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Published in:
Journal of Vacuum Science & Technology A

DOI:
[10.1116/1.578011](https://doi.org/10.1116/1.578011)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1992

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Ma, Y., Rudolf, P., Chen, C. T., & Sette, F. (1992). Potassium adsorption on the Si(100)(2×1) surface studied by Si and K core level photoemission and photoabsorption spectroscopy. *Journal of Vacuum Science & Technology A*, 10(4), 1965-1969. <https://doi.org/10.1116/1.578011>

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Potassium adsorption on the Si(100)(2×1) surface studied by Si and K core level photoemission and photoabsorption spectroscopy

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(Received 23 September 1991; accepted 9 October 1991)

The questions of K–Si bonding and the K adsorption site of the K/Si(100)(2×1) surface system are studied by Si and K 2*p* core level photoabsorption and photoemission spectroscopy as a function of K coverage and incident x-ray polarization. An unoccupied K 4*s* derived surface state is found in the K *L*-edge spectra that is coverage as well as polarization dependent. It is also found that the π^* state of the surface Si dimer is eliminated by the potassium adsorption, indicating that there is some degree of charge transfer from K to the substrate. The K–Si bond is thus characterized as of mixed covalent/ionic type. The polarization dependence suggests that the Si–K bond is inclined towards the surface plane.

Alkali metal adsorption on the Si(100)(2×1) surface has attracted great attention recently.^{1–19} Much of the interest is generated by the prospect of forming alkali atom chains^{2,3} on the dimerized Si(100)(2×1) surface and related issues such as metal-insulator transitions, metallization of the surface,⁴ and the Peierls distortion of one-dimensional structures.⁹ Current theoretical and experimental efforts are concentrated on two basic and interrelated questions: (1) the alkali adsorption sites and (2) the nature of the interaction between the alkali atoms and the Si surface. The most widely accepted alkali absorption site is the one proposed by Levine² which is favored by total energy calculations^{4,10} and a recent low-energy electron diffraction (LEED) study.¹⁴ On the other hand, Ling *et al.*, have concluded from cluster calculations that the most stable site is the cave site,¹⁴ while a photoelectron diffraction study suggested a double layer model with two alkali sites.⁷ Recent scanning tunneling microscopy (STM) investigations¹³ found that none of the previously discussed sites appears to explain the STM images. For example, it is found that the alkali chain direction formed at low coverage are along the direction perpendicular to the that of the dimer chain direction, contrary to the previous suggestions.

As for the nature of the alkali-Si bond, total energy calculations of Ciraci and Batra indicate⁴ that the bond is ionic because the outer valence electron of the alkali is found to be transferred to the dangling bond state of the surface Si dimer. A novel consequence of the result is that the charge transfer metallizes the substrate while the potassium overlayer remains insulating. Other calculations, however, have concluded that the Si–K bond is of mixed covalent/ionic type⁹ or even totally covalent with negligible alkali-to-Si charge transfer.^{6,10} Experimentally, the lack of appreciable alkali induced Si 2*p* x-ray photoemission (XPS) shifts has been interpreted to support the covalent bonding model.^{15,16,18} However conclusions derived solely from XPS core level measurements are debatable since other effects, e.g., the Madelung potential, also contribute to the core level binding

energy. Indeed, a recent Si core level XPS study concludes that the K–Si bond is partially ionic.¹⁹ Angle resolved photoemission¹¹ and inverse photoemission studies,⁵ while providing information on the alkali induced surface state, could not show where the charge is located and did not answer the question of the charge transfer.

Clearly much work needs to be done to fully understand this model system for metal/semiconductor interface. In this paper we address the questions of potassium bonding and adsorption site on the Si(100)(2×1) surface by analyzing the Si and K 2*p* core level spectra, especially the *L*-edge soft x-ray absorption (XAS) near edge spectra for both the Si and the K *L* edges. The novel aspect of the x-ray absorption technique is that, due to the dipole selection rule, these *L*-edge spectra provide information about the unoccupied, symmetry resolved, and local density of surface states, specifically, the K 4*s* and the Si dangling bond states. Because these states directly participate in the bonding between the potassium and the surface, the information we obtained is most relevant to the question of charge transfer. In addition, the polarization dependence of the x-ray absorption spectra has been extensively used to study the bond orientations of adsorbate systems.²⁰ We will use this technique here to get information on the K adsorption site. From the Si *L*-edge spectra as a function of K coverage, we observed that the K adsorption eliminates the Si dangling bond surface states of the (2×1) surface. Most importantly, the K 4*s* derived state is shown to be not only coverage but also polarization dependent, which implies a directional Si–K bond and that the bond is inclined in the surface plane. These results suggest a covalent Si–K bond with some degree of ionicity. The in-plane direction of the Si–K bond favors the cave site for K adsorption,⁹ but not the Levine site.² Implications of these results on the structure of the surface are discussed.

