Promoted oxidation of the K-modified Si(100) (2×1) surface: Electron-energy-loss-spectroscopy and thermal-desorption studies

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The interaction of the K-covered Si(100) (2×1) surface with oxygen has been investigated by the use of high-resolution electron-energy-loss spectroscopy and thermal-desorption spectroscopy. It was found that the mechanism of enhanced oxidation of the K-modified Si(100) (2×1) surface is dependent on the fractional K coverage Θ_K. At low coverage ($\Theta_K \leq 1$), K atoms reduce the work function of the Si surface, thus increasing the initial sticking probability of oxygen; the oxygen atoms are bonded to Si and potassium oxides are not formed. However, at high coverage ($\Theta_K > 1$), K adatoms are bonded to oxygen and potassium oxides (K_2O_2, KO_2) are formed; the promoting mechanism is related to the thermal decomposition of these oxides which play the role of an "oxygen reservoir."

I. INTRODUCTION

The effects of alkali metals on the physics and chemistry of Si surfaces have lately attracted considerable attention from both fundamental and technological points of view.[1,2] In particular, many works have been written concerning the interaction of an alkali-metal-modified Si(100) (2×1) surface with oxygen, because this is related to the alkali-metal-enhanced oxidation of Si and the formation of a negative-electron-affinity (NEA) surface.[1–7] As a result of these studies, it has been found that the oxygen uptake rate is drastically increased by alkali-metal additives, that alkali-metal additives (except for lithium) do not diffuse through the surface to form silicides, and that alkali-metal additives can be removed easily by heating the surface after oxidation up to 900 K.

However, details of the oxidation process remain unclear. (1) Is there direct bonding between K and O atoms at low-K coverage? (2) Does the enhanced oxidation occur by the local effect or by the (average) work-function change (nonlocal effect)? Michel *et al.*[4] have reported from their study, using Auger electron spectroscopy (AES) and photoelectron spectroscopy, that at fractional K coverage (number of K atoms per Si) $\Theta_K \leq 1$, there is direct bonding between K and O atoms (i.e., the K_xO_y species are formed) and, at $\Theta_K > 1$, both peroxide (K_2O_2) and superoxide (KO_2) are formed; the amount of oxides formed was linearly dependent upon the K coverage, which was interpreted to indicate that the local mechanism was operative. Nishigaki *et al.*[6] have also favored, from the study using metastable deexcitation spectroscopy, the local picture of the oxidation process which includes the formation of ionic bonding between K and O atoms at $\Theta_K \leq 1$. On the other hand, Starnberg, Soukiassian, and Hurych[7] observed, by using photoelectron spectroscopy, that the threshold coverage of alkali metals was required for the onset of the promoted oxidation of the Si(100) (2×1) surface, and hence, the promoting mechanism was considered nonlocal at $\Theta_K \leq 1$.

In this paper is reported our study on the interaction of the K-covered Si(100) (2×1) surface with oxygen mainly by means of high-resolution electron-energy-loss spectroscopy (EELS) and thermal-desorption spectroscopy (TDS). It is concluded that the process of promoted oxidation of the Si(100) (2×1) surface is different between the low-coverage ($\Theta_K \leq 1$) and high-coverage ($\Theta_K > 1$) regions, but that the local mechanism is operative in both regions.

II. EXPERIMENT

All experiments were made using an ultrahigh vacuum chamber which housed a high-resolution electron-energy-loss spectrometer, a quadrupole mass spectrometer for TDS and gas analysis, a four-grid retarding field analyzer with a normal-incidence electron gun for low-energy electron diffraction (LEED), and a spherical deflector analyzer for AES. For EELS measurements, a primary energy of $E_p = 4.4$ eV and an incident angle θ_i of 60° with respect to the surface normal were used. The ionizer of the mass spectrometer was enclosed in a Pyrex-glass envelope with a 4-mm-diam aperture. The aperture was located at 1 mm from the sample surface during the TDS measurements (heating rate 8 K/s).

