Coverage dependence of K adsorption on Si(100)2×1 by core-level photoemission: Structure, charge transfer, and metallization

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Using core-level photoemission, a coverage-dependent transition in the adsorption of K on Si(100)2×1 is observed. Below ~0.25 monolayers, a single adsorption is occupied, the asymmetry of the Si-dimer reconstruction is enhanced, and no more than ~0.05e is transferred from K to Si. Above this coverage, multiple sites are occupied, the dimer configuration becomes more symmetric, and the K overlayer becomes increasingly metallic. These findings resolve a number of conflicting studies of this system.

I. INTRODUCTION

Among the alkali-metal–semiconductor interfaces that have been studied, K on Si(100)2×1 has attracted the greatest attention. Nevertheless, some of the most basic questions concerning surface morphology, charge transfer, and interface metallization still remain unsettled. Regarding the morphology, recent work indicates that K occupies one adsorption site at low coverages[1] but two at saturation.[2,3] Little is known, however, about the effect of the adsorbed K on the structure of the underlying Si(100)2×1 surface. The amount of charge donated from K to Si has been a topic of intense discussion, but theoretical estimates[4-9] of this value vary by as much as an order of magnitude. The metallic character of the interface at saturation coverage has been variously ascribed to one-dimensional metallic chains of K,[4,10] metallization of the underlying Si,[5] or a bulklike K metal overlayer on a Si surface which remains semiconducting.[11]

Here we report core-level photoemission measurements that delineate the nature of this alkali-metal–semiconductor interface in each of these three fundamentally important areas. It is shown directly that K is responsible for coverage-dependent changes of not only the adsorption site but also of the Si surface reconstruction. In addition, the K adsorbate layer itself is explicitly seen to be metallic at saturation, whereas at low coverage, in the linear-chain regime, the K-K interaction is quite weak. From these combined results we show that there is very little charge transfer from K to Si at low coverage. These latter findings closely resemble the observed behavior of alkali metals on metal substrates.

II. EXPERIMENTAL DETAILS

Measurements were made using the AT&T Bell Laboratories–University of Oregon 6-m toroidal grating monochromator on beamline U4A at the National Synchrotron Light Source. The photoemitted electrons were analyzed with a 100-mm Vacuum Science Workshop hemispherical analyzer. For all spectra the total instrumental resolution was kept significantly smaller than the intrinsic width of the photopeaks. The Si substrates were cleaned by standard procedures of Ne$^+$ bombardment and annealing to 900 °C–1150 °C. Low-energy electron diffraction showed sharp 2×1 spots with no evidence of splitting. The majority of runs were taken on n-type samples (1.75 Ω cm), although no appreciable differences were observed in spectra from p-type wafers (0.045 Ω cm), indicating strong pinning of the Fermi level at all coverages. A clean Si surface was prepared before each K dose (from commercial dispensers) and all photoemission measurements were performed with the substrates at room temperature (RT).

Coverages quoted in this work were obtained from a careful work-function versus absolute-coverage (Θ) calibration,[12] which gave a maximum Θ of 0.70 monolayers (ML) at RT (not 1.0 ML as recently claimed[2,3]). In excellent agreement with this earlier study[12] and other work,[11,13] we measure a maximum lowering in work function of −3.32 eV and a change of −3.13 eV at saturation from the low kinetic-energy photoemission cutoff. Although we have not determined the absolute coverage directly, the integrated intensity of the K 3p photoemission features provides a measure of the relative K coverage. Figure 1, in which the K 3p integrated intensity is
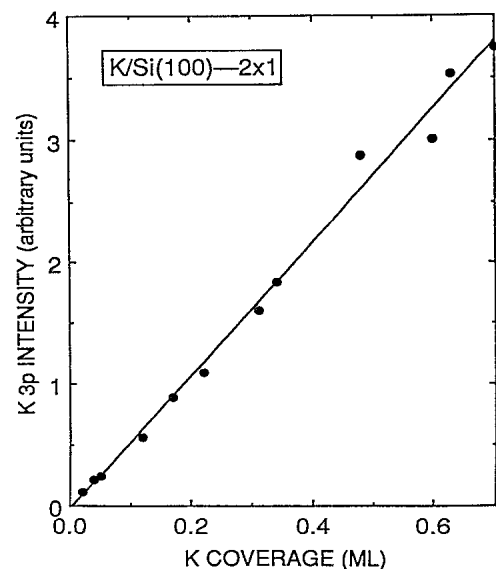

FIG. 1. K 3p integrated intensity vs K coverage deduced from the work function and Ref. 12.

plotted against the work-function-derived coverage, shows that our relative coverages are also in excellent agreement with those of Ref. 12. Specifically, the work-function minimum occurs at 90% of room-temperature saturation, i.e., $\Theta = 0.63$ ML.

