

Potassium-induced charge redistribution on Si(111) surfaces studied by core-level photoemission spectroscopy

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High-resolution core-level photoemission spectra of the K/Si(111)(7×7) surface system are presented. The Si 2*p* results show that potassium adsorption induces a Si 2*p* core level to shift to *higher* binding energy, i.e., to the opposite direction than that expected from the Si-K electronegativity differences. This result is compared with that of the K/Si(111)($\sqrt{3}\times\sqrt{3}$)R30°-B system and is interpreted in terms of the K-induced charge redistribution between the Si-adatom-rest-atom pair.

Alkali-metal adsorption on metal and semiconductor surfaces has attracted much attention recently.^{1,2} By studying these prototypical adsorbate systems one hopes to gain better understanding of the general metal-metal and metal-semiconductor interfaces. Yet despite the apparent simplicity of these systems and the large amount of theoretical and experimental efforts devoted to them, many fundamental issues are still not well understood. Among them is the nature of the interaction between the alkali-metal atoms and the substrate surfaces. Experimentally, characteristically similar behaviors are exhibited by the alkali-metal-adsorbate systems, regardless whether the substrate is a metal or a semiconductor, such as the alkali-metal-induced work-function changes, thermal desorption, and the substrate as well as the overlayer core-level photoemission spectra.^{1,2} While the Newns-Anderson model³ based on the coverage-dependent occupation of the alkali-metal *s* level could explain most of the experimental results, it is inconsistent, among other things, with the core-level photoemission results,^{4,5} i.e., the substrate core levels generally do not show appreciable alkali-metal-induced shifts. The revision of the model by emphasizing the covalent aspect of the alkali-metal-metal and alkali-metal-semiconductor interaction was then introduced, where the charge transfer from the alkali metals to the substrate is assumed to be not very substantial.⁶⁻⁸ For this model of alkali-metal adsorption, particularly on semiconductor, e.g., Si, surfaces, the covalent interaction between the alkali-metal valence electrons and the substrate surface states then implies varying degrees of ionicity for the alkali-metal-substrate bond depending on the nature of the substrate electronic structure.⁶⁻⁹ Yet previous experimental studies, e.g., core-level photoemission, of the alkali-metal adsorption on the Si(111) (7×7), Si(111)(2×1), Si(100)(2×1), and other surfaces have not showed such

dependences.⁵

In this paper we investigate the dependence of the alkali-metal-Si interaction on the substrate surface states by comparing high-resolution core-level photoemission results of potassium adsorption on the Si(111) (7×7) and Si(111)($\sqrt{3}\times\sqrt{3}$)R30°-B surfaces. As has been pointed out recently,^{10,11} these two surfaces have basically the same electronic structure, except that their dangling-bond states are somewhat different. Thus they offer a unique opportunity for investigating the role played by the surface dangling-bond states in bonding with alkali-metal atoms. This is especially true since recently we have observed potassium-induced core-level shifts on the Si(111)($\sqrt{3}\times\sqrt{3}$)R30°-B surface,¹² while previous photoemission work⁵ did not find such charge transfer for the alkali-metal adsorption on the (7×7) surface. In fact, our high-resolution measurements of the Si 2*p* spectra to be presented here suggest that potassium adsorption eliminates a low BE Si 2*p* component of the clean Si(111) (7×7) surface, i.e., the K-induced core-level shift is to the opposite direction than what was expected from the alkali-metal-to-Si charge-transfer picture. This low BE Si 2*p* component of the clean surface was assigned to the rest atoms in the Si(111) (7×7) unit cell, and its low BE was due to charge transfer from the Si adatoms. Our result thus suggests that such adatom-to-rest-atom charge transfer is changed by potassium adsorption. We speculate that this is because the Si adatoms recover electrons from the rest atoms to form bonds with the alkali-metal atoms. This interpretation suggests that in the case of Si(111) 7×7 surface, the alkali-metal-Si bonding is more covalent than in the case of the boron-doped Si(111) surface, demonstrating the dominating role played by the Si dangling-bond state in determining the degree of ionicity of the alkali-metal-Si bonding.

