130 eV.

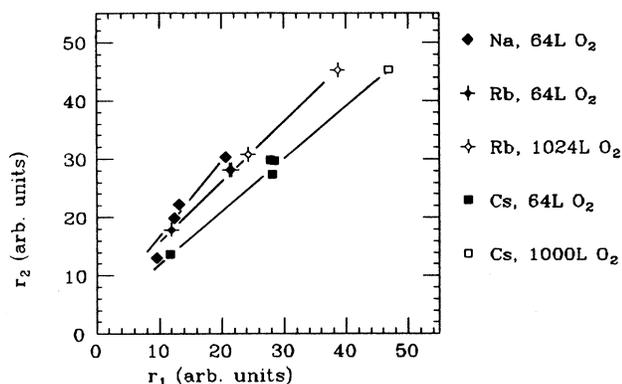


FIG. 6. Si 2*p* oxide-to-substrate ratios r_2 (after annealing) plotted vs corresponding ratios r_1 (before annealing), for different alkali metals at various coverages and various O₂ exposures.

tios r_1 before annealing versus the ratios r_2 after annealing for oxide films grown using all three metals under a variety of different growth conditions. It should be noted that for Rb- and Cs-covered surfaces, some oxide films were grown using 1024 and 1000 L of O₂, respectively, but even after such large exposures the changes were in close agreement with that was observed using smaller O₂ exposures. Some caution is, however, appropriate, since the samples were not all annealed at the same temperature. At low annealing temperatures, the oxide formation may not be complete, and furthermore, remaining alkali metal may affect the oxide-to-substrate ratio (as seen in the Si 2*p* spectra) indirectly through modifying the photoelectron escape depth. Excessively high temperature during annealing may reduce the oxide thickness by desorption. The results shown in Fig. 6 were obtained using the following annealing temperatures: 600 °C for samples with Na, 650–675 °C for samples with Rb, and 700 °C for samples with Cs (exception: 600 °C for the thinnest oxide). These annealing temperatures are high enough for complete alkali-metal desorption, and as we have not observed any notable reduction of oxide thickness at annealing below 800–850 °C, we are confident that the oxide films grown with Na, Rb, or Cs are safe to compare despite some variation in annealing temperature. Our comparison of oxides grown with different alkali metals can therefore be summarized as follows: the changes in oxide-to-substrate ratio upon annealing are relatively independent of alkali-metal coverage or oxygen exposure. Instead, they are specific for each alkali metal used. While annealing does not change the oxide-to-substrate ratios significantly for films grown with Cs, it results in an increase by $\approx 50\%$ for films grown with Na. For films grown with Rb, the changes in oxide-to-substrate ratios seem to be in the range between these extremes.

E. Time-dependent effects

We have observed spectral changes with time in Si 2*p* spectra recorded prior to annealing. Figure 7 illustrates how both thickness and stoichiometry of the oxide in-

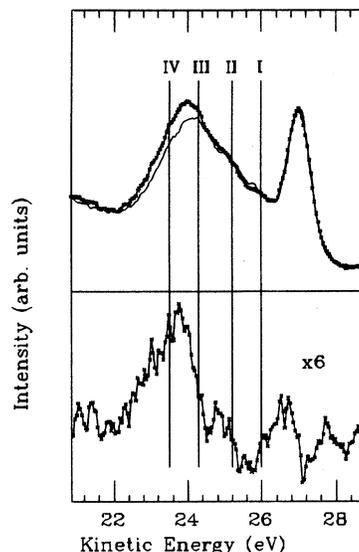


FIG. 7. 64 L O₂/Rb/Si(100)2×1: The top panel is a comparison of Si 2*p* core-level spectra from room-temperature oxidized (64 L O₂) Rb-covered (1 ML) Si(100)2×1 immediately after oxygen exposure (thin line) and 12 h later without annealing (crossed line). The spectra are scaled to have the same substrate peak height. The lower panel shows the differences of the two upper spectra. The Si 2*p*_{1/2} component has been subtracted numerically. The different oxidation states (Si⁺, Si²⁺, Si³⁺, and Si⁴⁺) are indicated as in Fig. 1. The photon energy was 130 eV.

creased as a sample was covered by 1 ML of Rb, exposed to 64 L of O₂, and then left at room temperature for 12 h.

