Early stages of the alkali-metal-promoted oxidation of silicon

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We have studied the potassium- and cesium-promoted oxidation of Si(100)2×1 with photoelectron and Auger-electron spectroscopies in the range of submonolayer alkali-metal-atom coverages. The alkali-metal atoms efficiently promote the oxidation of silicon. Our results demonstrate that there are two oxygen species on the surface during the oxidation reaction: oxygen atoms which are bonded to potassium from the very beginning of the process and oxygen atoms bonded to silicon. These two oxygen species are detected in core level O 1*s* and in valence-band photoemission spectra. Oxygen is transferred from K to Si, and this process is thermally activated and its efficiency is increased by heating the substrate. To explain these results we propose a model based on the decrease of local work function produced by potassium, which reduces the activation barrier for oxygen dissociation. Oxygen reacts with potassium, forming a potassium oxide which efficiently transfers oxygen to silicon.

I. INTRODUCTION

The preeminence of silicon in modern microelectronics is based on the quality of the SiO_2-Si interface which is atomically abrupt, with less than one defect site per 10^4-10^5 interfacial bonds. During formation of the SiO_2-Si interface the electrically active sites are almost completely removed.[1] The aim of understanding and controlling this process has made the oxidation of silicon a subject of permanent interest in the last years.

The oxidation of single crystals of silicon is a difficult process. The rate-limiting step seems to be the trapping and dissociation of O_2 molecules. Thus, high oxygen pressures and elevated temperatures are required to speed the reaction.[2]

It has been recently observed that the oxidation rate of silicon can be enhanced by many orders of magnitude by the presence of metals at the surface.[3-8] Problems of chemical reaction between silicon and most of the metal catalysts can be overcome by the use of alkali metals as oxidation promoters.[9-15] Thus, an adlayer of Na, K, or Cs deposited on the surface, which enhances the oxidation rate of silicon up to 10^5-10^6 times, can be removed from the surface by mild heating of the substrate to about 900 K. However, the role played by the alkali metal in the promotion, i.e., the oxidation mechanism, is currently a matter of controversy. For instance, it has been proposed that the oxidation rate is enhanced by dissociation of O_2 molecules due to the average metal-silicon dipole moment.[9] In order to justify the maintenance of the catalytic behavior upon substrate oxidation, it has been argued that the metal-silicon surface dipole is replaced by an equally effective metal-oxygen surface dipole. We have already shown that this assumption is not supported by experimental results on the Cs-promoted oxidation of silicon, because the average work function actually increases above its level for a Cs-covered surface, for O_2 exposures larger than 0.8 L (1 L$\equiv 10^{-6}$ Torr sec).[12] We will present here analogous experimental evidence for such a behavior in K- and Cs-covered Si(100)2×1. On the other hand, a mechanism based on the trapping of oxygen molecules by the alkali-metal film and their transfer to the substrate upon annealing has been proposed for the multilayer adsorption case.[13]

In this work we present measurements of the silicon-promoted oxidation by the alkali metals potassium and cesium. Our measurements cover the range from less than one monolayer (ML) coverage to the multilayer regime. We found the existence of two different oxidation regimes depending on metal coverage, which we attribute to the predominance of two different mechanisms. In the low-coverage regime, the alkali-metal adatoms, bonded to oxygen, act as an efficient promoter of the silicon oxidation. Oxygen is transferred to silicon with a temperature-dependent rate. Both alkali metals behave in essentially the same way, although with different efficiency. On the basis of the experimental data we propose a mechanism with strongly local character.

II. EXPERIMENTAL

The measurements have been carried out in two different chambers already described.[10-12] Briefly, the first contains a four-grid low-energy electron diffraction (LEED) optics, a cylindrical mirror analyzer (CMA) for Auger-electron spectroscopy (AES), and a Kelvin probe to measure work-function changes. In the second chamber, ultraviolet-photoelectron spectroscopy (UPS) was carried out with a He-discharge lamp ($h\nu=21.2$ eV), and x-ray photoelectron spectroscopy (XPS) with a Mg $K\alpha$ x-ray source ($h\nu=1253.6$ eV). Spectra were taken in the constant resolution mode of the analyzer, at a pass energy of 5 eV for UPS and 50 eV for XPS. The photoemission intensities were reproducible within 10%. The

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base pressure in both chambers was in the low 10^{-10} Torr range, even during potassium deposition. Auger electrons were excited with a 1.8 keV, 5 μA electron beam. The electron current was kept as low as possible, and was maintained on the target only during measurements in order to minimize electron-bombardment-induced effects. The Si(100) sample, cut from a commercial wafer (*n*-doped type, 30–50 Ω cm), was fixed on a tungsten wire by means of another tantalum wire. Temperature was measured by means of a Chromel-Alumel thermocouple, spot welded to the tantalum wire. Silicon was cleaned through cycles of 1.5 keV Ar^+ bombardment and annealing to 1100 K. Temperature was slowly reduced, and after these treatments the sample regularly showed a clear 2×1 LEED pattern. Carbon contamination on the surface was always below an AES intensity ratio less than $\frac{1}{250}$ for the Auger peaks of C (at a kinetic energy of 272 eV) and of Si (at a kinetic energy of 92 eV), and no other contaminants could be detected. The alkali metal was deposited from commercially available dispensers (SAES Getters). Alkali-metal-atom coverages were determined from the Auger peak-to-peak intensity in the first chamber[16] and from the area of the K 2*p* and the attenuation of the Si 2*p* levels in the second one. A complete monolayer of K will be defined in this work as 6.78×10^{14} atoms/cm^2, i.e., a 1:1 relationship with the atomic density of the Si(100)2×1 surface.