The sample used in this experiment was a B-doped

Si(111) crystal. The (7×7) surface was produced by annealing to above 900°C to desorb the protective oxide layer. The sample cleanliness was checked by monitoring the C 1s and O 1s photoemission spectra as well as the line shape of the Si 2p spectra. Potassium was evaporated onto the Si(111) (7×7) surface using commercial SAES dispensers. The potassium coverage, relative to the room-temperature saturation coverage, was estimated from the evaporation time, K 2p photoemission spectra, and work-function measurements. The absolute saturation coverage is not exactly known. An estimate based on the K 2p photoemission spectra gave a coverage of approximately 0.3–0.4 monolayer, where a monolayer (ML) is defined as the number of atoms in an ideal Si(111) layer. Work-function changes, measured from the secondary-electron cutoff, showed the characteristic drop with increasing coverage to -3.1 eV at about 75% of the saturation coverage, and stayed essentially constant at higher coverages. Low-energy electron diffraction (LEED) showed that the (7×7) pattern persisted but the intensity has been changed with increasing coverage, in agreement with an earlier reflection high-energy electron diffraction (RHEED) observation of a (7×7) superstructure for the alkali-metal–Si(111) (7×7) system.¹³ The photoemission spectra were measured at the AT&T Bell Laboratories high-resolution soft x-ray beamline U4B located at the National Synchrotron Light Source,¹⁴ using a Vacuum Science Workshop HA150 electron-energy analyzer equipped with multichannel detectors. The overall energy resolution of the Si 2p spectra was better than 100 meV. The potassium evaporation and photoemission measurements were done at both 100 K and room temperature. No appreciable differences were observed in the x-ray photoemission spectroscopy (XPS) spectra for samples prepared at these two temperatures.

The Si 2p spectra at several K coverages are shown in Fig. 1. The spectrum for the clean surface is similar to those reported previously.¹⁵ The spectrum is composed of several spin-orbit doublets due to different Si sites in the large Si(111) (7×7) unit cell. Most of the doublets are not resolved in Fig. 1 from that of the bulk Si due to the small differences in their Si 2p BE's. The partially resolved component at the kinetic energy of about 32.5 eV in Fig. 1 is the most interesting one. It was assigned to the so-called rest atoms in the *second* layer of the (7×7) unit cell.¹⁵ Detailed electronic-structure calculations¹⁶ suggested that there is some degree of charge transfer from the dangling-bond state of the Si adatoms to the dangling-bond state of the rest atoms, essentially filling up these states. This picture of charge distribution on the clean Si(111) (7×7) surface has been further confirmed by spatially resolved scanning tunneling microscopy (STM) studies^{17,18} which show an occupied state located on the rest atoms with binding energy of -0.8 eV, and a dangling-bond state located on the Si adatoms, near the Fermi level. This charge transfer causes the rest-atom Si 2p core level to shift to lower binding energy; this is the basis for assigning the low BE component to the rest atoms.¹⁵

Upon K adsorption, no significant changes are observed in the Si 2p spectra except in the region of the low

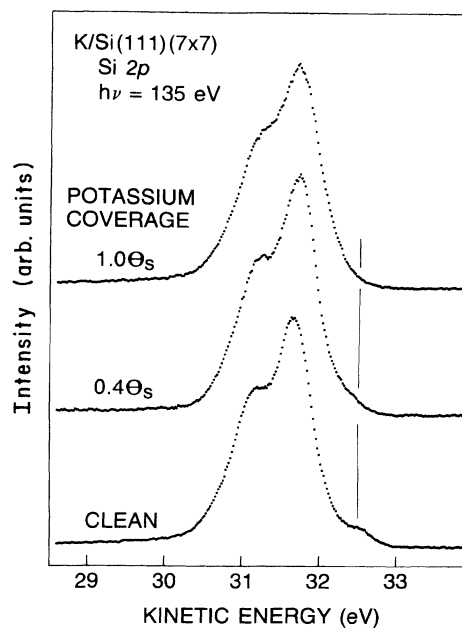


FIG. 1. High-resolution Si 2p photoemission spectra at several coverages on the Si(111) (7×7) surface. All the spectra are measured at 100 K with overall instrumental energy resolution better than 100 meV.