Boron doped Si(100) samples were used in this study. The (2×1) surface was prepared by heating the Si sample to above 900 °C to desorb the protective oxide layer. The quality of the surface was inspected by low-energy electron dif-

fraction (LEED) which showed the usual two-domain (2×1) pattern and by the Si 2*p* x-ray photoemission spectra (XPS).²¹ The potassium was evaporated onto the surface using commercial getter sources. The substrate temperature during evaporation and the measurements were held at 100 K. The sample work function was monitored by the secondary electron cutoff of the photoelectron spectra. The measured work function change agrees with previous studies,^{11,12} amounting to about -3.0 eV at saturation and a work function minimum of about -3.1 eV at about 60% of the saturation coverage. Since there is some disagreement in the literature about the absolute saturation coverage of this system,^{11,12,17} we will only use the work function change as the measure of coverage in this paper.

The experiment was performed at the AT&T Bell Labs Dragon beamline at the National Synchrotron Light Source.²² The x-ray absorption measurements were carried out with electron yield methods: Auger electron yield detection (Kinetic energy: 87 eV for Si *L*-edge spectra and 245 eV for K *L*-edge spectra) for surface sensitive spectra and partial electron yield (electron kinetic energy of 10 eV) for bulk sensitive spectra. Together with the absorption measurements, we monitored the XPS spectra of the K 2*p* and Si 2*p* core levels. The overall energy resolution of the XPS measurements was better than 0.3 eV, while for the XAS measurements the photon energy resolution was better than 0.15 eV. The XPS results agree with previous studies.¹² The K 2*p* core level shifts to lower binding energy with increasing K coverage. The total shift, from that of lowest coverage, amounts to 0.5 eV at saturation coverage. The Si 2*p* XPS spectra showed minor change upon potassium adsorption at the region of the surface peaks.^{15,16,19}

In Fig. 1, we plotted the Si *L*-edge spectra at several K coverages. For comparison, a bulk sensitive Si *L*-edge spectrum (curve A) is shown at the bottom of Fig. 1(a). The Si *L*₃ and *L*₂ thresholds are separated by 0.6 eV. We note that the surface sensitive spectrum (curve B) for the clean surface is substantially different from curve A due to the contribution of the surface states. In particular, the two peaks at photon energy of 98.5 and 99.1 eV are clearly of surface origin. Since their separation is the 2*p*_{1/2} - 2*p*_{3/2} spin-orbit splitting these two peaks were assigned to the transitions to the dangling bond states of the Si dimer (the antibonding π^* state) at the *L*₃ and *L*₂ edges, respectively.²¹ According to model calculations of the surface electronic structure, this state should be at the middle of the band gap.²³ Note that, due to the dipole selection rule, we are probing only the *s* part of this *sp*³ hybridized state, which explains the weak intensity of the two peaks. In addition, no appreciable polarization dependence has been observed for these two peaks.

As potassium is deposited on the surface, the peak intensity of this dangling bond state gradually decreases, becoming undetectable above about half the saturation coverage. This indicates that these empty dangling bond state states have been eliminated by the potassium adsorption. At the same time, as shown more clearly in Fig. 1(b), the shape of the *L*-edge threshold changes with increasing coverage, indicating the modification of the surface state near the conduction-band minimum (CBM). The increase in intensity in that

FIG. 1. (a) Si *L*-edge spectra for clean Si(100)(2×1) measured with bulk sensitive partial (curve A) and surface sensitive (curve B) electron yield methods; potassium covered surfaces with work function changes of $\Delta\phi = -2.1$ eV (curve C) and $\Delta\phi = -3.0$ eV (curve D). (b) Overlap plot of curves B (solid) and D (dashed) in (a).

region suggests that new states are created near the CBM. From the energy separation, we believed that this state is due to hybridization with the K 3*d* or K 4*p* states.

These results are in good agreement with the band structure calculations of the K/Si(100)2×1 system,^{4,10} i.e., upon K adsorption, the energies of the π and π^* states are lowered and these states become occupied by the electron from the K. The filling of the dangling bond state has been used as an indication for the charge transfer from potassium to the Si substrate.⁴ However, it is also argued that the downward shift of the π states may be due to the hybridization between the Si and K orbitals.¹⁰ Since the XAS technique has the advantage of being sensitive to the local density of states, we conclude that the unoccupied state of localized on the Si atoms are being filled after K deposition. This conclusion can be argued to indicate that there is some degree of charge transfer from the K atoms to the Si dimer atoms on the surface.