III. RESULTS AND ANALYSIS

The most striking result to emerge from this work is the existence of a coverage-dependent transition in adsorption behavior at ~ 0.25 ML, which is not at all evident in the coverage-dependent behavior of the work function. As will be shown, both the K $3p$ and Si $2p$ photoemission data bear out this transition. We first discuss the K results. Raw spectra in the K $3p$ region for coverages spanning 0 to 0.7 ML are displayed in Fig. 2. In addition to the K $3p$ photopeak are two Si valence-band (VB) plasmon features, which are also present on the clean surface. The figure shows that for coverages ≤ 0.22 ML the binding energy is constant and the line shape is rather symmetric. At higher coverages the data are broader, shifted, and significantly more asymmetric than those below 0.22 ML.

Analysis quantifies these observations. For all coverages less than ~ 0.25 ML the K $3p$ data are well characterized by a single spin-orbit doublet [ratio is 0.5, splitting is 256 meV (Ref. 14)] whose components have identical Gaussian width (930 $\pm$ 30 meV), Lorentzian width (30 $\pm$ 3 meV), and Doniach-Šunjić singularity index ($\alpha = 0.05 \pm 0.01$). (The quoted uncertaintes are determined from the scatter of values obtained from the analysis of independent data sets.) Figure 3 illustrates
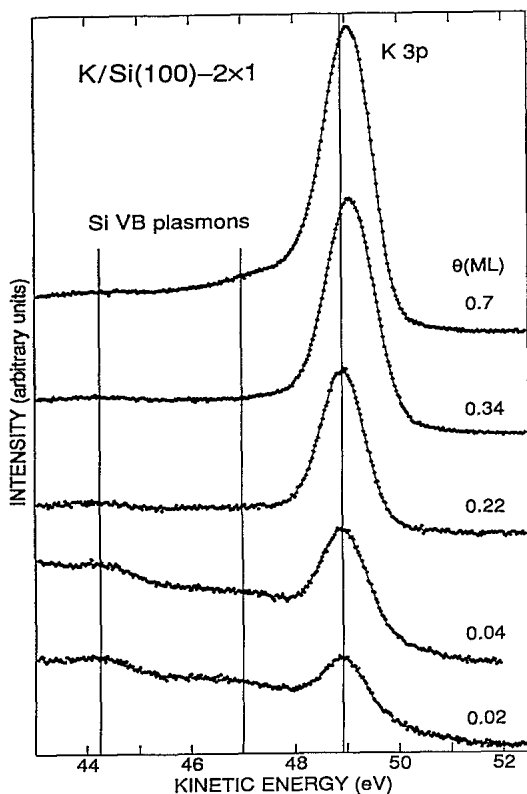
this line shape for spectra at 0.02, 0.04, and 0.22 ML.[15,16] As Θ increases beyond 0.22 ML, this simple model function becomes increasingly inadequate. A good fit to these data requires two spin-orbit doublets. In Fig. 4 saturation-coverage data are fitted with both a single (a) and two (b) spin-orbit doublet features. Clearly two components are required to produce residuals that are near statistical in nature. The larger asymmetry of the photopeaks here relative to the low-coverage data is reflected in their larger singularity index α of ~ 0.18, which is comparable to that found in bulk K and other alkali metals.[17] In Fig. 5 we show both α and the binding-energy (BE) shift for data extending over the full range of coverage, determined from fits with a single doublet. The transition, which begins at $\Theta = \sim 0.25$, is well defined in each parameter. It does not cause a break in the coverage dependence of the work function, indicating that the dipole moment of the K adsorbate atoms remains constant through the transition.