III. RESULTS

A. Oxidation of clean silicon

In order to compare with the oxidation of the alkali-metal-covered substrate, the oxygen uptake by the clean Si(100)2×1 surface at 700 K as a function of the O_2 exposure has been measured, and is depicted in Fig. 1 in terms of the intensity ratio of the Auger peaks O_{512} and Si_{92}. From these ratios, the number of oxygen atoms adsorbed per silicon surface atom is calculated (left-hand scale), following a procedure developed in Ref. 17. The data presented here are in excellent agreement with previous reports and illustrate the two stages (fast and slow) of oxidation of silicon surfaces as described by many other authors.[17]

In Fig. 2, XPS O 1*s* core-level spectra are shown for increasing O_2 exposures at 100 and 300 K. At both temperatures the adsorption is dissociative, and the O 1*s* binding energy (BE) at 532.0 eV below the Fermi energy (E_F) is typical for bonds between atomic oxygen and silicon. The uptake is only moderate.

B. Oxidation of K-covered silicon

We have shown previously that when K is deposited on the Si(100) surface, the kinetics of adsorption of oxygen is enhanced by a factor of 10^4 (in terms of oxygen exposure) with respect to the clean Si surface.[10] Upon annealing to 900 K, the alkali-metal adatoms are removed from the surface, leaving behind a SiO_2 film on the Si substrate whose thickness depends linearly on the K coverage previously deposited. Quantitative experimental evidence was presented for the range of K coverages above 1 ML.[10,11]

The mechanism responsible for the alkali-metal-promoted oxidation of silicon at alkali-metal-atom coverages larger than 1 ML has already been described in de-

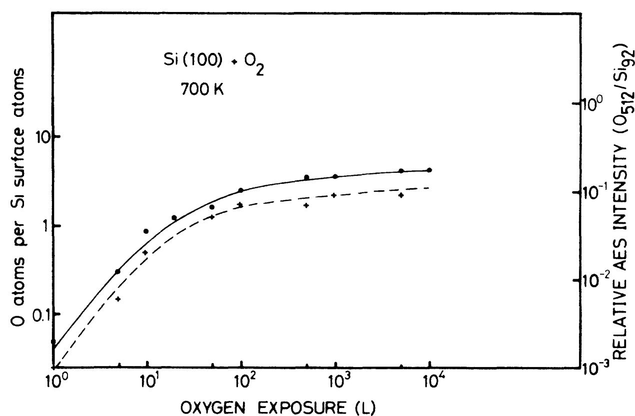

FIG. 1. Oxygen uptake at 700 K as measured by AES intensities (right-hand scale) for a clean Si(100) surface. The uptake is also given in number of oxygen atoms per Si surface atom, following a procedure described in Ref. 17. The dots represent subsequent O_2 exposures while the crosses correspond to single exposures.

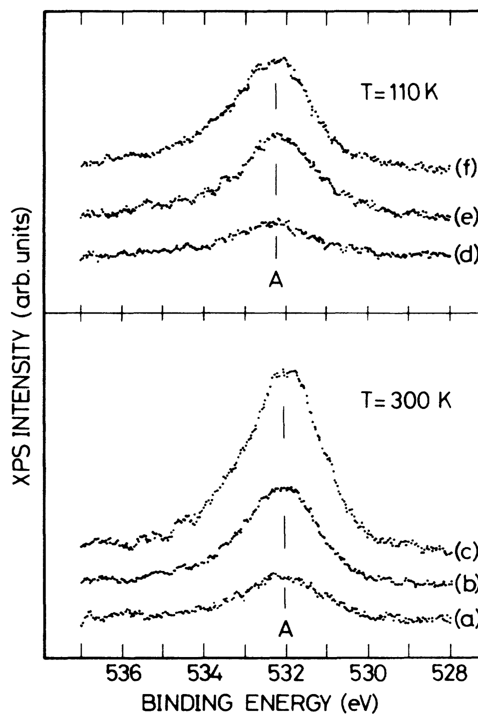

FIG. 2. O 1*s* XPS spectra for increasing O_2 exposures on a clean Si(100) surface. Only one peak (denoted as *A*) can be observed, and corresponds to atomic oxygen bonded to silicon. The temperature of the sample is 300 K for curves *a*–*c* and 110 K for curves *d*–*f*. The oxygen exposures are (a) 10 L, (b) 10^3 L, (c) 10^5 L, (d) 1 L, (e) 10^2 L, and (f) 10^4 L.

tail.[11,13] It can be summarized as follows: the impinging oxygen molecules react with the thick alkali-metal film (grown at 110 K), forming potassium oxides. For sequential deposition at low temperature, a thick K_2O_2 layer can be formed, with a surface KO_2 layer on it. This process does not affect the silicon substrate, until the temperature is raised sufficiently for an oxygen transfer to the silicon. During such a thermal-annealing procedure the K disappears in the photoemission signal and the silicon surface is oxidized.