The sample used ($7 \times 8 \times 0.1$ mm^3) was p type, boron doped, and 3000 Ω cm. The sample surface was cleaned by several cycles of Ne^+-ion bombardment and annealing to 1150 K. The sample cleanliness was monitored by EELS. The sample heating was done by electron bombardment from the rear. The sample temperature was measured by using an Alumel-Chromel thermocouple inserted between the Si sample and the mount. The sample temperature was calibrated by the desorption temperatures of H_2 from the Si(100)-(2×1)-H and Si(100)-(1×1)-H surfaces.[8]

The K atoms were deposited on the Si surface using a chromate dispenser (SAES Getters S.p.A.) which was located at 3 cm from the sample surface. The fractional K coverage Θ_K was estimated by the K-TDS peak area assuming that the room-temperature saturation coverage

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corresponds to $\Theta_K=1$ on the basis of the double-layer model.[9] During the deposition, the sample temperature was kept at 100 K and the background pressure was $<1\times10^{-10}$ Torr. The sample with $\Theta_K\leq1$ was prepared by heating the surface (after deposition at 100 K) up to 400 K (heating rate 8 K/s). The sample with $\Theta_K>1$ was prepared by the K deposition on the Si surface with $\Theta_K=1$. The oxygen gas was introduced into the vacuum chamber via a multichannel array doser. The work-function change ($\Delta\Phi$) was measured by the threshold of the secondary-electron emission.

III. RESULTS AND DISCUSSION

A. Oxidation of the Si(100) surface at a low-K coverage ($\Theta_K\leq1$)

Figure 1 shows EELS spectra in the specular mode of the Si(100)-(2×1)-K surface ($\Theta_K=1$) and of the same surface subsequently exposed to an increasing amount of O_2 at 300 K.

The EELS spectrum for the Si(100)-(2×1)-K surface has a loss continuum similar to that for the Si(111) (7×7) surface [Fig. 1(a)].[10] The loss continuum is decreased in intensity at 100 K and disappears by 0.5-L-O_2 exposure (1 L$=10^{-6}$ Torr s) [Fig. 1(b)]. The loss continuum is ascribed mainly to the electronic transitions between the surface-state bands which are broadened by the electron-phonon coupling. In contrast to the spectrum for the Si(111) (7×7) surface, however, no broadening of the elastic peak was observed for the Si(100)-(2×1)-K surface.[10] This may be related to the finding that the Si(100)-(2×1)-K surface does not have a metallic character.[11] No vibrational loss associated with the Si—K bonding was observed due possibly to the low energy or low intensity. It is noted that the vibrational energy of the Si—K stretching mode has been estimated to be 111 cm^{-1}.[12]

For O_2 exposure $\lesssim1$ L, a loss peak is observed at 950 cm^{-1} [Figs. 1(b) and 1(c)]. With increasing exposure (1–200 L), three peaks at 450, 670, and 1100 cm^{-1} grow

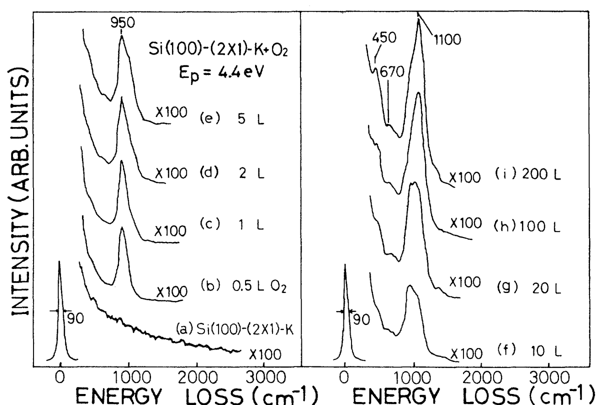

FIG. 1. EELS spectra in the specular mode of (a) the Si(100)-(2×1)-K surface and of (b)–(i) the same surface subsequently exposed to an increasing amount of O_2 at 300 K. $E_p=4.4$ eV.

in intensity and the 950-cm^{-1} loss is increasingly hidden in the 1100-cm^{-1} loss [Figs. 1(d)–1(i)]. All observed losses are excited mainly by the dipole mechanism according to the angle-dependent measurements. The $\Delta\Phi$ measurements indicate that initially, the work function is decreased, has a minimum ($\Delta\Phi\sim-0.5$ eV) for ~1-L O_2, and is increased ($\Delta\Phi\sim0.4$ eV for 100-L O_2). All LEED spots are decreased in intensity and the diffuse background is increased for O_2 exposure >1 L. It is noted that ~1-L exposure corresponds to the formation of the NEA surface.[3] These results indicate that the O_2 adsorption on the Si(100)-(2×1)-K surface occurs in two stages.