Although the Si $2p$ spectra exhibit more subtle changes, the distinction between low- versus high-coverage behavior is clearly evident. Figure 6 shows raw Si $2p$ spectra for a clean, a 0.22-ML-covered, and a sa-
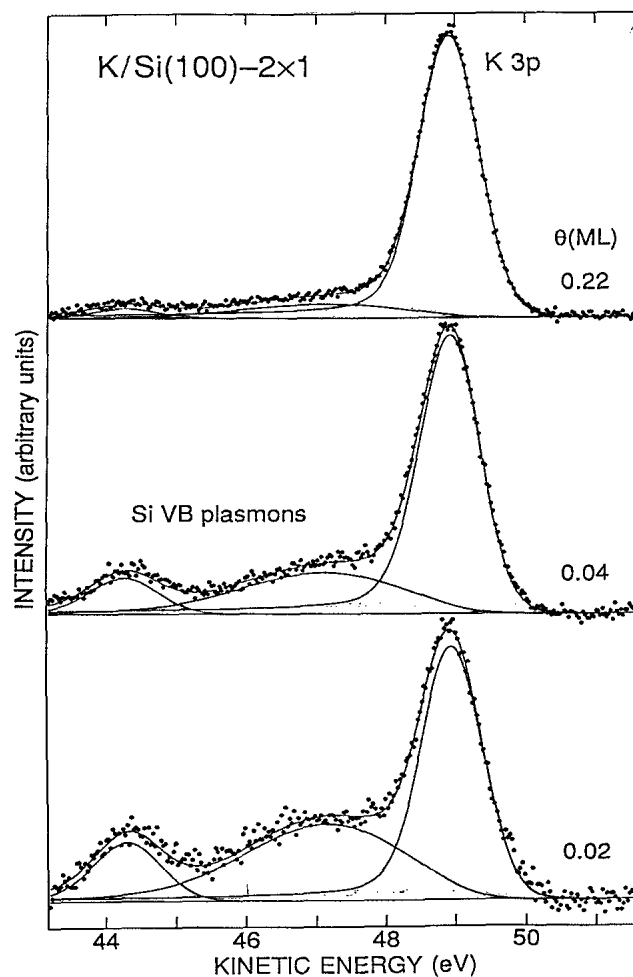

FIG. 3. Analysis of low-coverage K $3p$ region. All three data sets are least squares fit with identical spin-orbit doublet line shapes for the K $3p$ feature and identical line shapes for the Si VB plasmon peaks.
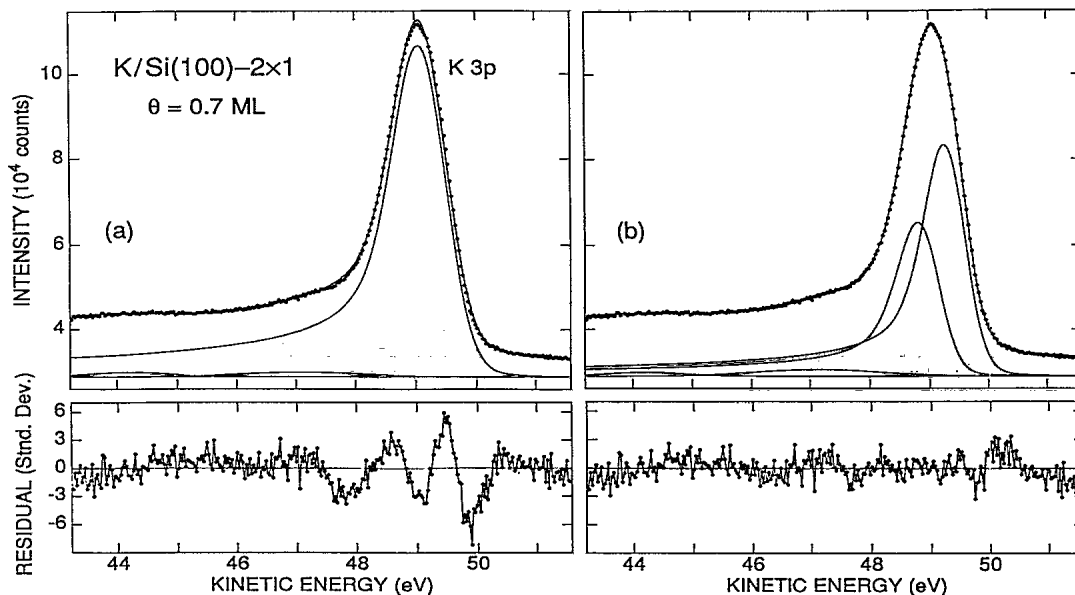

FIG. 2. K $3p$ spectra for K adsorption on RF Si(100)2×1. Photon energy is 72 eV; instrumental resolution is 220 meV.