In the following we will present the results of oxidation of a Si(100)2×1 substrate by K deposition, O_2 exposure and annealing, at K coverages below 1.5 ML, which indicate that a different mechanism is operating at submonolayer alkali-metal coverages. In Fig. 3 the ratio between Auger intensities corresponding to SiO_2 (at a kinetic energy of 75 eV) and Si (at 92 eV) after the oxidation process is shown as a function of the K coverage. For each point, after the calibrated evaporation of K (Ref. 16) on the clean Si(100)2×1 surface, the sample is exposed either to 200 or to 2000 L of oxygen, and heated afterwards to 900 K in order to remove the potassium atoms. Although at these oxygen exposures full saturation was not achieved, there is no significant difference between the two types of points in Fig. 3. Two different behaviors are evident above and below a K coverage around one monolayer. The simple attenuation of the clean Si AES peak by the growing SiO_2 layer cannot explain quantitatively the sudden change in the slope. Actually, the data begin to deviate from the initial linear proportionality between SiO_2 production and K coverage at coverages above 0.6 ML, reaching a second linear region with a much larger slope that coincides with that already published for K multilayers.[11] We propose that these two different slopes observed upon increasing the alkali-metal coverage reflect two different oxidation mechanisms, the transition from one to the other being related to the formation of metallic K on the surface. In the rest of this work we will concentrate on the oxidation process for submonolayer K coverages.

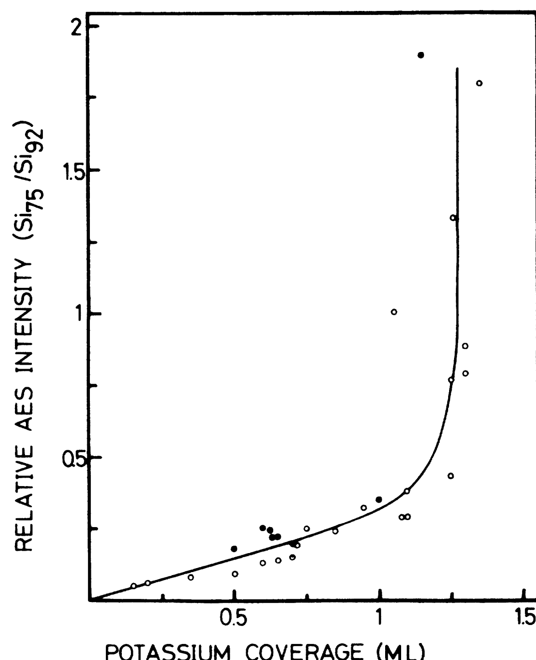

FIG. 3. Amount of SiO_2 produced as given by the intensity ratio of the AES peaks of Si at 75 and 92 eV kinetic energy (corresponding to SiO_2 and Si, respectively). Each dot represents a measurement of AES intensities after K deposition, O_2 exposure, and annealing to 900 K as a function of the initial K coverage. The solid dots correspond to 2000 L O_2 exposure while the open dots have been obtained with 200 L O_2 exposure. The continuous line is a guide to the eye.

1. Identification of two oxygen species at $\theta_K < 0.5$ ML

It should be noted first that the adsorption of oxygen on a Si surface partially covered with K produces *two* different oxygen species, due to bonds either with Si or with K. Figure 4 shows two representative series of XPS spectra corresponding to increasing O_2 exposures for 0.30 and 0.45 ML of potassium, at room temperature and 110 K, respectively. *Two* O 1s peaks are present in *both* series, peak *A* at a BE of 532.0 eV and peak *B* at a BE of

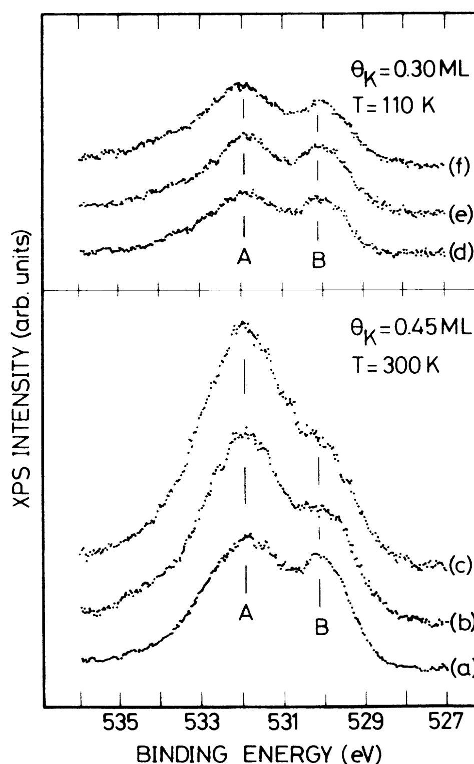

FIG. 4. O 1s XPS spectra for increasing O_2 exposure on Si(100) surfaces partially covered with K. In curves *a–c* the temperature is 300 K and θ_K=0.45 ML. The oxygen exposures are (a) 10 L, (b) 10^2 L, and (c) 10^3 L. In curves *d–f*, the temperature is 110 K and θ_K=0.35 ML. The exposures are (d) 1 L; (e) 10 L, and (f) 10^2 L. Two atomic oxygen species are observed. Oxygen bonded to silicon is denoted *A* while the one bonded to potassium is designated as *B*. Vertical scale is the same for all the spectra.