IV. DISCUSSION

It is now clear that a threshold alkali-metal coverage is required for promoted oxidation of the Si(100)2×1 surface. The exact value of the threshold coverage is somewhat a matter of definition, since the onset of promoted oxidation is not absolutely sharp. It seems reasonable, however, to define the threshold as the coverage where the straight lines drawn through the data points above the insets in Figs. 2(b), 3(b), and 4(b) intersect the horizontal lines marking the oxide-to-substrate ratios without the alkali-metals. Following this procedure we obtain the threshold values 0.40, 0.33, and 0.65 ML for Na, Rb, and Cs, respectively. Considering the uncertainties involved, however, it seems reasonable to talk of a general threshold coverage of 0.5 ± 0.2 ML for alkali-metal-promoted oxidation. It must be stressed that the existence of an threshold coverage is far more important than its precise value.

The proportionality between Cs coverage and oxide thickness claimed by Ortega *et al.*¹⁸ seems to be founded on the failure to separate promoted oxidation from alkali-metal-independent oxidation. Actually, the amount of oxide is fairly constant for the four lowest coverages shown in Fig. 4 of Ref. 18. Also, since Auger-electron spectroscopy (AES) was the main tool in this study, there is a significant possibility that the results

were affected by electron-beam-induced oxidation. We have found that these types of overlayer systems are very much affected by electron beams as well as unmonochromatized synchrotron radiation. Surnev has, in a study of alkali-metal-promoted oxidation of Ge(111),³⁸ demonstrated that AES-type electron beams cause a major increase in the uptake of oxygen. Similarly, Carriere *et al.* have shown that the exciting beam of an Auger spectrometer induced oxidation of a Si(100) surface at room temperature in the presence of oxygen.^{39,40} The importance of using experimental probes that affect the system under study as little as possible should therefore be stressed. What has been said above about confusion of promoted and alkali-independent oxidation should apply also to the low-coverage data in the studies of K-promoted oxidation of Si(100)2×1.^{15–17} The corresponding high-coverage data are less relevant in this discussion, for reasons discussed in the Introduction. Our present results mean that the strictly local scenario can be excluded from the discussion without doubt, since it is completely incompatible with the onset of alkali-metal-promoted oxidation at ≈0.5 ML. The onset is, however, not completely abrupt. The data in Figs. 2–4 do allow for some kind of gradual transition from the alkali-metal-independent oxidation to the region of rapidly increasing promoted oxidation, although the experimental uncertainty does not permit a precise classification of the onset. Such a gradual onset could indicate that promoted oxidation starts in small areas having higher than average alkali-metal density. The smaller the area (or equivalently, the lower the number of alkali-metal atoms) required for promoter activity, the more gradual the onset. Another factor that may influence the onset of promoted oxidation is the density of defects on the substrate surface. In a scanning-tunneling-microscope (STM) study of the Si(100)2×1 surface, Hamers *et al.*⁴¹ confirmed the dimer-type reconstruction of this surface,⁴² but found that ≈10% of the dimers were missing. The reactivity of adsorption sites associated with such defects can be anticipated to differ significantly from that of regular adsorption sites, both with and without alkali metals present. The defects may therefore have a strong influence on both the alkali-metal-independent oxidation and on the abruptness of the onset of promoted oxidation.

There is an intriguing correlation between the onset of promoted oxidation and the appearance of plasmon-like structures in the core-level spectra, signifying a metallic overlayer (or metallization of the top Si layer through charge transfer from alkali metal to the substrate if one adopts Ciraci and Batra's picture.²⁹ It is, however, not primarily the metallic character of the surface that is responsible for promoted oxidation, since O₂ exposures as low as 1 L destroy the metallic character of the surface, while the oxidation process continues at far higher exposures.^{13,19} The mechanism suggested by Franciosi *et al.*,¹⁰ based on surface-dipole-induced charge transfer to antibonding molecular O₂ orbitals, is more compatible with this finding than models involving surface metallization,²⁹ which recently have been questioned on other grounds.^{13,27,43,44} Since this mechanism is closely connected with the reduced work function and the formation

of a dipole layer at the surface, it would be illuminating to study if there is any strong correlation between oxygen uptake and work-function changes. It should be noted that a strong correlation between initial sticking coefficients and work-function changes was found by Surnev in his study of the oxidation of alkali-metal-covered Ge(111).³⁸

