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Existence of two adsorbed states for K on the Si(100)(2×1) surface: A thermal desorption study

S. Tanaka, N. Takagi, N. Minami, and M. Nishijima
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

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Thermal desorption spectroscopy (TDS) was applied to the investigation of the adsorbed state of K on the Si(100)(2×1) surface. Two K desorption peaks were observed and were attributed to the desorption of K atoms from two different chemisorbed states on the Si(100)(2×1) surface. The results strongly suggest that the fractional saturation coverage of K atoms in the chemisorbed state is one. The coverage dependences of the peak temperatures and shapes of the TDS spectra are discussed.

I. INTRODUCTION

The adsorption of alkali metals on Si surfaces has been studied for many years not only because it is a prototype of metal adsorption on semiconductor surfaces but also because it is important from the viewpoint of the technological applications, e.g., alkali-metal-promoted oxidation of Si (Ref. 1) and formation of a negative-electron-affinity (NEA) surface.[2] Recently, much work has been done on the adsorption of alkali metals (especially K) on the Si(100)(2×1) surface. However, the structures of these systems are still controversial. The first model was proposed by Levine[2] who, assuming that the dimer structure of the Si(100)(2×1) clean surface remains intact, proposed that alkali-metal atoms (Cs) are adsorbed in the four-coordinated hollow sites of the dimer rows ("pedestal sites"). Several experimental and theoretical studies have been made assuming this model.[3-5] According to the Levine model, the fractional coverage Θ of alkali metal at the saturation is 0.5 [one alkali-metal atom per Si(100)(2×1) unit cell]. However, recently, Abukawa and Kono[6] claimed that $\Theta = 1$ based on their photoemission and photoelectron diffraction studies, and proposed a double-layer model for the Si(100)(2×1)-alkali-metal system.

Reported in this paper is our study of the Si(100)(2×1)-K system mainly by means of thermal desorption spectroscopy (TDS). Clear evidence has been found for the existence of two chemisorbed states of K atoms on the Si(100)(2×1) surface.

II. EXPERIMENT

All experiments were carried out by the use of an ultrahigh-vacuum chamber in which is housed a quadrupole mass spectrometer for TDS and gas analysis, a high-resolution electron-energy-loss spectrometer, a four-grid retarding-field analyzer with a normal-incidence electron gun for low-energy electron diffraction, and a spherical deflector analyzer with a normal-incidence electron gun for Auger electron spectroscopy. 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.

The sample used ($7 \times 8 \times 0.1$ mm^3) was *p*-type, boron doped, and had specific resistivity 3000 Ω cm. The sample surface was cleaned by several cycles of Ne$^+$-ion bombardment and annealing (1150 K). The sample heating was made 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 temperature of H_2 from the Si(100)(2×1)-H and Si(100)(1×1)-H surfaces.[7] The K atoms were deposited using a chromate dispenser (SAES Getters S.p.A.) which was located 3 cm from the sample surface. During the deposition, the sample temperature was 100 K and the background pressure was less than 1×10^{-10} Torr.

III. RESULTS AND DISCUSSION

Thermal desorption spectra of K (mass number 39) were measured with increasing K coverage. The heating rate was 7.7 K/s. Results are shown in Figs. 1(a)–1(g) for the low-coverage range, and in the inset of Fig. 1 for the high-coverage range. In Fig. 1, it is assumed that the fractional coverage Θ of K atoms in the chemisorbed state is one at the saturation, as will be discussed later. The intensity of the peak near 370 K (labeled α_0) is increased with increasing coverage and is not saturated. The α_0 peak is ascribed to the desorption from the "bulk" K in islands by comparison with TDS studies for alkali-metal atoms chemisorbed on transition-metal surfaces.[8,9] This result indicates that the "bulk" K formation occurs at room temperature but that it is desorbed at a temperature slightly higher than the room temperature.

Our main interest is on the spectra in the low-coverage range [Figs. 1(a)–1(f)]; these spectra correspond to the desorption from the chemisorbed K. In the low-coverage region, a high-temperature desorption peak β is observed to grow in intensity and is shifted towards lower temperatures with increasing coverage ($T = 880$–700 K) [Figs. 1(a)–1(d)]. The β peak has a characteristic shoulder at the high-temperature edge. The origin of the peak shift and the shape of the β peak will be discussed later. After the saturation of the β peak, a new desorption peak α grows in intensity at a lower temperature; this peak is also