530.1 eV. At 300 K only peak A grows with increasing oxygen exposure, while peak B is already saturated at the lowest exposure presented here (10 L). In contrast, at 110 K both peaks are almost saturated at 1 L of O_2 exposure, and do not grow noticeably upon subsequent oxygen exposure.

Oxygen atoms bonded to potassium should be charged more negatively than those bonded to silicon, because of the larger charge transfer from potassium to oxygen. Accordingly, the O 1s signal at lower BE (peak B) is tentatively identified as atomic oxygen bonded to K, while the species at higher BE (peak A), which appears at the same BE as oxygen atoms adsorbed on *clean* silicon (see Fig. 2), is ascribed to atomic oxygen bonded to silicon. Further support for this identification comes from the intensity behavior of both O 1s signals with K coverage, as will be discussed in the following.

Figures 5 and 6 show selected XPS and UPS spectra taken for increasing potassium coverages at the same oxygen exposure (10 L). Both series have been taken at 110 K. The O 1s XPS spectrum for 0.15 ML shows again two peaks at BE of and 531.9 eV (denoted as A) and 530.0 eV (denoted as B). For higher K coverages (e.g., at $\theta_K = 0.55$ ML), peak B assigned to atomic oxygen bonded to K is proportionally larger. This proportionality can be observed also in Fig. 4: the almost saturated emission B is more intense at 300 K due to the higher K coverage in this case. The UPS series corresponding to the XPS

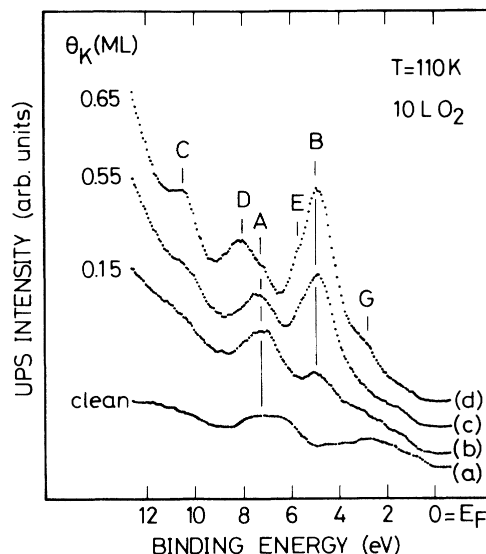

FIG. 6. Series of UPS spectra corresponding to the same conditions as in Fig. 5. The Si(100) surface was covered with different amounts of potassium, and subsequently exposed to 10 L of O_2 at 110 K. The coverages are, as indicated in the figure, (a) clean Si(100), (b) 0.15 ML, (c) 0.55 ML, and (d) 0.65 ML. Peaks A and B correspond to the lines marked A and B in the O 1s spectra of Fig. 5, respectively, while peaks C, D, and E correspond to the O 1s feature at C. Vertical scale is the same for all the spectra.

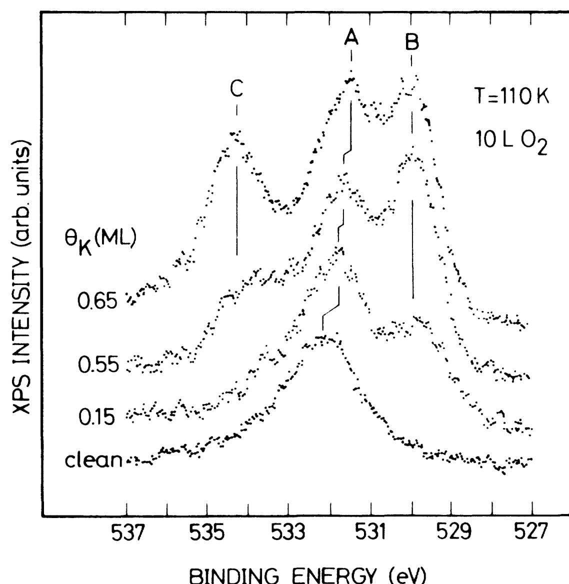

FIG. 5. O 1s XPS spectra taken for different K coverages on a Si(100) surface after subsequent exposure to 10 L of O_2, at 110 K. The curves correspond to (a) clean Si(100). (b) $\theta_K = 0.15$ ML, (c) $\theta_K = 0.55$ ML, and (d) $\theta_K = 0.65$ ML. Peak A corresponds to oxygen bonded to Si and peak B to oxygen bonded to K. Peak C signals the formation of KO_2 which is found at K coverages larger than 0.5 ML. Vertical scale is the same for all the spectra. The shifts in binding energies are probably related to changes in the location of the species within the surface dipole.

series of Fig. 5 is presented in Fig. 6. For 0.15 ML of K, the UPS spectrum shows *two* O 2p emissions at BE of 7.1 eV (denoted as A) and 5.0 eV (denoted as B). Peak A has about the same BE as the main peak in the spectrum of oxygen on clean silicon (also plotted in Fig. 6). Emission B grows (for constant oxygen exposure) with increasing K coverage. Thus, peaks A and B in the UPS spectra may be identified in a similar way as the O 1s peaks: the one at lower binding energy (B) corresponds to the O 2p level of atomic oxygen bonded to potassium in agreement with previous data for oxygen chemisorbed on alkali-metal-covered metallic surfaces.[18] and the one at higher binding energy (A) to the O 2p level of oxygen bonded to silicon. It should be noted that the existence of two oxygen species could not be concluded in previous works[9,15] due to the lack of O 1s spectra, although valence-band data presented in Ref. 9 and 15 clearly show *two* O 2p-derived peaks in the UPS spectra.

