Dangling-bond adsorption site for potassium on Si(100)-(2×1)

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Surface extended x-ray-absorption fine structure (SEXAFS) has been used to determine the adsorption geometry of potassium on Si(100)-(2×1) in the single-site regime at a half monolayer coverage. Measurements indicate that potassium adsorbs in a low-symmetry dangling-bond site, with a K-Si bond length of 3.20±0.03 Å. Moreover, normal-incidence SEXAFS data evidence potassium backscatterers at 3.81±0.04 Å, which is consistent with potassium adsorption in adjacent sites along the dimer rows.

Alkali-metal-semiconductor interfaces have been extensively studied in recent years. This work is primarily motivated by interest in the physics of charge transfer, metallization, and Schottky barrier formation. Alkali metal-semiconductor interfaces make good model systems with which to study metal-semiconductor contacts due to the simple electronic structure of the alkali metal. Additional interest is provided by the important technological applications of alkali-metal-semiconductor interfaces in, for instance, negative electron affinity devices and promoted substrate oxidation. Despite the attention that this area has received, certain fundamental properties of alkali-metal-semiconductor interfaces remain matters of controversy, including the surface morphology. In this paper we describe a structural study, employing surface extended x-ray-absorption fine structure (SEXAFS), of one such geometrically ill-determined interface, the prototypical K/Si(100)-(2×1) system.

The phase diagram for K/Si(100)-(2×1) has recently been explored by Michel et al.[1] They find that up to 0.5 ML [1-ML coverage of K is defined here as the density of atoms equal to the atomic density of the Si(100) surface, i.e., 6.78×10^{14} atoms/cm²], K adsorbs in a unique site at room temperature; above this coverage an additional site is occupied. However, there is no consensus view as to the identity of the adsorption site in the single-site regime, with a variety of K adsorption sites being proposed in previous experimental studies. The sites previously considered are shown in Fig. 1. These include the pedestal site, which was suggested[2] on the basis of Levine's model for Cs/Si(100)-(2×1) (Ref. 3) as well as the valley bridge and cave sites. The cave and/or valley sites have been proposed by diffraction studies,[4] scanning-tunneling-microscopy (STM) measurements,[5] a photo-

emission study,[6] as well as by photoemission of adsorbed Xe and thermal-desorption-spectroscopy measurements.[1] Two lower-symmetry geometries have been proposed on the basis of very-low-coverage (<0.1 ML) STM data,[7,8] which we describe here as dangling-bond sites. As for the K-Si bond length, an earlier SEXAFS study arrived at a value of 3.14±0.1 Å.[9]

Corresponding theoretical studies[10−14] have attempted to deduce the most favorable adsorption site by total-energy minimization. As in the experimental work, the results are at variance with one another, both in terms of the adsorption site and the derived K-Si bond length (2.59–3.53 Å).
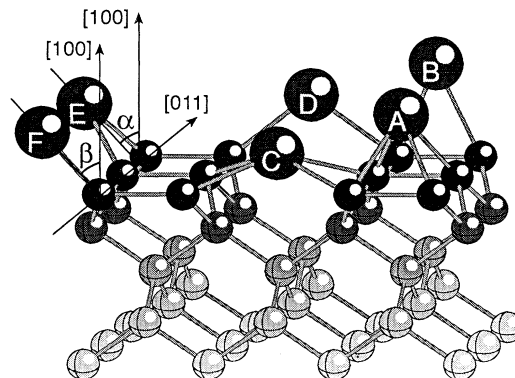

FIG. 1. Adsorption sites of potassium on Si(100)-(2×1) considered in earlier work. Symmetric Si dimers are shown for simplicity (see text). The sites include the pedestal (A), bridge (B), cave (C), valley bridge (D), and dangling bond sites (E and F). The angles α and β are discussed in the text.

Here, we use a proven structural technique[15] to address the key issue of the discrepancy between the very-low-coverage STM results[7,8] and other structural measurements in the single-site regime. We find that the same type of site evidenced at very low coverage by STM is occupied at about 0.5 ML.

Potassium K-edge SEXAFS measurements were performed using a Ge(111) crystal pair in the double-crystal monochromator of station 6.3 at the Synchrotron Radiation Source, Daresbury Laboratory.[16] Measurements were recorded at grazing (20°) and normal (90°) photon incidence. In both geometries, the photon E vector was in the [011] azimuth.[17] A double-pass cylindrical mirror analyzer (CMA) (Physical Electronics Inc.) operated in the nonretard mode was used to record the K LMM Auger yield as a monitor of the surface x-ray-absorption coefficient. The CMA axis was at 90° to the incident photon beam. Normalization of the SEXAFS data to the incident photon flux was accomplished by measuring the drain current from a thin Al foil placed between the monochromator and sample chamber. During the SEXAFS measurements the sample temperature was maintained at about 150 K to reduce Debye-Waller-like attenuation of the SEXAFS amplitude.[15]

The Si(100) wafer sample (n-type, P-doped, $\rho = 1-10$ Ω cm, UniSil Corporation) was cleaned in situ by several cycles of annealing to 1400 K for 10 sec. This was sufficient to produce an almost contaminant free ($<1\%$ ML carbon) well-ordered two-domain 2×1 surface, as judged by Auger electron spectroscopy and low-energy electron diffraction (LEED).