BE component. We observe here that the intensity of the low BE peak decreases roughly proportionally to the increased potassium coverage, indicating that this component has been shifted towards higher BE and merged into the bulk and other surface Si components. This potassium-induced change was not observed in previous photoemission studies of this system due to their inadequate energy resolution.⁵ We note that the lack of Si 2p core-level shift towards lower BE suggests the absence of substantial charge transfer from the potassium to the Si substrate. In fact, the observed shift to high BE is in the opposite direction from what is expected from the electronegativity differences between the K and the Si atoms. The observed shift for the Si rest atoms is also interesting, since the rest atoms are located in the second layer of the Si surface, and thus are not expected to interact directly with the potassium atoms. Indeed, STM results¹⁹ show that the potassium atoms interact mostly with the topmost Si adatoms. Clearly the Si 2p spectra indicated a very complicated charge redistribution induced by the potassium adsorption.

The core-level BE shift can be due to several factors. The presence of the potassium atoms in the neighborhood of the rest atoms is expected to shift the Si 2p core level to *lower* BE through both initial-state (charge transfer) and final-state effects (screening). Therefore, this is not the reason for the observed shift to *higher* BE. On the other hand, a change in the coordination of the rest atoms is unlikely, because STM and LEED-RHEED studies indicate that the potassium adsorption does not disrupt the (7×7) surface structure. Since, as noted above, the low Si 2p BE of the Si rest atoms is due to the excess charge resulted from adatom–rest-atom charge transfer, the shifting to *higher* Be is then most likely due

to the K-induced charge redistribution around the rest atoms, i.e., the charge density near the rest atoms is reduced as a result of the potassium adsorption. In the absence of direction contact between potassium and the rest atoms, and without major surface reconstruction, we speculate that the excess charge on the rest atom is transferred back to the adatoms. This suggested that the reverse charge transfer process is presumably necessary because of the bonding-charge requirement between the adatoms and the potassium adsorbates. Energetically, the reverse charge transfer is favorable: the transfer of an electron from the adatom to the rest atom results in a gain of energy of about 0.6 eV in the case of the clean Si(111) (7×7) surface, i.e., the energy separation between the dangling bond states of the adatom and rest atoms,¹⁶⁻¹⁸ while the bonding energy of K with Si surfaces is more than 2 eV.⁸

The rest-atom–adatom reverse charge transfer has also been suggested before for the $\text{NH}_3/\text{Si}(111)$ (7×7) system,¹⁸ using evidence from STM studies. However, in the case of ammonia adsorption, it was postulated that the reason for the charge redistribution is due to the bonding of atomic hydrogen with the rest atoms, sending the excess electrons back to the Si adatoms, which then form bonds with NH_2 species. We do not expect that there is direct interaction between the potassium atoms and the Si rest atoms. We also emphasize that the Si-H and Si- NH_2 interactions are expected to be covalent. Thus the observation of the reverse charge transfer on both the NH_3 and $\text{K}/\text{Si}(111)$ (7×7) systems indicates that the Si-K interaction is similar in nature to that of Si-H and Si- NH_2 , i.e., covalent. In any case, considering the electronegativity differences, the similarity observed in these two cases is indeed very surprising. Clearly, STM investigation can further confirm this picture of charge redistribution.