2. Transition to a second regime at $\theta_K > 0.5$ ML

In Fig. 5 we also display photoelectron spectra at $\theta_K > 0.5$ ML showing the appearance of a different K-O species, which may be associated to the transition from the first linear regime in Fig. 3 to the alkali-metal-multilayer regime described elsewhere.[11,13] We note that for $\theta_K > 0.5$ ML, when the K rows on the Si(100)2$\times$1 surface have been completed and the surface becomes metallic,[19] a new O 1s emission at a BE of 534.3 eV (peak C) appears, growing in intensity with increasing K coverage and dominating at large K coverage. This peak C can be

assigned to KO_2 based on the following facts: (1) An O 1*s* emission with a similar BE of 534.0 eV has also been observed in thick KO_2 layers grown by codeposition of K and O_2,[13] and (2) during the oxidation of metallic Cs, CsO_2 has been identified by peaks in the UPS spectrum at a BE of 10.7, 8.5, 5.8, and 4.7 eV below E_F (Refs. 18 and 20–22) in excellent agreement with features *C* (10.5 eV), D (8.0 eV), and *E* (5.8 eV) in our data. The peak at 4.7 eV overlaps with peak *B*, characteristic of the lower coverage regime, giving rise to the strong emission at a BE of 5 eV. Finally it should be mentioned that peak *G* at 2.8 eV below E_F, which is only observed at $\theta_K > 0.5$ ML, reflects the presence of a small amount of O^{2-} ions (i.e., K_2O) at the surface, as found for the oxidation of thick metallic Cs (Refs. 18, 21, and 22) and K films.[11] O^{2-} ion is characterized by emissions at a BE of 2.7, 4.4, and 5.4 eV in the case of Cs_2O.[18,21,22] In our case, only the more intense emission (at 2.8 eV) is observed. K_2O does not play a significant role in the oxidation of Si for $\theta_K < 0.5$ ML. At these low coverages, the promoter role is taken by the potassium bonded to oxygen atoms (species denoted as *B*).

C. Influence of the temperature in the transfer of oxygen from potassium to silicon

Our identification of two oxygen species present during the oxidation of Si at submonolayer coverages of K allows us to follow the kinetic evolution of the reaction. We propose that in this coverage range the oxidation reaction proceeds by dissociation of oxygen molecules at K sites (to be demonstrated elsewhere[23]), bonding of oxygen to K (producing mostly the *B* species), and a partial transfer of oxygen from K to Si, the latter being strongly temperature dependent as will be demonstrated in the following.

The O 1*s* spectra in Fig. 4 show that, at 300 K, the emission corresponding to oxygen bonded to silicon (*A*) grows continuously with O_2 exposure, indicating that the Si substrate *is oxidized* with a much larger rate than without K. The enhancement of the oxygen uptake in K-covered silicon can be directly estimated from the area of the O 1*s* peak (*a*) in Fig. 4, which is twice as large (for an O_2 exposure to 10 L at room temperature) as the one obtained for clean silicon at 10^5 L [see Fig. 2(c)], displaying an enhancement factor of 10^4 in terms of the kinetics mentioned above. The transfer process can be frozen by cooling down the sample as shown by comparison of the data taken at 110 K and room temperature (see Fig. 4), both in amount of oxygen uptake and transfer of oxygen from potassium to silicon. Although both oxygen species are present in both cases, the intensity of the signal from oxygen bonded to silicon (*A*) does not increase significantly with exposure for the lower temperature, indicating that the oxidation process of the substrate is limited by a thermal barrier that cannot be overcome at 110 K.

The existence of oxygen bonded to alkali-metal atoms that can be transferred to Si is directly proven by the observed increase in the amount of SiO_2 present on the surface upon thermal treatment. If a silicon surface covered with a certain amount of an alkali metal and exposed to a given oxygen dose is thermally annealed, the photoemission signal from the alkali-metal core levels disappears, while the signal from the silicon oxide simultaneously increases. This is illustrated in Fig. 7 for a Cs coverage of 0.55 ML and a subsequent O_2 exposure of 400 L by means of the corresponding AES peak height variations versus substrate temperature. An *additional* oxidation of the silicon crystal during annealing has already been reported,[14,15] but was not properly associated to previously alkali-metal-bonded oxygen transferred to the silicon substrate. This point is proven in Figs. 8 and 9 where the evolution of both O 1*s* peaks and UPS spectra during annealing is shown. The disappearance of the O 1*s* signals related to oxygen bonded to K, at BE of 534.3 and 530.0 eV, respectively, results in an intensity increase of the peak related to silicon oxide, which is shifted to higher BE with increasing temperature (i.e., decreasing K content). At 550 K the process of K elimination and transfer of oxygen is not yet finished, and a small amount of K-bonded oxygen still remains on the surface. By comparing the total O 1*s* area before and after annealing it is concluded that the transfer of oxygen from K to Si is almost complete. The UPS spectra corresponding to this process are shown in Fig. 9. The emission *B*, ascribed to K-bonded atomic oxygen, decreases in intensity and shifts to higher BE, while the peaks at 7.5 and 11.5 eV below E_F, characteristic for silicon dioxide[24,25] grow simultaneously.