FIG. 4. Analysis of saturation coverage (0.7 ML) K $3p$ data. (a) Fit with one spin-orbit component. Note highly nonstatistical fluctuations in residuals. (b) Fit with two spin-orbit doublet components. Residuals are now much more random, indicating a much higher quality of the fit compared to (a).

turated 0.70-ML K surface. Aside from increased inelastic scattering for the saturated surface, the most obvious changes occur on the high-kinetic-energy (low-BE) side of the bulk peak. At small K coverage the low-BE feature moves to a slightly lower value, while at high K coverage it moves back towards the bulk line and increases in area.
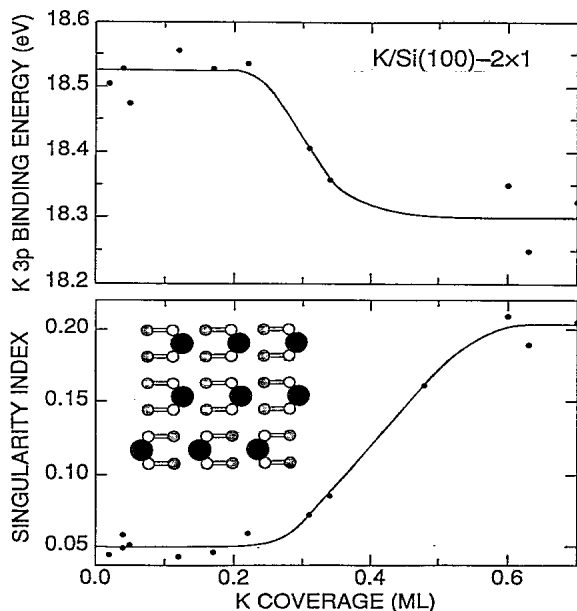

FIG. 5. K $3p$ binding energy and singularity index vs K coverage. The reference level for the BE is the Fermi level of Ni(100) crystal held at the same potential as the Si sample. The singularity index is for fits with one spin-orbit doublet. Better two-doublet fits at high Θ yield comparable values. Inset: Low-coverage adsorption site at $\Theta = \frac{1}{4}$ ML. Large shaded circles are K, small shaded circles are Si down atoms, and small open circles are Si up atoms.

Also apparent at saturation is a decrease in area on the high-BE side of the bulk line.

In order to assess more fully the influence of K on the Si spectra, further analysis is required. We have recently shown[18] that deconvolution of the phonon broadening from $2p$ spectra of the clean Si(100)2×1 surface gives a reliable determination of the surface-atom peak positions. The bottom trace in Fig. 7 shows such a deconvolved spectrum in which the bulk $2p_{3/2}$ feature, labeled B, is used as a reference point for the binding energies. The two lowest-BE features at -0.33 and -0.56 eV, labeled S_u, have been assigned[18] to crystal-field-split up atoms of the asymmetric dimers of the reconstructed Si surface. The higher-BE $2p_{3/2}$ feature at 0.25 eV, labeled S_d, has been assigned to the down atoms of the dimers. The splitting between the up- and down-atom BE's and the crystal-field splitting both come from the charge
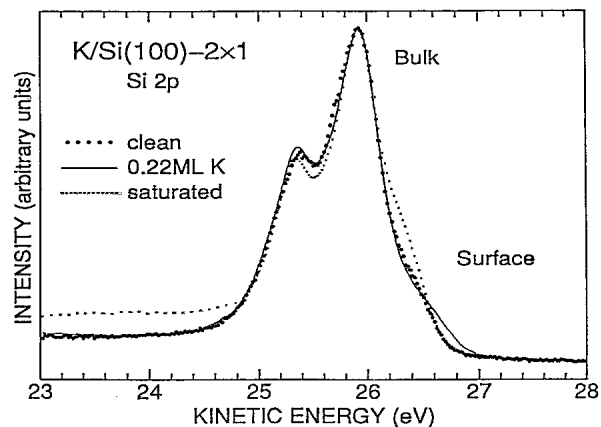