FIG. 2. K L -edge spectra as a function of K coverage: samples with the work function change of $\Delta\phi = -1.2$ eV (curve A); $\Delta\phi = -2.1$ eV (curve B); $\Delta\phi = -2.7$ eV (curve C); $\Delta\phi = -3.1$ eV (curve D); $\Delta\phi = -3.0$ eV (curve E), which is approximately the saturation coverage, and multilayer (curve F). The Fermi level position in each spectrum, estimated from XPS K $2p$ core level shifts as discussed in the text, are indicated by the vertical lines. The spectra were taken at an incident angle of 10° , i.e., the polarization vector is almost perpendicular to the surface normal direction.

The K L_3 edge absorption spectra as a function of K coverage are shown in Fig. 2. Due to the dipole selection rule, the allowed transitions are from K $2p$ to final states with s and d symmetries. Therefore the main feature at about 297 eV is assigned to the transition to the $3d$ and the smaller feature at around 295 eV is to the K $4s$ derived states. With increasing potassium coverage, it is seen that both peaks, especially the K $4s$ state, become increasingly broad. This is not unexpected and we ascribe this to the K–K bond formation: as the potassium atoms get close to each other with increasing coverage, the K–K interaction becomes dominating; consequently both the s and d states become bands with increasingly broader bandwidth.

With increasing coverage, we note that the $3d$ state remains at same position while the $4s$ derived state shifts to lower photon energy. Since the XPS binding energy of the K $2p$ level decreases with potassium coverage, it may be argued that the downward shift of the K $4s$ state is due to the shift of the $2p$ level. However, this should also cause the $3d$ states to shift downward which is not observed. We thus conclude that the main reason for the observed shift of K $4s$ peak is the coverage dependent K–Si and K–K interactions.

The positions of the Fermi level in these spectra are of

special interest because they are related to the question of the metallicity of the surface. To find the Fermi levels we start with the spectrum (curve F in Fig. 2) for the potassium multilayer. In solid potassium the Fermi level bisects the $4s$ conduction band; therefore the Fermi level in these spectra should be at the onset of the $4s$ band continuum, i.e., at 294.5 eV as indicated in Fig. 2. To estimate the Fermi level positions in other spectra, we use the measured energy shifts of K $2p$ XPS peak relative to that of the bulk potassium. The Fermi levels obtained this way are shown in Fig. 2. It is seen that the $4s$ state is about 0.5 eV above the Fermi level at low coverages, and gradually shifts toward the Fermi level with increasing coverage. However, we caution here that the estimation is true only in the single particle picture, neglecting the core hole screening effects that are clearly different for the cases of solid and submonolayer potassium. Since in the final state of the XAS the photoelectron is the screening charge while in the XPS spectra the screening is done by electrons from neighboring potassium or substrate Si atoms, the screening is more efficient in the XAS. This may introduce an error of a few tenths of an eV in our determination of the Fermi levels.

Although we could not establish the precise positions of the Fermi level in these spectra, it is established at near or below the onset of the absorption threshold from the above arguments. The peak position of the $4s$ derived state, which is clearly a peak in the low potassium coverage spectra, is about 0.5 eV from the approximate position of the Fermi level, indicating that the K $4s$ derived state is above the Fermi level, and consequently less than half occupied. This is consistent with the results of the Si L -edge spectra which

FIG. 3. K L -edge spectra measured at incident angles of 80° (curve A), 50° (curve B), and 10° (curve C) for a K/Si(100) sample with work function change of $\Delta\phi = -2.1$ eV. The spectra were normalized by the $3d$ peak intensities at 297 eV which is expected to show little angular dependence.

suggests that there is some charge transfer from the K 4s state to the dangling bond states of the Si substrate. At higher coverages, the K 4s peak is seen to broaden and shift towards the Fermi level, in agreement with our expectation that the overlayer become more metallic due to the band formation of the K 4s states.