At 300 K there is an oxygen transfer from potassium to silicon (from oxygen species *B* to oxygen *A*). There is always, however, a certain amount of oxygen bonded to K that can be transferred to Si by annealing. This is demonstrated in Fig. 10, where the amount of SiO_2 produced at 300 K, as given by the Si_{75}/Si_{92} AES intensity ratio, is shown as a function of the O_2 exposure (in logarithmic scale), for $\theta_K = 0.7$ ML. Annealing of a given sample to 900 K results in an oxygen transfer from K to Si producing further SiO_2 as shown by the arrows in the figure, and the complete elimination of the potassium Auger *LMM* signal. Although the total amount of SiO_2

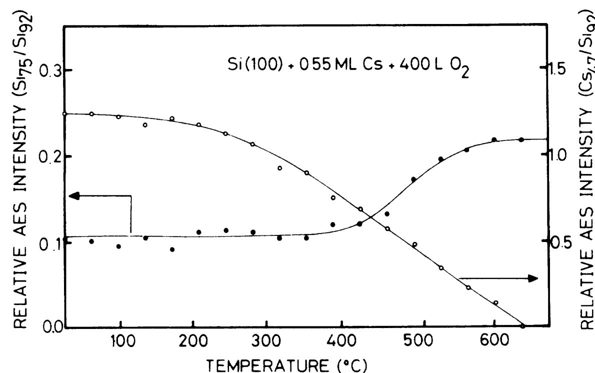

FIG. 7. Growth of SiO_2 (solid dots) and disappearance of the Cs signal (open dots), as given by AES intensity ratios, during thermal annealing of a Si(100) surface, covered with 0.55 ML of Cs, exposed to 400 L of O_2 at 300 K and subsequently annealed for 2 min at each (increasing) temperature.

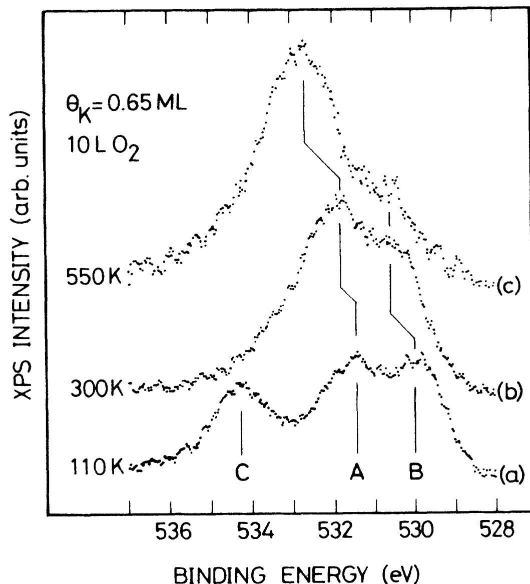

FIG. 8. O 1s XPS spectra for a Si(100) surface covered with 0.65 ML of K and exposed to 10 L of O_2 and subsequently annealed to increasing temperatures, illustrating the transfer of oxygen from the K-bonded species (*B* and *C*) to the Si-bonded species (*A*). Vertical scale is the same for all the spectra. Binding energy shifts are related to changes in the stoichiometry of the various species and/or different locations within the surface dipole.

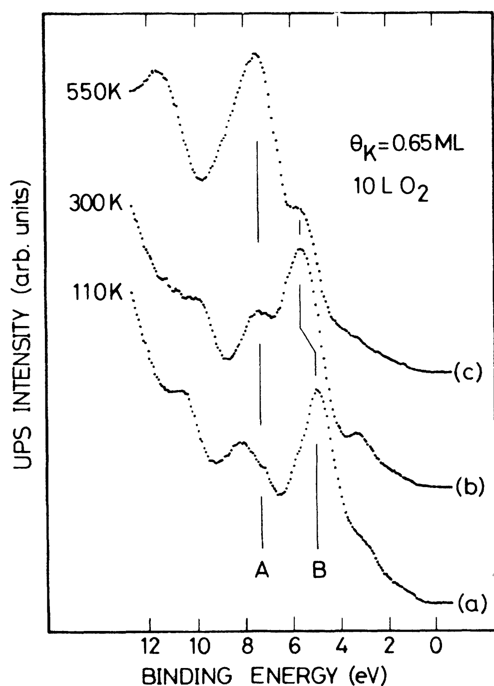

FIG. 9. Series of UPS spectra corresponding to the XPS data of Fig. 8. The surface was covered with 0.65 ML of K and expressed to 10 L of O_2 and subsequently annealed to increasing temperatures. The transfer of oxygen from the *B* species to the *A* species takes place with increasing temperature. Vertical scale is the same for all the spectra.