In this discussion we have so far not distinguished between the different alkali metals. Although the basic mechanism of promotion most likely is identical, there are significant quantitative differences, in particular between Na and Cs, concerning the transfer of oxygen to silicon during annealing. Our data show the amount of oxide formed at room temperature using Na to be significantly smaller than what is obtained using a comparable Cs coverage. Upon annealing, the thickness of the Na-grown oxide increases by ≈50%, and becomes more comparable to what is obtained using Cs. It appears that the Cs-grown oxide is still thicker after the annealing,^{11,12} but the difficulty in determining when Na and Cs coverages are equal makes this conclusion somewhat uncertain. A somewhat trivial explanation to the observed differences would be that suppression of the substrate peak through alkali-metal-induced reduction of the photoelectron escape depth is more accentuated when using Cs. This is, however, unlikely, for two reasons: first, considering how easily the alkali-metals desorb we expect them to stay on top of the oxide layer,^{11,12,19} and consequently to suppress substrate and oxide structure equally in the Si 2*p* spectra. Second, the damping of the Si 2*p* emission seen after deposition of 1 ML is not very different, slightly more than 50% for Cs, slightly less for Na. Not even in an extreme situation, with the alkali-metal atoms residing entirely below the oxide layer, would this difference be sufficient to explain why the oxide thickness increase during annealing is so much smaller with Cs than with Na. The only possible conclusion therefore seems to be that, with the overlayer consisting of Na, fewer Si—O bonds are formed at room temperature, and a larger portion of the adsorbed oxygen remains bonded primarily to the Na atoms until the temperature is increased. In contrast, with the Cs overlayer, more of the oxygen reacts with the substrate at room temperature. Assuming that Na and Cs monolayers by themselves are able to hold about the same amount of oxygen, this will eventually result in somewhat thicker oxide layers before annealing using Cs. However, the lower desorption temperature for Na implies that the oxygen is not more tightly bound to Na than to Cs. Instead, it appears reasonable to suggest that Na does not increase the reactivity of the silicon surface to the same extent as Cs. Also, this is possibly associated with the work-function lowering and the different dipole moments of adsorbed Na and Cs. The fact that similar results were obtained over a wide range of alkali-metal coverage and oxygen exposures implies a delicate partitioning of oxygen between overlayer and substrate.

The observed increase with time of oxide thickness and stoichiometry (Fig. 7) indicates that, even at room temperature, some of the oxygen trapped by the alkali metal (Rb in this case) is transferred to the silicon substrate. To

some extent, the annealing can be replaced by waiting for a sufficiently long time. A similar effect was also observed with Cs and K overlayers. This observation suggests that the main role of temperature in this process is to accelerate the migration of oxygen atoms through the silicon substrate, thus leading to the improvement of the oxide thickness and stoichiometry.

V. CONCLUSIONS

We have established that a threshold coverage of ≈ 0.5 ML of Na, Rb, or Cs is required for promoted oxidation of the Si(100) 2×1 surface by alkali metals. A certain amount of oxide is, however, formed independently of the alkali-metal coverage, and confusion on this point is probably also responsible for contradictory reports. Also, we stress the importance of avoiding electron-beam exposure in this kind of study since such exposure may cause additional surface reactions. The existence of a coverage threshold means that the mechanism of alkali-metal-promoted oxidation is essentially of nonlocal nature. This is in very good agreement with our previous study of the Cs-promoted oxidation of the Si(111) 7×7 surface,¹⁹ where we showed that the dangling bonds do not play a crucial role in the catalytic mechanism, and also stressed the nonlocal nature of the catalytic mechanism. These results add to the credibility of the mechanism proposed by Franciosi *et al.*¹⁰ Our study does not support a local mechanism of promotion suggested in the recent Auger-spectroscopy work by Ortega *et al.*¹⁸

Comparing the effects of annealing on oxides grown with different alkali metals, we found that the thickness of Na-grown oxides increased $\approx 50\%$ upon annealing, in contrast to the thickness of Cs-grown oxides, which did

not increase appreciably. The stoichiometry of the oxides showed similar improvements in the two cases, however. Intermediate results were found using Rb. The differences implies that Na does not increase the reactivity of the substrate to the same extent as Cs. These results were established over a wide range of alkali-metal coverages and oxygen exposures.

The mechanism by which annealing leads to more complete oxidation was found to some extent to be active also at room temperature.

Note added in proof. In a previous paper,¹⁹ we pointed out that for Cs coverage in the monolayer range, oxygen seems to interact more strongly with the Si substrate than with the Cs overlayer, and we expressed the opinion that formation of strong cesium-oxygen bonds is not an important step in the mechanism of promoted Si oxidation. The readers should be made aware that this has been misquoted in a recent paper by Michel *et al.*⁴⁵ to mean that there is no reaction at all between alkali metal and oxygen. This must be considered as a serious distortion of our original statements.

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