Let us consider the assignment of the 950-cm^{-1} loss. According to the infrared studies of potassium oxides in Ar matrix, the K—O stretching mode ν(K—O) is observed at 307–502 cm^{-1} depending upon the valency of oxygen.[13] The energy of the 950-cm^{-1} loss is obviously out of this range. One might ascribe the 950-cm^{-1} loss to the O—O stretching mode of the peroxidelike O_2 admolecule which is expected to be observed at 790–932 cm^{-1}.[14] However, this can be ruled out because the assignment requires also the observation of the ν(K—O) mode. One might argue that the ν(K—O) mode was not observed because it is located on a very steep slope or because of the low intensity. Although we cannot completely exclude this possibility, we emphasize the following points. (1) Detailed measurements in the low-energy region were made in both specular and off-specular modes, but the ~300–500-cm^{-1} loss was not observed. (2) The ν(K—O) mode of KO_2 is observed at 320 (~280) cm^{-1} with a high intensity in the high-K-coverage region ($\Theta_K>1$) as will be discussed in Sec. III B. Therefore, the 950-cm^{-1} loss is ascribed to the bonding between Si and O. The 950-cm^{-1} loss may be attributed to the Si—O stretching mode of the O atom located in the on-top site[15,16] or to the SiOSi antisymmetric stretching mode of the O atom located in the bridge site,[16,17] but the former is preferable for the following reasons. (It is noted that the SiOSi species is formed by the Si—Si bond scission followed by the insertion of an O atom.) (1) Losses which can be associated with the SiOSi symmetric stretching and bending modes are not observed. The cross section for dipole scattering is proportional to the surface loss function which is simply given by $\mathrm{Im}[-1/\epsilon_s(\omega)]$ [$\epsilon_s(\omega)$ is the dielectric constant of the surface layer in the two-layer model].[18] By comparison with the loss function derived from the optical data for bulk vitreous SiO_2,[19] it is considered that these two modes should have enough cross sections to be observed if the SiOSi antisymmetric stretching mode is observable. (2) The formation of the SiOSi species should be accompanied with the distortion of the Si(100)-(2×1)-K superstructure which is expected to produce a diffuse LEED background. However, this is ruled out by our LEED measurement for ~1-L-O_2 exposure.

The 450-, 670-, and 1100-cm^{-1} losses are typical of the SiOSi species, and are assigned to the SiOSi bending, symmetric stretching, and antisymmetric stretching modes, respectively.[16,17]

The above assignment of the 950-cm^{-1} loss is confirmed by Fig. 2, which shows EELS spectra in the

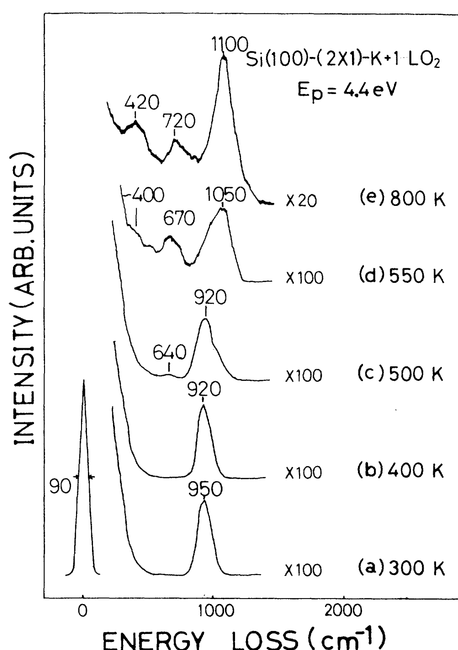

FIG. 2. EELS spectra in the specular mode of (a) the Si(100)-(2×1)-K surface exposed to 1-L O_2 at 300 K and of (b)–(e) the same surface subsequently heated to high temperatures. $E_p=4.4$ eV.