K was deposited from a carefully degassed commercial source (SAES Getters), the pressure during evaporation remaining below 2×10^{-10} mbar. The chamber base pressure was below 7×10^{-11} mbar. Calibration of the absolute K coverage employed the K_{LMM}/Si_{LMM} Auger intensity ratio in conjunction with a procedure described in Ref. 1 to form a surface with a coverage of 0.6 ML. All the SEXAFS data shown in this paper were recorded at a K coverage of 0.55 ± 0.1 ML. This overlayer was formed by K deposition at 150 K, with subsequent flashing to about 273 K to ensure adsorption in a single site.[1] The 2×1 LEED pattern was found to persist after K deposition, consistent with earlier work.[1] Auger electron spectroscopy measurements showed no evidence of a significant increase in surface contamination after K deposition, although a low level ($\ll 1\%$ ML) of O contamination was noted following SEXAFS data acquisition.

Surface extended x-ray-absorption fine-structure data recorded at grazing and normal incidence are shown in Fig. 2. Background subtraction and normalization of these data to their respective edge-jumps yields the EXAFS oscillations $\chi(k)k^2$ and their corresponding Fourier transforms shown in Fig. 3 (solid lines). Surface extended x-ray-absorption fine-structure spectra were analyzed using EXCURV90, a curve-fitting procedure based on the rapid curved wave computational scheme.[18] The theoretical phase shifts and backscattering amplitudes used in the analysis[19] have already proved adequate in previous studies.[20,21] E_0,[18] employed as an adjustable
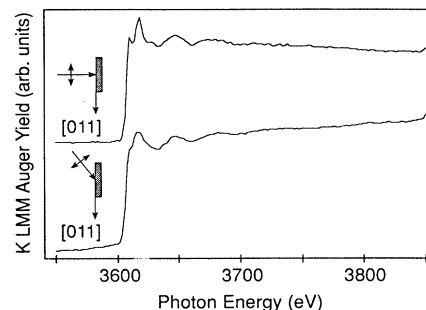

FIG. 2. K LMM Auger yield K K-edge SEXAFS spectra of K/Si(100)-(2×1) at a coverage of 0.55±0.1 ML, recorded at 150 K. The relative edge step in the grazing (normal) incidence data is 0.86 (1.01), where the relative edge step is the difference in count rate above and below the absorption edge divided by the count rate below the edge.
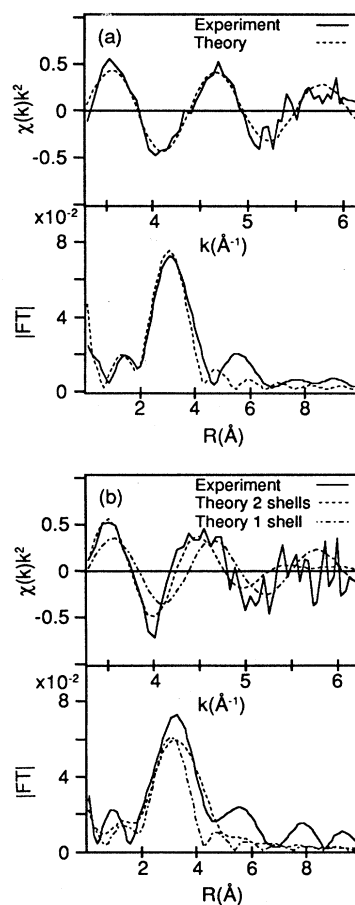

FIG. 3. K LMM Auger yield K K-edge SEXAFS spectra of K/Si(100)-(2×1) at a coverage of 0.55±0.1 ML, recorded at 150 K. Data were recorded at an angle of incidence of 20° (a) and 90° (b) with the E vector in the [011] azimuth. The EXAFS function $\chi(k)$ weighted by k^2 (solid line) and the best fit (dashed line) are compared in the upper part of the diagrams. The corresponding lower sections contain the modulus of the Fourier transform. In (b), the best fit employing only one shell (Si) at 3.20 Å, the K-Si distance determined from the grazing incidence data, is also shown (dot-dashed line).

parameter in the analysis, was constrained to have the same value, 7.4 eV, in the analysis of data recorded in both measurement geometries.

Successful fitting of the grazing incidence data required a single shell of Si backscatterers at 3.20 ± 0.03 Å (Debye-Waller-like factor $=0.035$ Å^2). The normal-incidence data required an additional shell of K backscatterers at 3.81 ± 0.04 Å (Debye-Waller-like factor $=0.058$ Å^2) to adequately fit the data. Inclusion of further backscattering shells of Si or K did not significantly improve the fits to the grazing or normal-incidence data. The best fits to the data are shown in Fig. 3, along with the best fit to the normal-incidence data using only the first shell of (silicon) backscatterers at 3.20 Å.