FIG. 6. Raw Si $2p$ spectra from Si(100)2×1 illustrating the effect of K adsorption. Photon energy is 130 eV; instrumental resolution is 90 meV.
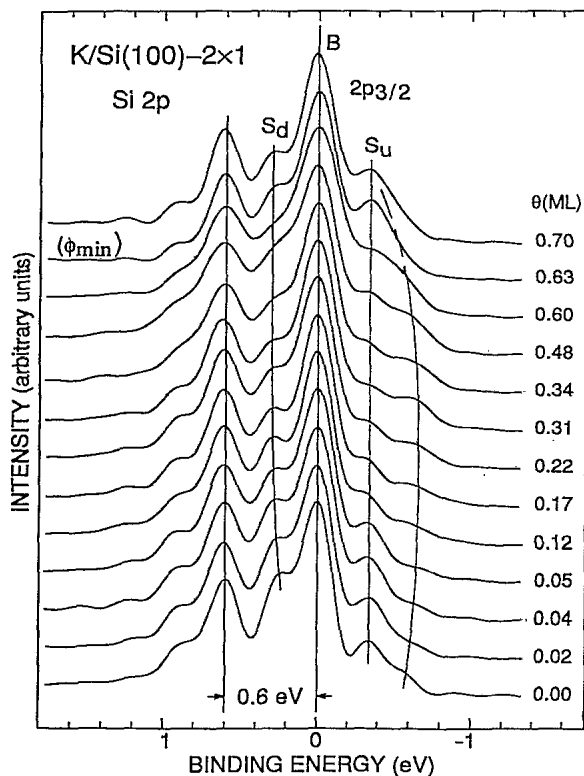
FIG. 7. Deconvolved Si $2p$ spectra vs K coverage. Peaks are labeled by their origin (B is bulk, S_d is down atom, and S_u is up atom) on the clean surface. ϕ_{min} labels the spectrum obtained at the work-function minimum.

transferred from the down atoms into the empty dangling-bond state of the up atoms. Note that the intensities of these features are consistent with all surface atoms being reconstructed into asymmetric-dimer units.[18] The $2p_{1/2}$ counterparts of B and S_d are readily identified by the 0.60-eV spin-orbit splitting.

The rest of Fig. 7 reveals, in more detail, the effects that increasing amounts of K have on the Si $2p$ core levels. The average change in up-atom core-level BE is seen to come largely from movement of the lowest-BE crystal-field component. As Θ increases to $\sim$0.25 ML, the BE of this component decreases by $\sim$0.10 eV. Beyond this critical coverage, the peak increases in BE until near saturation when it merges with the other crystal-field component. The BE of the down atoms of the dimers is also affected by K. As Θ increases to $\sim$0.25 ML, the down-atom peak position increases from +0.25 to +0.30 eV. The change in relative area between low- and high-BE surface features is also apparent, with the former increasing at the expense of the latter.

IV. DISCUSSION

A. Low-coverage regime

In discussing our results, we focus first on the low-coverage region, i.e., Θ < 0.25 ML. Recent scanning-tunneling-microscopy (STM) work[1] shows that for Θ < 0.1 ML, K occupies a single adsorption site and tends to form one-dimensional chains perpendicular to

the Si-dimer rows. The condensation into chains, even for Θ as small as 0.05 ML, is consistent with our observation that the K $3p$ BE remains constant for all coverages less than $\sim$0.25 ML. Our result, together with the identical line shapes found for the K $3p$ spectra in this range of coverage, extends the STM finding that K occupies the off-center bridge between two up atoms of the reconstructed Si surface over the full range of $\Theta \lesssim 0.25$ ML. Note that this adsorption site is fully consistent with a transition at $\sim$0.25 ML, because at this coverage every up atom can be bridge bonded to a K atom. The inset in Fig. 5 illustrates this low-coverage binding site[1] for Θ = 0.25 ML. The fact that we observe no high-order LEED spots (apart from those due to the Si-dimer reconstruction) is reflected in the inset by the uncorrelated positions of the K atoms along the Si-dimer rows.

Additional insight is provided by the effect of K on the Si $2p$ spectrum. There are two major contributions to an adsorbate-induced shift in surface-atom BE: a chemical one due to adsorbate-substrate charge transfer, and a structural one due to adsorbate-induced changes in reconstruction of the surface.[19] One possible contribution to the average up-atom BE decrease at low coverages is simple charge donation from the electropositive K to the dangling bonds of the up atoms. If such a chemical shift were the only effect, then comparison with the induced shifts caused by a wide range of electronegative and electropositive adsorbates (F, O, Cl, S, H, As, Al, and Ca) on Si surfaces,[20] which suggest a Si-atom core-level shift of 1.8 eV/e, implies a charge transfer per K of only 0.05e. However, K charge donation to the up atoms—with no accompanying change in Si reconstruction—would also shift the down-atom BE back towards the bulk value because the dangling bonds of the up atoms (now saturated with K 4s charge) would be less capable of accepting charge from the down atoms. Since the binding energy of the down atoms exhibits the *opposite* behavior, we conclude that the K-induced surface shifts are due primarily to changes in Si surface *structure* rather than to adsorbate-substrate charge transfer. Viewed in this way, the adsorption of K for $\Theta \lesssim 0.25$ ML is seen to increase the buckling of the Si surface dimers. STM observations show that alkali metals[1] (as well as defects[21]) stabilize the dynamically oscillating dimers of the clean surface. More precisely, then, the shifts observed here show that the K-induced static buckling is larger than the time-averaged buckling of the clean surface. From this discussion we see that the above assignment of a transfer of $\sim$0.05e (0.025e to each Si atom) is actually an *upper limit* on the charge flow at these low coverages. Our observation of little, if any, K charge donation and the STM finding of the low coordination and directional nature of the K atoms in the bridge site,[1] as well as the K-Si bond length of 3.1 Å derived from surface-extended x-ray fine-structure data,[22] each support the picture of *covalent* rather than ionic bonding between the K and surface Si atoms for Θ < 0.25 ML.