specular mode of the Si(100)-(2×1)-K surface ($\Theta_K=1$) exposed to 1-L O_2 and of the same surface subsequently heated to high temperatures at the heating rate 8 K/s. All spectra were recorded at 300 K. A loss peak is observed at 950-cm^{-1}, characteristic of the NEA surface as discussed above [Fig. 2(a)]. By heating up to 500 K, the EELS spectrum is changed somewhat: a new loss peak is observed at 640 cm^{-1} and the 950-cm^{-1} loss is shifted to 920 cm^{-1} accompanied with the tailing of the high-energy side [Fig. 2(c)]. Since the 640-cm^{-1} loss is attributed to the symmetric stretching mode of the SiOSi species, this tailing is ascribed to the antisymmetric stretching mode of the SiOSi species. After 550 K heating, the EELS spectrum is drastically changed: two loss peaks are observed at 670 and 1050 cm^{-1} with the shoulder at $\sim$400 cm^{-1}; residue of the 950 (920)-cm^{-1} loss is hidden in the low-energy side of the 1050-cm^{-1} loss peak [Fig. 2(d)]. By heating to 800 K, three peaks are observed at 420, 720, and 1100 cm^{-1} which are typical of the SiOSi species [Fig. 2(e)].[16,17] These results indicate that the O atoms located in the on-top sites of the first-layer Si atoms break the Si—Si bonds to form the SiOSi species by heating.

Abukawa *et al.*[5] have proposed a model for the Si(100)-(2×1)-K/O NEA structure from the study using x-ray photoelectron diffraction (XPD). According to this model, oxygen atoms are located in the on-top sites of the first-layer Si atoms, which is consistent with our EELS measurements. Michel *et al.*[4] and Nishigaki *et al.*[6] have concluded that O atoms are bonded to K adatoms as described in the Introduction. Their conclusion is essentially based on the experimental results which show the existence of a large charge transfer from K to O. However, the charge transfer may occur through the Si substrate if the K and O atoms are located nearby, and thus, the formation of the K—O bond can be ruled out as discussed above.

Figure 3 shows oxygen-uptake curves for the Si(100)-(2×1)-K ($\Theta_K=1$) and Si(100) clean ($\Theta_K=0$) surfaces. The amount of the adsorbed oxygen is estimated by the TDS peak area associated with the SiO desorption. Figure 3 clearly indicates that the preadsorbed K atoms drastically promote the oxygen adsorption. The initial sticking probability of oxygen for the K-covered surface is about 10 times as large as that for the clean surface. As the fractional O coverage for $\sim$1-L-O_2 exposure (where the NEA structure is formed) is unity,[5] the initial sticking probability for the K-covered surface is almost unity. This is consisted with the initial sticking probability ($\sim$0.8), measured by the use of molecular beam technique, for the Cs-covered Si(100) surface ($\Theta_{Cs}=0.9$).[20] For O_2 exposure >1 L, the oxygen-uptake rate for the K-covered surface is almost comparable with that for the clean surface. This means that the promotion mechanism is mainly associated with the drastic enhancement of the initial sticking probability.

The amount of the adsorbed oxygen after 500-L-O_2 exposure at 90 K is plotted as a function of the fractional K coverage Θ_K in Fig. 4. The inset of Fig. 4 shows the development of the TDS spectra associated with the SiO desorption with increasing K coverage ($\Theta_K=0-1.4$). It is noted that the TDS spectrum for $\Theta_K=1.4$ has a tail at the high-temperature side, and hence, the oxygen coverage was estimated by the peak area below 1100 K assuming the same background as the others. In the range of $\Theta_K \leq 1$, the amount of oxygen is linearly dependent upon the K coverage, and there is no threshold reported by Starnberg, Soukiassian, and Hurych.[7] It is considered that the linear dependence reflects the "local" work-function change near K adatoms. There is a threshold at $\Theta_K=1$ which implies that the oxidation mechanism at a