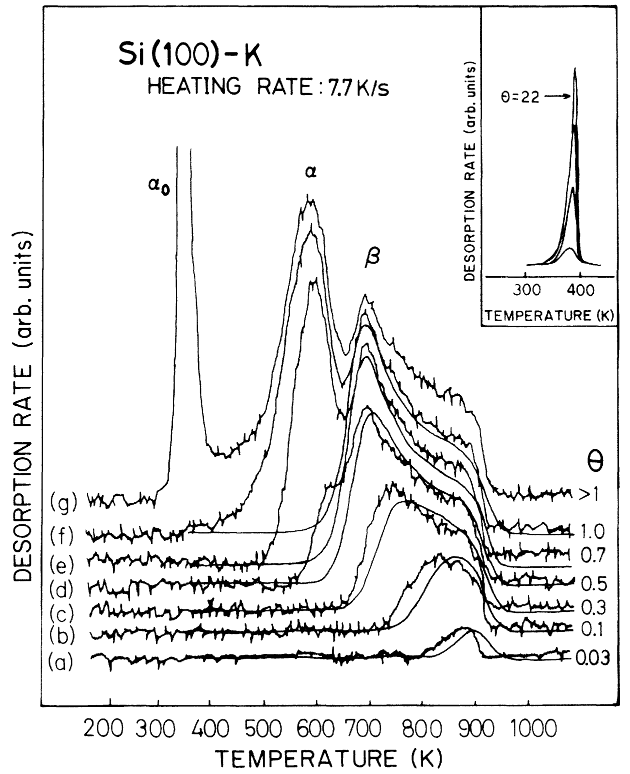

FIG. 1. TDS spectra of K atoms from the Si(100) surface with increasing fractional K coverage Θ. K atoms were deposited on the Si(100) surface at 100 K. The solid curves show the results calculated according to the model proposed by Albano (Ref. 13).

(but only slightly) shifted towards lower temperatures with increasing coverage (T=630-600 K) [Figs. 1(d)-1(f)]. The α_0 peak is observed after the α and β peaks are saturated [Fig. 1(g)]. It is noted that the TDS spectra of the K-covered Si(100) surface formed by the K deposition at 350 K were similar to those shown in Fig. 1 except for the absence of the α_0 peak.

From the presence of the two desorption peaks α and β, it is considered that there are two different chemisorbed states for K atoms on the Si(100)(2×1) surface and that K in the α state has a lower binding energy and that K in the β state has a higher binding energy. It is difficult to understand the TDS results by the Levine model which has a single chemisorbed state. The presence of two chemisorbed states implies the existence of two different chemisorbed sites. According to this model, for low coverages the adsorbed K atoms are desorbed only from the stable sites. It is noted for low coverages that the K atoms are not required to occupy only the stable sites by deposition at a lower temperature (e.g., room temperature), because the adatoms on the less-stable sites are expected to move to the stable sites before the desorption takes place. For high coverages, the K atoms adsorbed in the less-stable sites cannot move to the stable sites which are occupied, and are desorbed directly from the less-stable sites.

There are four possible adsorbed sites of high symmetry on Si(100)(2×1); these are cave, valley-bridge, pedestal, and bridge sites.[10] We call the first two sites lower sites and the last two sites upper sites. It is considered that the two desorption states α and β correspond to desorption from both upper and lower sites, because the K occupation of an upper (lower) site hinders adsorption into the neighboring upper (lower) sites due to the steric effect. Ling, Freeman, and Delley[10] and Ramírez[11] calculated the binding energy of a K atom in each site, and concluded that K atoms are more stable in the lower sites than in the upper sites. Thus, it is considered that the α state corresponds to the upper sites and the β state, the lower sites.

Our TDS results are compatible with the double-layer model proposed by Abukawa and Kono.[6] On the basis of their model, the fractional coverages associated with the α state (pedestal sites) and β state (valley-bridge sites) are 0.5, and the total fractional coverage is one. This is consistent with the fact that the area intensities of the α and β desorption peaks at saturation are nearly the same. (Peak deconvolution has been performed, and the intensity ratio between the two peaks is 50:50.) However, according to the calculations of Ling *et al.*[10] and Ramírez,[11] K atoms are most stable in the cave sites where K atoms can saturate the Si dangling bonds, and the order of increasing stability is given by the sequence bridge, pedestal, valley-bridge, and cave sites. Thus, the α state may be associated with the pedestal sites and the β state, the cave sites. It is noted that the one-dimensional chains of K atoms (which are adsorbed only in the lower sites) may be formed by heating of the sample to 600 K after (or during) the deposition.

The shift of the α and β peaks towards lower temperatures with increasing coverage indicates that the desorption energies of K atoms decrease with the increase of the K coverage. Figure 2 shows coverage dependences of the desorption energies for the α and β states estimated from the peak temperatures, assuming the prefactor ν_0 of 10^{13} s^{-1}, by the use of the Redhead method.[12] The indicated coverages were evaluated from the (deconvoluted) peak-area intensities. The desorption energy in the limit of zero coverage is estimated to be 38 kcal/mol for the α state and 56 kcal/mol for the β state. [These estimates are considered reasonable in spite of the fact that the Redhead method is based on the assumption of a constant desorption energy (independent of the coverage variation during the desorption), because (i) for lower coverages, the desorption reaction is only slightly perturbed compared to the case of the $\Theta=0$ limit, and (ii) for higher coverages, the desorption peak has a large peak at the low-temperature side (Fig. 1), and the coverage at the peak is not very much altered compared to the initial coverage.] It is noted that, for the α state, the total fractional K coverage in the zero limit is 0.5 due to the presence of K atoms associated with the β state.