Before elucidating the K adsorption site, we compare our K-Si bond length (and error bar) with that obtained in earlier work, 3.14 ± 0.1 Å.[9] The magnitude of the error bar quoted in the earlier study is based on an assessment of phase-shift reliability and the effect of anharmonic vibrations. However, the generally accepted uncertainty associated with phase-shift transferability is ±0.02 Å,[22] and we estimate the potential error from anharmonicity to be of the same order.[23] As for the bond distance, a likely origin for the discrepancy is the use of a negative E_0 (Ref. 18) value in the previous study.

To determine the adsorption site of K, we employ the effective coordination numbers obtained from the best fits to the polarization-dependent data, comparing them to the calculated effective coordination numbers for each of the six adsorption sites in Fig. 1. These, together with their respective ratios, are listed in Table I. For simplicity, Table I contains the effective coordination numbers calculated on the basis of a frozen substrate containing symmetric Si dimers with a bond length of 2.5 Å.[13] Effective coordination numbers were calculated for several dimer geometries, both symmetric and buckled, but no significant differences between these values and those shown in Table I were found. Comparison of the calculated and experimental effective coordination ratios allows us to discount the bridge, cave, and valley bridge sites as possible K adsorption sites.

In assessing the possibility that K adsorbs in the pedestal site, we first note that there is a significant discrepancy between the experimental and calculated absolute effective coordination numbers in Table I. Other evidence to rule out the pedestal site is found by considering the expected contribution to the EXAFS from the second shell of Si backscatterers. As noted above, such a contribution is not observed. On the basis of approximately equal Debye-Waller-like factors for the first two Si shells, calculations indicate that a second shell contribution should be observed well above the noise level for all sites in Fig. 1. Its absence can be understood in the case of the dangling-bond sites by recognizing that libration of K about the nearest-neighbor Si atoms need not change the K nearest-neighbor distance, but would change the distance to the second Si shell, increasing Debye-Waller-like attenuation of its backscattering amplitude. A similar mechanism does not apply in the case of the pedestal site.

Of the sites considered, the SEXAFS data are, therefore, only consistent with the dangling-bond sites E and F in Fig. 1. A satisfactory agreement between the experimental and calculated effective coordination numbers and their ratios for these sites is obtained within the range $20°\leq\alpha\leq40°$ and $45°\leq\beta\leq50°$, where α and β are defined as the angle between the surface normal and the K-Si bonding plane for sites E and F, respectively (see Fig. 1).

On the basis of the SEXAFS data, there is no reason to prefer either site E or F. However, on the basis of the more recent interpretation of very-low-coverage (<0.1 ML) STM data,[8] it seems likely that the bridging site E is occupied. Of the other experimental studies which have assigned an adsorption site,[1,2,4-6] none explicitly considered the dangling-bond sites, but we have no reason to believe that their data are inconsistent with one of these sites.

The K-K bond distance of 3.81 ± 0.04 Å evidenced in normal-incidence data is, within experimental error, identical to the surface lattice vector parallel to the dimer rows (3.84 Å), indicating that K atoms adsorb in adjacent sites along the dimer rows. The effective coordination number for K backscatterers, 3.4 ± 1.0, is consistent with that expected for this geometry (3.0), as is the 2×1 LEED pattern.

Finally, we note that both the K-Si bond length, which is equal to the sum of the covalent radii of Si and K [1.17 Å$+2.03$ Å$=3.20$ Å (Ref. 24)], and the dangling-bond adsorption site suggest covalent rather than ionic bonding to the substrate. This is consistent with results from recent studies which have directly probed the electronic structure of the interface in the single-site regime.[6,25]

In summary, SEXAFS measurements from the K/Si(100)-(2×1) interface in the single-site regime show that K adsorbs in a low-symmetry dangling-bond site, with a K-Si bond length of 3.20 ± 0.03 Å. The data also

TABLE I. The effective coordination numbers obtained for the best fits to the normal and grazing incidence SEXAFS data from K/Si(100)-(2×1), and the theoretically calculated effective coordination number for sites $A-F$ (Fig. 1). For sites E and F, the angles in brackets are the values of α and β employed for the calculated effective coordination numbers shown. Also tabulated are the effective coordination number ratios.

| Angle of incidence | Experimental | | Calculated 1st silicon shell | | | | | |
	silicon	potassium	A	B	C	D	$E(30°)$	$F(45°)$
90°	1.6 ± 1.0	3.4 ± 1.0	3.10	0.47	5.94	1.90	1.57	0.75
20°	2.6 ± 1.0		5.48	4.52	0.82	2.11	2.71	1.41
90°/20°	0.62 ± 0.17		0.57	0.10	7.24	0.90	0.58	0.53

indicate that K atoms are adsorbed in adjacent sites along the dimer rows. This work resolves the discrepancy between the very-low-coverage STM results[7,8] and other structural measurements in the single-site regime.

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