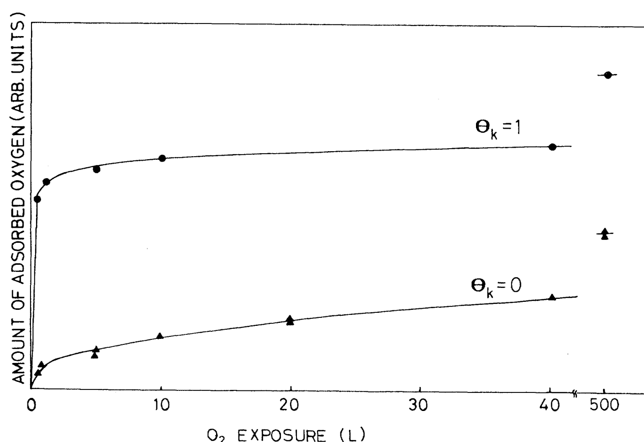

FIG. 3. Oxygen-uptake curves for the Si(100)-(2×1)-K ($\Theta_K=1$) and Si(100) clean ($\Theta_K=0$) surfaces at 300 K. The amount of the adsorbed oxygen was estimated by the TDS peak area associated with the SiO desorption.

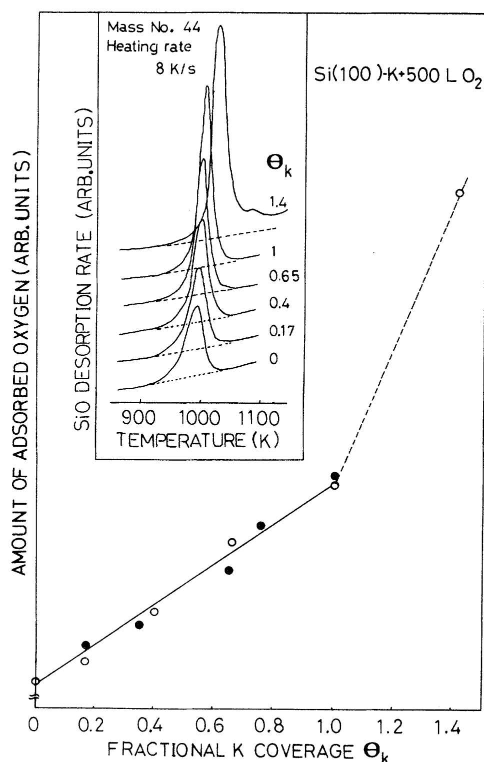

FIG. 4. The amount of adsorbed oxygen after 500-L-O_2 exposure at 90 K is plotted as a function of the fractional K coverage ($\Theta_K=0\sim1.4$). The inset shows TDS spectra for the SiO desorption from the K-covered surfaces (heating rate 8 K/s). The open circles correspond to the TDS spectra in the inset.

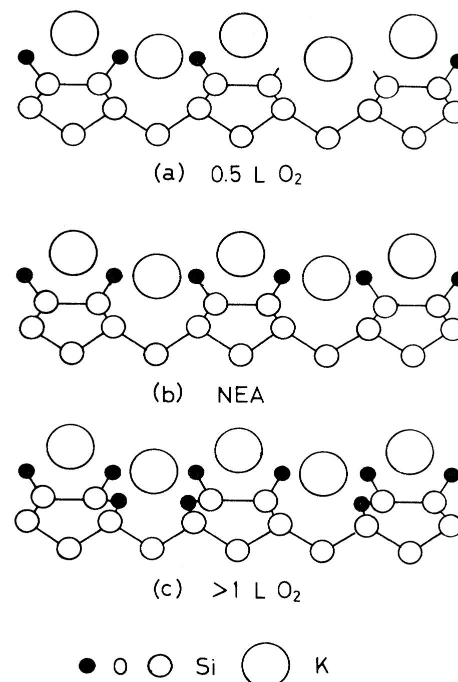

FIG. 5. Schematic representation of the oxidation process for the K-covered Si(100) (2×1) surface ($\Theta_K\leq1$).

low-K coverage is different from that at a high coverage. The oxidation mechanism at a high coverage will be discussed in Sec. III B.