The β peak shifts towards lower temperatures with increasing initial coverage, and has a characteristic shoulder at the high-temperature side [Figs. 1(a)-1(d)]. In order to understand these results, we made a simulation calculation according to the model proposed by Albano[13] in which it is assumed that the desorption energy of an adatom is decreased by the dipole-dipole repulsion of the chemisorbed atoms. The desorption rate $R(N,T)$ of a K

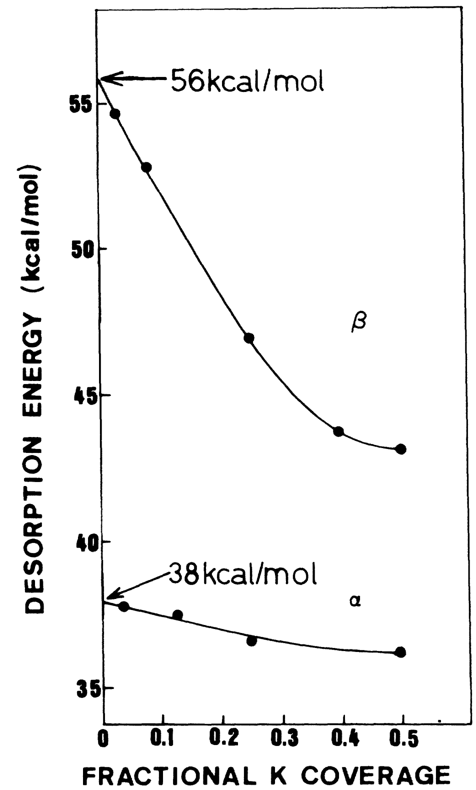

FIG. 2. Coverage dependences of the desorption energies of K atoms in the α and β states.

atom from Si(100) is, assuming a first-order desorption, given by

$$R(N,T) = -dN/dt = \nu_0 N \exp[-E_d(N)/RT] , \quad (1)$$

where N is the number of K adatoms per unit area, T is the surface temperature, t is the time, E_d is the desorption energy, and R is the gas constant. The desorption energy is changed by the interaction between a dipole [with the dipole moment $\mu(N)$] and the depolarizing electric field [$\varepsilon_d(N)$] created by the surrounding dipoles, and hence,

$$E_d(N) = E_d(0) + \mu(N)\varepsilon_d(N) , \quad (2)$$

where $E_d(0)$ is the desorption energy in the limit of $\Theta = 0$ (56 kcal/mol) and $\mu(N)$ and $\varepsilon_d(N)$ can be calculated by applying the "breathing lattice" approximation to the (2×1) rectangular array.[14] Thus, the desorption energy $E_d(N)$ is given by

$$E_d(N) = E_d(0) - 11.4[\mu(0)]^2 N^{3/2} \times (1 + 11.4\eta N^{3/2})^{-2} , \quad (3)$$

where $\mu(0)$ is the dipole moment of an isolated K adatom and η is the effective polarizability (assumed to be independent of N). By use of the Runge-Kutta method, the TDS spectra were numerically calculated for the case of a heating rate of 7.7 K/s. Results of the calculation are shown by the solid curves in Figs. 1(a)–1(f). The agreement between the computed spectra and the experimental results are reasonable.

The values of the dipole moment of an isolated K adatom $\mu(0)$ and the effective polarizability η, which were chosen such that the shape and shift of the peak were fitted to the experimental results, are 5.7 D and 8.6 Å^3, respectively. These values are in reasonable agreement with those for K chemisorbed on transition metals obtained by TDS and work-function change measurements.[13] However, they are not similar to the values (2.0 D and 3.0 Å^3, respectively) for K chemisorbed on Si(100)(2×1) estimated from the work-function-change measurements by using a similar model.[15] [The values reported by Oellig and Miranda[15] are 3.6 D and 9.2 Å^3, respectively, but the (hexagonal) array and K coverage which they assumed for the estimation are different from ours, and the data were reinterpreted according to our model.] This may indicate that the K-desorption process is different from the adsorption process. For example, K atoms may occupy multiple sites from the initial stage of adsorption.

The above-mentioned phenomenological analysis does not necessarily indicate that the dipole-dipole repulsion within the adlayer is indeed responsible for the coverage dependence of the TDS spectra. A detailed theoretical study is needed by which we can understand microscopically the TDS spectra.[16]

IV. SUMMARY

Thermal desorption spectroscopy was applied to the investigation of the adsorbed state of K on the Si(100)(2×1) surface. Two desorption peaks were observed which are attributed to the desorption of K atoms from two different chemisorbed states (associated with the upper and lower sites) on the Si(100)(2×1) surface. The desorption energy of K atoms from the two states were estimated for various coverages. The coverage dependences of the peak temperatures and shapes of the TDS spectra were discussed.

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