Next we compare the Si 2*p* photoemission results with those of the $\text{K}/\text{Si}(111)$ ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B system. Figure 2 displays the Si 2*p* core-level spectra of the $\text{K}/\text{Si}(111)$ ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B system. (Detailed discussion of these spectra as well as that of B 1*s* level has been presented elsewhere.)¹² In contrast to the case of the Si(111) (7×7) surface shown in Fig. 1, the K adsorption is shown to induce shifts of Si 2*p* core levels to lower BE. The B 1*s* photoemission spectra also show a K-induced component with 1.1-eV lower binding energy. These results provided strong evidence for charge transfer from potassium to the substrate,¹² which is consistent with the electronegativity differences between Si and K. The very different behavior of potassium adsorption on the two surfaces is especially interesting, since the two surface systems have very similar electronic structures—both are Si(111) surfaces with adatom on the surface. The (3×3) surface is a derivative of the (7×7) surface, modified by boron doping in the subsurface region.¹⁰⁻¹¹ As discussed in the introduction, the covalent aspect of the alkali-metal–Si interaction is expected to be dominated by the dangling bonds on the surfaces. It is precisely these dangling bonds that are modified by the subsurface doping of the boron atoms;¹¹ this forms the basis for our explanation of the opposite K-induced Si 2*p* core-levels shifts on these

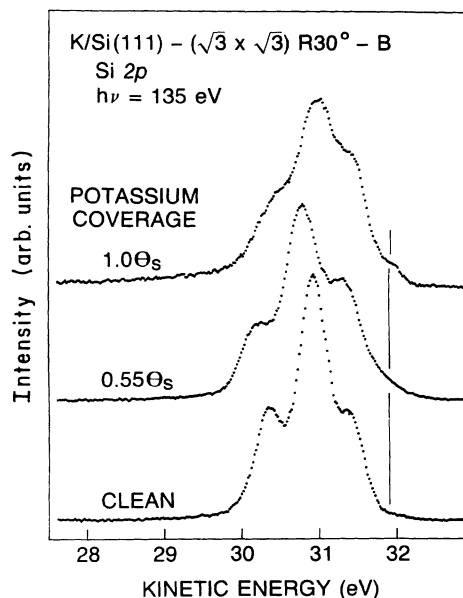


FIG. 2. High-resolution Si 2*p* photoemission spectra of the $\text{K}/\text{Si}(111)$ ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B surface. Experimental conditions are the same as in Fig. 1.

two surfaces.

On the (7×7) surface, both the adatoms and the rest atoms are threefold coordinated; each has one dangling bond per atom. The interaction between the adatom and the rest atom filled the rest-atom dangling-bond state with some electrons from that of the adatoms. Since the rest atoms and the adatoms are far apart, this interaction is weak. The energy separation of the dangling-bond states of the adatom and rest atom is only about 0.6–0.8 eV, and both states are in the band gap.¹⁶⁻¹⁸ In the case of the Si(111) ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B surface, however, the boron atom is directly below the Si adatoms and is more electronegative. Therefore, Si adatom–boron interaction is very strong. The separation of the bonding–antibonding band is more than 2.5 eV, and the filled bonding state is deep in the valence band, while the empty antibonding state (which is mostly of dangling-bond nature located on the Si adatoms) is the only state in the band gap.¹¹ Therefore, we speculate that, upon K adsorption, the rehybridization process breaks the adatom–rest-atom “bond” in the Si(111) (7×7) surface, and the charge is redistributed to the alkali-metal–adatom interface. On the Si(111) ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B surface, the adatom–boron bond is also preserved because of the energetics. It is unfavorable to break the strong B–adatom bond; the alkali metal interacts mostly with the empty antibonding adatom–boron state in the Si(111) ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B surface, resulting in effective charge transfer from the k atoms to the substrate,¹² i.e., a much more ionic bond.

In summary, we have observed K-induced Si 2*p* core-level shifts on the Si(111) (7×7) and on the Si(111) ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ -B surfaces that are in opposite directions. The results on the (7×7) surface suggests a charge redistribution between the Si adatom–rest-atom pairs are in-

duced by the potassium adsorption. We also conclude that, in the case of Si(111) ($\sqrt{3}\times\sqrt{3}$) $R30^\circ$ - B surface, charge is transferred from potassium to the substrate through the interaction of the K 4s orbital with an empty surface state, while for the Si(111) (7 \times 7) surface the alkali-metal-Si bonds are less ionic. This work demonstrates that the nature of the bonding between alkali-

metal atoms and semiconductor surfaces depends critically on the occupation and the energy positions of the dangling-bond states.

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