From the above discussion, the oxidation in the K-covered domains at $\Theta_K\leq1$ is thought to proceed in two stages as schematically shown in Fig. 5. In the first stage, oxygen molecules approaching the surface are dissociatively chemisorbed in the on-top sites of the first-layer Si atoms near K adatoms. In the second stage, O atoms chemisorbed in the on-top sites are transferred to the substrate near K adatoms and break the Si—Si backbonds to form SiOSi species. The oxidation rate of the second stage is slow compared with that of the first stage as shown in Fig. 3. The Si—Si bond weakening which also promotes the O-atom insertion into the Si—Si bond may occur near the K adatoms because of the charge transfer to the antibonding states of the Si—Si bond. However, we have no evidence for this. [It is noted that the Si—Si bond weakening is observed for the Y-covered Si(100) surface.[21]] The oxidation in the K-free domains is thought to proceed in the same way as that on the clean surface.[16,17]

Let us consider why the sticking probability of O_2 is much higher for the K-covered surface than that for the clean surface. It has been found, by the use of the modulated molecular-beam reactive scattering technique, that the initial sticking probability of atomic oxygen on the Si(100) surface is unity but that of the O_2 molecule is very low.[22] Thus, it is considered that the dissociation of molecular oxygen is the rate-limiting process in the oxidation of the Si surface. The dissociation is induced by a charge transfer from the dangling π-bond band to the $2\pi^*$ antibonding orbital of molecular oxygen.[1,2,4,6,7,23] On the K-covered surface, the work function is greatly reduced in comparison with that on the clean surface as described above, and the electron flow to the $2\pi^*$ antibonding orbital of molecular oxygen is highly promoted. Therefore, the dissociation probability of O_2 is drastically enhanced.

In the oxidation of the clean Si(111) surface the intermediate molecular precursor species, which is identified as the peroxy-bridge-like or superoxidelike species, has been found by several groups by using EELS and near-edge x-ray absorption fine structure (NEXAFS).[16,17,22,24] It is very difficult to answer the question of whether or not there is such an intermediate species on the K-covered surface. Since the dissociation probability is markedly enhanced on the K-covered surface by comparison with that on the clean surface, the lifetime of such a precursor species is probably too short to be observed by the conventional spectroscopic methods, and a time-resolved technique will be needed for the detection.

B. Oxidation of the Si(100) surface at a high-K coverage ($\Theta_K>1$)

Figure 6 shows EELS spectra in the specular mode of the "bulk" K in islands ($\Theta_K=1.4$) on the Si(100) (2×1) surface exposed to an increasing amount of O_2 at 90 K.

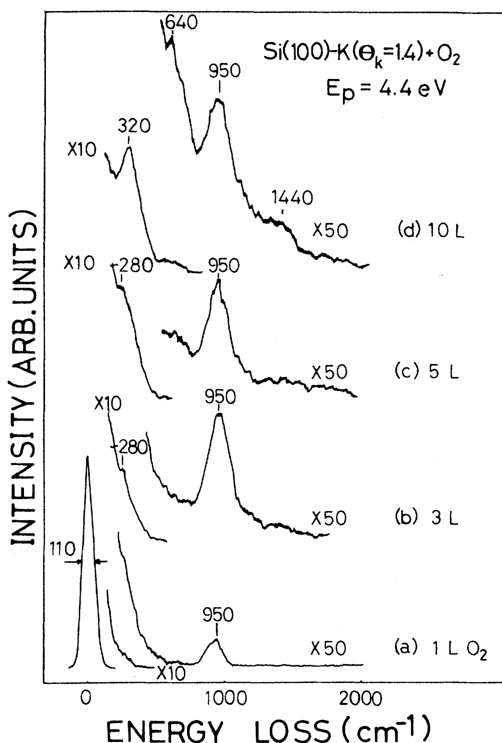

FIG. 6. EELS spectra in the specular mode of the "bulk" K in islands ($\Theta_K = 1.4$) on the Si(100) (2×1) surface exposed to an increasing amount of O_2 at 90 K. $E_p = 4.4$ eV.