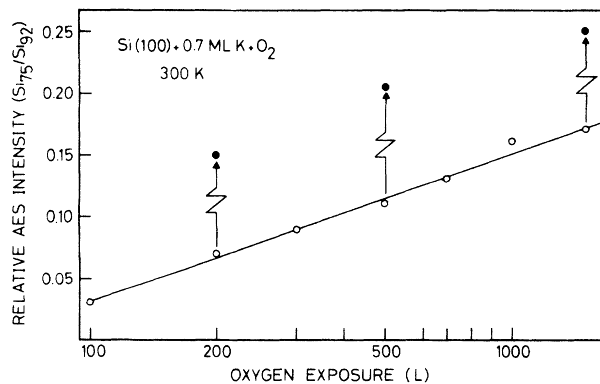

FIG. 10. Ratio of intensities of the AES peaks for SiO_2 (at 75 eV) and Si (at 92 eV) as a function of the O_2 exposure (in logarithmic scale) for 0.7 ML of K deposited on Si(100) at 300 K. The arrows indicate the increase in the amount of oxide produced if the respective sample is heated to 900 K, which results in complete disappearance of the K signal. The absolute increase in the amount of SiO_2 produced is almost constant, independently of the oxygen exposure, for the range presented here.

depends on the oxygen exposure, the additional oxide produced upon heating is almost independent of the oxygen exposure, indicating (1), that the K adlayer is already saturated with oxygen at the lowest oxygen exposure presented here, and (2), that this K-bonded oxygen is transferred to silicon upon heating.

Finally, it should be mentioned that the oxidation procedure described above (alkali-metal deposition, oxygen exposure, and annealing) can be repeated as illustrated in Fig. 11, where the resulting amounts of SiO_2, as given by AES intensities, have been plotted as a function of the

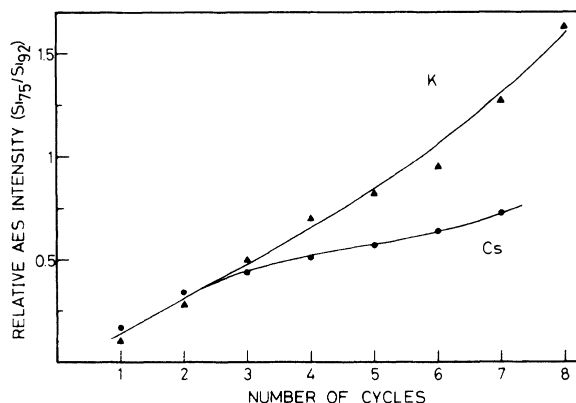

FIG. 11. Amount of silicon dioxide produced (as given by the corresponding AES intensity) as a function of the number of cycles. One cycle consists of K deposition (0.68 ML), O_2 exposure (200 L), and annealing (3 min to 900 K). The triangles represent data for K. Solid dots represent the results of similar cycles (0.55 ML, 200 L of O_2, 3 min annealing to 900 K) for Cs. The effectiveness of this oxidation process is slightly larger for K than for Cs when a relatively thick SiO_2 layer is present.

number of cycles both for the cases of K and Cs on Si(100). In the case of K each cycle consists in a K deposition of 0.68 ML, subsequent oxygen exposure of 200 L, and annealing to 900 K for 3 min. For the case of cesium, 0.5 ML were deposited and subsequently exposed to 200 L of O_2 and annealed at 900 K for 3 min. The data show an almost linear increase of the SiO_2 signal with the number of cycles, but in this case, and once the oxide layer is thick enough, the transfer of oxygen from K to Si should take place mainly during the annealing. The results shown in Fig. 11 confirm the overall similarity in the behavior of the different alkali metals, except for a slightly lower efficiency for cesium as compared to potassium after the first few cycles.

IV. DISCUSSION

We propose the the following model to explain the experimental results, based on the assumption that the chemisorption of oxygen on a Si(100)2$\times$1 surface is limited by the instantaneous formation of O_2 ions.[26] To this end, charge must be transferred from the Si substrate into the empty levels of the O_2 molecule.[27] It was proposed that this charge transfer is favored by the average work-function decrease produced by K deposition, which is assumed not to change upon O_2 adsorption.[9] This mechanism should produce a strong nonlocal promoter effect. In Fig. 12 we show the work-function changes induced by oxygen adsorption on clean and K-covered Si(100) surfaces. For sufficiently high oxygen exposures, the average work function increases in all cases, i.e., the surface dipole decreases after oxygen adsorption. For K coverages below 0.5 ML the average work function *increases* upon adsorption of oxygen above its value (which depends on the potassium coverage of the surface). On the other hand, at $\theta_K > 0.5$ ML an additional decrease of the average work function is observed for O_2 exposures below 0.2 L. At exposures larger than 1 L the average work function increases by 1.5 eV above its initial value on a K-covered surface. This behavior is typical for thick alkali-metal films, and has been attributed in this case to the existence of oxygen ions below the last atomic layer of alkali-metal atoms.[18] It has been observed as well for the case of Cs/Si(100)2$\times$1,[12] where it was also attributed to the formation of oxygen ions below the metallic cesium layer. As in that case, the K-Si surface dipole is not replaced by an equally large K-O surface dipole, as has been proposed.[9,15] However, recent photoemission of adsorbed xenon (PAX) measurements in this system[23] show that upon submonolayer deposition of potassium the work function of the surface is reduced *locally* around the potassium adatoms. The lowering of the vacuum level around the K adatoms therefore may enhance the charge transfer via electron tunneling from the K-covered substrate to the empty levels of oxygen molecules resulting in increased formation of O_2^- ions. As a result, the dissociation rate should increase due to the presence of K adatoms because less energy is required to dissociate an O_2^- ion (3.8 eV) than to break the O_2 molecule (5.2 eV),[28] thus reducing the activation barrier for the observed oxygen dissociation. This type of mechanism has a local character, at least at low K coverages where adsorbed K atoms do not interact with each other, which is expected for $\theta_K < 0.5$ ML. An experimental differentiation between the promotion effect due to local versus nonlocal mechanisms usually depends on the linearity of the measured relationship between reaction rate and the amount of the promoter (K coverage). Only for local mechanisms a linear behavior may be expected. On the basis of the present data it is difficult to settle this question. However, the clear linear relationship between the total amount of oxide grown and the coverage of potassium (see Fig. 3) supports a model assuming a strongly local character. It should also be mentioned that for oxygen on Cs-covered Si(111)7$\times$7, the initial sticking coefficient increases almost linearly with the Cs coverage[29] further pointing to a local mechanism. Additional work is required to clarify this issue.