In Fig. 3, we show the K *L*-edge spectra as a function of the x-ray incidence angle, i.e., the angle between the surface normal and the polarization direction of the incident photon was varied in these spectra. As is clear from the figure, where we have normalized the spectra by the intensity of the 3*d* state,²⁴ the 4s state is strongly dependent on the polarization direction of the incident photon. The intensity of the 4s peak is the largest for normal incidence, i.e., when the polarization vector of the x ray is parallel to the surface plane. Thus the K 4s state is substantially modified upon adsorption on the surface to have a large nonspherical component. Since the polarization dependence is observed starting at low K coverages, the nonspherical contribution cannot be due to the interaction between the neighboring potassium atoms. An explanation is that it is due to the in-plane K 3*d* state which, due to hybridization with the substrate orbitals, is pulled down about 2 eV compared with other *d* orbitals to have the same energy as that of the 4s state. Since a shift of 2 eV for the in-plane 3*d* orbitals is rather large, we believe instead that the major contribution for the nonspherical components comes from the transition from K 2*p* to the substrate Si orbitals that are hybridizing with the K 4s orbital, e.g., the dangling bond state. The wave functions of these Si orbitals are fairly extended so that they will have finite amplitudes at the core of the potassium atoms for this transition to occur. This kind of explanation is routinely used to interpret the polarization dependence of the near edge x-ray absorption spectra (NEXAFS) of adsorbate systems.²⁰

This conclusion provides the strongest experimental proof for the hybridization between the Si dangling bond state and those of the potassium. It also suggests that the Si–K bond is highly directional. The directional nature of the Si–K bond characterizes it as covalent (at least at low K coverages where the polarization dependence is clearly observed). However, as suggested earlier, the elimination of the Si π^* state by the potassium adsorption and the fact that the K 4s state is located about 0.5 eV above the Fermi level, we believe that there is some degree of charge transfer from K to the substrate. The combination of the two facts then characterizes the bond as of mixed covalent/ionic type.⁹

The observed polarization dependence has also important implications on the allowed K sites on this surface because it suggests that the Si–K bond direction is inclined towards the surface.²⁵ There are several possible potassium adsorption sites that have been considered. Here we only consider two representative examples. The most widely discussed site is called the pedestal site² and is shown schematically in Fig. 4(a). More recently Ling *et al.* suggested that the cave site [also shown in Fig. 4(a)] to be the most stable.⁹ Our results agree with this type of sites where K atoms occupy sites between the Si dimer chain since the potassium atoms can form bonds with Si which is inclined in the surface plane. We also note that in the cave site, the potassium atoms occupy

FIG. 4. (a) The pedestal and cave sites for K adsorption on the Si(100)(2×1) surface. In the pedestal site, the Si–K bonds are much more vertical than that in the cave site. (b) Proposed low coverage structure model for the K/Si(100)(2×1) surface showing K chains perpendicular to the Si dimer chain direction.

positions in the direction of the Si dangling bond, which facilitates the hybridization between the orbitals of the K and the Si atoms. On the other hand potassium atoms in the pedestal site form nearly vertical bonds with Si atoms, which would show opposite angular dependence than that exhibited in Fig. 3.

Putting the potassium atoms in the cave site also offers an explanation for the STM observation that the potassium chains are perpendicular to the Si dimer chains at low K coverages.¹³ Previous discussions all suggest alkali chains to be parallel to the Si dimer chains. A model is shown in Fig. 4(b) where the K chains are placed perpendicular to the Si dimer chain. Since STM only probes the charge density of the surface, the model depicted in Fig. 4(b) will produce alkali chain images perpendicular to the Si dimer chains. In addition, the arrangement shown in Fig. 4(b) is also energetically more favorable than the parallel chains, because the in-plane components of K–Si dipoles in a K chain are parallel, minimizing the electrostatic energy.

In summary, we studied the unoccupied, in particular the K 4s derived states, surface states of the K/Si(100)(2×1) surface by polarization dependent soft x-ray absorption spectroscopy. The observed directional bonding between the Si substrate and the potassium atoms, the position of the K 4s state, and the elimination of the Si dangling bond states together characterized the bond as covalent with some degree of ionicity. It is found that the bond is inclined towards the plane of the surface, favoring the type of K sites like the cave site over the pedestal site.

Acknowledgments: We acknowledge useful discussions with S. Kevan and J. Rowe. Assistance of L. H. Tjeng in the experiments is appreciated. The National Synchrotron Light Source is supported by the U. S. DOE under Contract No. DE-AC02-76CH00016.

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²⁴ Since the K 3d states are far higher in energy than that of the K 4s state, and since there are five 3d states, we believe that the hybridization with the substrate states should have much smaller effect on the anisotropy of the 3d peak than that of the 4s peak. Thus our normalization procedure is reasonable.

²⁵ Work is in progress to determine the precise angle of the Si-K bond relative to the surface plane.