By the exposure to 1-L oxygen, a loss peak is observed at 950 cm^{-1} [Fig. 6(a)]. With increasing exposure, a shoulder appears at ~ 280 cm^{-1} [Figs. 6(b) and 6(c)]. For 10-L exposure, losses are observed at 320, 640, 950, and 1440 cm^{-1} [Fig. 6(d)]. The 950-cm^{-1} loss is attributed to the Si—O stretching mode of the O atoms chemisorbed in the on-top sites of the first-layer Si atoms in the (2×1)-K domains. The 320 (~ 280)-cm^{-1} loss is assigned as the K—O stretching mode of KO_2 referring to the infrared studies of potassium oxides.[13] (The corresponding O—O stretching mode is not observed well due, perhaps, to the low-excitation cross section.) The 640-cm^{-1} loss is ascribed to the multiple or overtone excitation of the 320-cm^{-1} loss. The energy of the 1440-cm^{-1} loss is out of the range that is expected for the O-O stretching mode of peroxidelike or superoxidelike O_2 admolecules[13,14] and for SiOSi species.[16,17] Therefore, this loss is related to the residual gases (CO,CO_2). The 1440-cm^{-1} loss is ascribed to the vibrational mode (ν_3) of CO_3^{2-} formed by the adsorption of CO_2.[25,26] Michel *et al.*[4] observed the existence of K_2O_2 and KO_2 by using photoelectron spectroscopy for the K film deposited on the Si(100) (2×1) surface, but only losses associated with KO_2 were observed in our EELS measurements; losses associated with K_2O_2 are not observed, probably due to the low-excitation cross section.

A series of thermal desorption spectra of K from the K-covered Si(100) surface ($\Theta_K = 1.4$) with increasing O_2 exposure at 90 K is shown in Fig. 7. The spectrum for

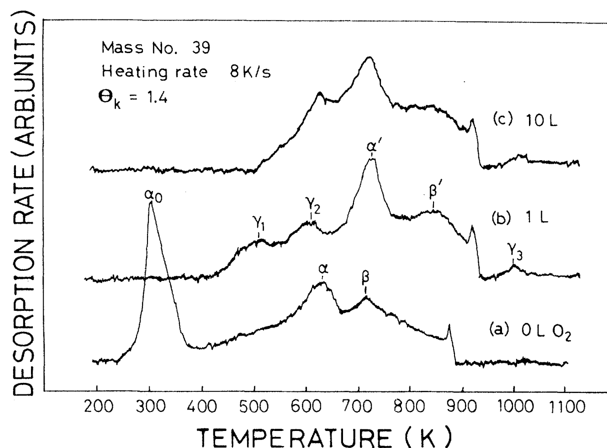

FIG. 7. A series of TDS spectra of K atoms from the K-covered Si(100) (2×1) surface ($\Theta_K = 1.4$) with increasing O_2 exposure at 90 K: (a) oxygen-free, (b) 1 L, (c) 10-L O_2 (heating rate 8 K/s).

the oxygen-free Si(100) surface shows three peaks: α_0, α, and β [Fig. 7(a)]. The origin of the sharp peak at ~ 880 K (which has been observed in our recent experiments) is not well understood, but is attributed to the K^+-ion desorption which has been observed for the K-covered Ni(111) surface.[27] (It is noted that the shift of the sharp peak after O_2 exposure [Figs. 7(b) and 7(c)] reflects the work-function change.) The α_0 peak is ascribed to the desorption from the "bulk" K islands by comparison with the TDS studies for alkali-metal atoms on transition-metal surfaces.[28] The α and β peaks correspond to the chemisorbed states of K and are indicative of the existence of two different chemisorbed states which are associated with the double-layer model.[11] The development of TDS spectra for the various K coverage was previously discussed in detail.[29] [The difference in peak temperatures (α_0, α, and β) between the previous and this work is attributed to the difference in the position of the thermocouple.]

By 1-L-O_2 exposure, the spectrum is drastically changed [Fig. 7(b)]. The α_0 peak disappears, the α and β peaks are shifted towards higher temperatures, and new peaks (γ_1, γ_2, and γ_3) appear.