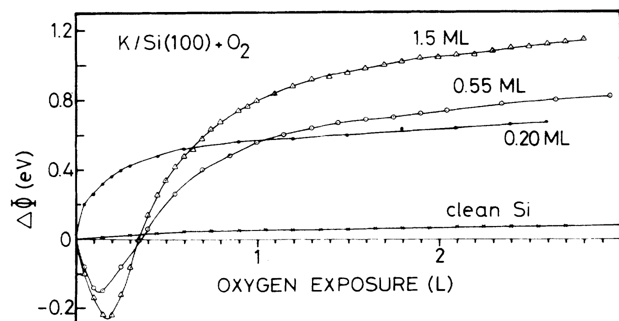

FIG. 12. Work-function changes measured by a Kelvin probe, produced by O_2 adsorption on Si(100) surfaces at 300 K, previously covered with K, as a function of O_2 exposure. The data points correspond to clean surface, 0.20 ML, 0.55 ML, and 1.5 ML. Note that the initial value of the work function (prior to oxygen exposure) depends on the respective value of OK.

After dissociation, some oxygen atoms remain bonded to potassium while other oxygen atoms diffuse away from the potassium sites and become trapped at clean patches of the silicon surfaces, giving rise to the two oxygen species *A* and *B* identified in this work with both UPS and XPS.

The temperature dependence of the oxidation rate is attributed to the freezing of the diffusion of oxygen atoms from the potassium sites to the patches of clean silicon taking place as the temperature is lowered. In this case, also the intensity ratio between the two oxygen species is frozen, and remains constant at a value corresponding to a higher percentage of oxygen bonded to potassium than to silicon (Fig. 4). Upon heating, the transfer process is accelerated and an increasing amount of K-bonded oxygen is transferred to silicon resulting in an increase in substrate oxidation.

For alkali-metal coverages above 0.5 ML (completion of the alkali-metal rows on the Si(100)2$\times$1 surface), the average work function of the surface increases with K coverage,[16] and metallization of the surface takes place.[19] Thus, an impinging O_2 molecule interacts with a metallic K layer and a potassium oxide of well-defined composi-

tion (like the one of the bulk oxide) is produced. When the initial K film is thick enough (which requires low substrate temperatures), the oxygen is trapped by the alkali-metal film by forming an oxide, and thermal annealing is required to produce oxidation of the Si substrate. The different oxidation mechanism explains well the transition to the second oxidation regime in Fig. 3. As shown in these data, above $\theta_K = 0.5$ ML the transition from the first to the second oxidation regime begins in close relationship with the presence of the KO_2 species, which plays a relevant role in the promoted oxidation at higher K coverages.[10]

V. CONCLUSIONS

The experimental data presented here indicate the following points.

(i) The presence of K on the surface of Si(100) strongly enhances the oxidation of the substrate.

(ii) The mechanism of the enhanced oxidation at submonolayer coverages of K is different from that described for K multilayer.[11,13] The transition from one to the other is correlated with the metallization of the surface, induced by K deposition.

(iii) Contrary to previous statements[9,14] the alkali metal participates in the reaction with impinging oxygen molecules at submonolayer coverages. Indeed, there are *two* different oxygen species during the promotion reaction: oxygen atoms bonded to K *and* bonded to Si.

(iv) At 300 K the amount of oxygen atoms bonded to silicon grows with O_2 exposure, while that of K-bonded oxygen atoms saturates. There is a thermal activation barrier in the oxidation reaction of the substrate, possibly related to the diffusion of activated oxygen from K sites to free Si patches. This diffusion is inhibited at low temperatures (e.g., 110 K).

(v) The promoted substrate oxidation by submonolayer coverages of potassium neither requires the metallization of the surface nor involves dissociation induced by the decrease in average work function. Instead, we propose a strongly local mechanism, where dissociation takes place in the vicinity of the K sites.

(vi) The behavior of different alkali metals (K,Cs) is basically similar, except for minor differences in effectiveness.

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