B. High-coverage regime

Beyond 0.25 ML the adsorption behavior of K becomes more complex. The two-doublet fit of the K $3p$

spectrum for $\Theta = 0.7$ in Fig. 1 indicates that K occupies two (or more) inequivalent sites. Photoelectron diffraction[2] results from the saturated surface are indeed consistent with a two-adsorption model of K adsorption. Moreover, recent thermal-desorption data[3] show the appearance of a second desorption peak at a coverage somewhere between 0.21 and 0.35 ML (assuming 0.7 ML is saturation), in accord with our observed transition at 0.25 ML and a two-site model at high coverage.

In this high-coverage regime, K has the opposite effect on the Si $2p$ spectrum that it had below 0.25 ML. Recall in Figs. 6 and 7 that with increasing coverage above 0.25 ML both the crystal-field splitting and the down-atom–up-atom BE splitting decrease. Such behavior is consistent with the dimers becoming more symmetric as more K is adsorbed. However, it is also evident in both figures that the surface-atom feature associated with the up atoms increases in area at the expense of the surface-atom feature at higher binding energy. Since all the dimers are buckled on the clean surface, this last observation requires some other type of surface atom to be associated with the low-BE surface peak. One simple possibility is that near saturation K induces some fraction of the Si dimers to become very nearly symmetric. This structural rearrangement is accompanied by the donation of a small amount of charge so that the binding energy of these symmetric dimer pairs approaches that of the remaining up atoms. With this interpretation, the $2p$ data at saturation coverage indicate (upon fitting) that about 50% of the dimers are in a symmetric configuration and that $\sim 0.15e$ is transferred to each Si atom in a symmetric pair.

Our results also address the metallic state of the K/Si(100) interface. The large value of the K $3p$ singularity index in the saturation coverage region, $\alpha \simeq 0.18$, demonstrates that the K layer is metallic. This is as expected for a condensed overlayer of K that has donated little charge to the Si surface, and is thus consistent with the small charge transfer deduced from the Si-atom shifts. The smaller value of $\alpha \simeq 0.05$ in the low-coverage

region is consistent with the weaker screening response expected from widely spaced adatoms in linear chains. Earlier studies [3,11,23] have suggested that excess K growing on top of the first-layer K is responsible for the high-coverage metallic response and that the true first-layer saturation occurs just before the work-function minimum at 0.63 ML.[11] The present K $3p$ results show that neither claim is correct: the transition to metallic behavior of the K overlayer is observed (Fig. 5) close to, if not coincident with, the other transitional behavior at ~ 0.25 ML, well before the work-function minimum. The absence of separate, sharper K $3p$ features (characteristic of bulk K metal[15]) in the 0.7-ML spectra (top curve, Fig. 2) demonstrates that bulklike K metal does not appear on this surface at RT. Very recent second-harmonic-generation experiments[24] support the low-coverage onset of metallic behavior in the K overlayer observed here. Using 0.63 ML as the work-function-minimum coverage, the metallic transition is observed to occur at 0.18 ML, fully consistent with the behavior of α in Fig. 5.

In summary, two different K adsorption regimes, with a crossover at a coverage of ~ 0.25 ML, have been experimentally observed. The low-coverage regime is characterized by a single K adsorption site, little or no charge transfer to the substrate, an enhanced asymmetry of the Si surface dimers, and very weak K-K interactions. At high coverages, multisite K adsorption with a small amount of charge transfer to the Si substrate, more symmetric dimers and strong metallic character of the K overlayer are favored. The estimates of charge flow presented here should serve as a guide for evaluating theoretical methods of calculating adsorbate charge donation in this system.

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