The shift of the α and β peaks toward higher temperatures indicates that the K—Si bond becomes stronger, which is opposed to the result of a theoretical calculation.[30] It is considered that the shift of K desorption temperatures is related to the interaction between the adsorbed K and O. According to a number of theoretical models, the adsorbate-adsorbate interaction is classified into two groups: one is the direct interaction (i.e., dipole-dipole interaction, overlap of the adsorbate electronic orbitals, and Coulomb interaction), and the other is the indirect interaction (i.e., interaction through electrons in the substrate).[31] According to the effective-medium theory by Nørskov, Holloway, and Lang,[32] the adsorbate-adsorbate interaction is mainly due to the direct Coulomb interaction of the adsorbates. Especially, K and O atoms are electropositive and electronegative,

respectively, and hence, the direct Coulomb interaction is considered to induce the shift of K desorption temperatures. Additionally, there may exist the contribution from the through-substrate interaction between the adsorbed K and O.

The total area of the γ_1 and γ_2 peaks is almost equal to the α_0 peak area and, therefore, the γ_1 and γ_2 peaks are associated with the bulk-K islands. For 10-L-O_2 exposure, the γ_1 peak disappears and the γ_2 peak shifts slightly toward higher temperature. Since our EELS measurements show the formation of superoxide species (KO_2) for 10-L exposure, the γ_2 peak is ascribed to the K desorption by the decomposition of KO_2. The γ_1 peak is related to the K desorption by the decomposition of K_2O_2 on the basis of the photoelectron spectroscopy study by Michel *et al.*[4] With increasing O_2 exposure the γ_1 peak disappears, which is attributed to the conversion from K_2O_2 to KO_2 [Fig. 7(c)].

The temperature of the γ_3 peak (1020 K) is identical to that of the SiO desorption (inset, Fig. 4). This means that the complete removal of K atoms has to be accompanied by the SiO desorption, which is contrary to the fact that an alkali metal is called a "good catalyst" because it can be easily removed by heating the surface after oxidation up to 900 K,[1,2] and which may imply the existence of potassium silicate $K_xSi_yO_z$ on the Si(100) surface. [It is noted that cerium silicate $Ce_2Si_2O_7$ is observed for the Ce-deposited Si(100) surface.[33]]

As shown in Fig. 4, the oxidation for the Si(100) surface ($\Theta_K=1.4$) is more promoted than that for the Si(100)-(2×1)-K surface ($\Theta_K=1$) and the linear dependence upon the K coverage has a threshold at $\Theta_K=1$. This indicates that the promotion mechanism for high coverage ($\Theta_K>1$) is different from that for low coverage ($\Theta_K\leq1$).

From the above discussion, it is concluded that the promotion mechanism at $\Theta_K>1$ is the thermal decomposition of potassium oxides (K_2O_2,KO_2). The K adatoms play a role as an oxygen reservoir at a high coverage which is different from the promotion mechanism for a low coverage where there is no direct bonding between K and O. It is noted that heat treatment is needed for the Si-substrate oxidation in the high-coverage region ($\Theta_K>1$).

IV. CONCLUSION

The promoted oxidation of the K-covered Si(100) (2×1) surface has been studied. It is concluded that there is a difference in the oxidation process between the low-coverage ($\Theta_K\leq1$) and high-coverage ($\Theta_K>1$) regions.

At a low coverage, the oxidation occurs in two stages. In the first stage, oxygen molecules are dissociatively chemisorbed in the on-top sites of the first-layer Si atoms, and there is no direct bonding between K and O. This process is drastically enhanced by the existence of the K adatoms which reduce the local work function. In the second stage, O atoms break the Si—Si bonds (near K adatoms) to form SiOSi species. The promotion mechanism is explained by the local picture.

At high coverage, there is direct bonding between K and O, and peroxide (K_2O_2) and superoxide (KO_2) are formed. The promotion mechanism is explained by the thermal decomposition of these potassium oxides. It is noted that K adatoms in the "bulk" islands play a role as an "oxygen reservoir."

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