

Adsorption of potassium on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface: Observation of an insulating surface at submonolayer coverage

T. M. Grehk

Materials Science, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

L. S. O. Johansson

Department of Synchrotron Radiation Research, Institute of Physics, University of Lund, Sölvegatan 14, S-223 62 Lund, Sweden

U. O. Karlsson and A. S. Flodström

Materials Science, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

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The $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface with submonolayer coverages of potassium has been studied with angle-resolved photoelectron spectroscopy. Deposition of potassium leads to the formation of a state 0.7 eV below the Fermi level. The energy position of this state showed only a minor dependence on the actual potassium coverage and the state displayed a small dispersion of 0.1 eV when probed along the $\bar{\Gamma}\text{-}\bar{M}'$ direction in the $\sqrt{3}\times\sqrt{3}R\ 30^\circ$ -surface Brillouin zone. These results support the idea that a mainly covalent bonding exists between the potassium atoms and the Si surface.

Interface systems of alkali metals on silicon surfaces have in recent years been studied extensively as model systems for metal-semiconductor interfaces.¹ Despite the simple electronic structure of the alkali metals, with one s electron in their outer electronic shell, there still exists some controversy about the binding mechanisms associated with the formation of the silicon-alkali-metal interfaces and the absolute coverage at saturation.²⁻¹² Two main, differing pictures of the alkali-metal bond have been proposed.² In the ionic-bond picture,³⁻⁶ there is a complete (or nearly complete) charge transfer of the alkali-metal valence electron to the semiconductor surface, causing a strong dipole-induced electrical field at the surface and, consequently, a strong reduction in the work function. The metallization of the surface occurs through the partial filling of the surface-state bands and hence the surface is metallic over a wide coverage range.

In the polarized-covalent-bond picture,⁷⁻⁹ a small, fractional charge is transferred from the adsorbate atom to the substrate surface and changes in the work function are caused by a weak, polarized covalent bond between the alkali metal and the semiconductor substrate. The metallization occurs when the valence-electron orbital of the metal atoms overlaps. Therefore, in contrast to the ionic-bond picture, a critical adsorbate concentration is needed for metallization. In some studies^{10,11} a mixed bonding model has been favored with almost ionic bindings at low coverage, whereas an increase in the adsorbate coverage led to a higher degree of covalence.

To get a better understanding of the electronic structure associated with alkali-metal silicon bonding, the adsorption system, potassium on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ has been studied. This surface has the advantage of possessing only one type of Si adatom and it is well established that the B atom on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface occupies the B-S₅ position directly below the Si adatom.¹²⁻¹⁵ The Si adatom in this configuration forms

three bonds to its nearest, first-layer Si neighbors and donates one electron to the boron atom directly below it. Experimentally, an empty dangling-bond state, two filled back bond states, and one filled surface state, connected with boron bonded beneath the surface top layer, have been observed on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface.^{16,17}

In a recent high-resolution core-level x-ray photoemission and photoabsorption study (XPS and XAS) of K adsorption on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surfaces, it was argued that the adsorbate substrate bonding is determined primarily by the hybridization of the K $4s$ orbitals with an empty surface state.¹⁸ Due to the existence of an empty surface state on the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface, a larger amount of charge is transferred from the potassium atoms to the surface than would be the case for a surface with half-filled surface state. It was further proposed¹⁸ that one potassium atom interacts with each $\sqrt{3}\times\sqrt{3}$ surface cell and that the resulting band would be half-filled, i.e., a metallic surface is formed.

In this paper, data from an angle-resolved photoemission spectroscopy (ARPES) study of the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface, with different amount of deposited potassium, is presented. The K-saturated surface has also been investigated along the $\bar{\Gamma}\text{-}\bar{M}'$ direction, in the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone (SBZ). It was found that the filled surface bands of the $\text{Si}(111)\sqrt{3}\times\sqrt{3}R\ 30^\circ\text{:B}$ surface were unaffected by the K adsorption. Instead, a new state was observed developing 0.7 eV below the Fermi level. Surprisingly, no density of states was observed in the vicinity of the Fermi level. Only after exposure well beyond the saturation of the work-function change could the development of a metallic Fermi edge be seen.

The ARPES spectra and the K $3p$ data were collected simultaneously using planar polarized synchrotron radiation of 21 eV and second-order light of 42 eV energy, respectively, at beamline 41 at the MAX-LAB synchro-

tron light source, Lund, Sweden. Emitted electrons were collected with an angle acceptance of $\pm 1^\circ$, using a 180° hemispherical analyzer. A total energy resolution of 0.18 eV was used in experiment, as measured from the Fermi-level onset of a tantalum foil in electrical contact with the sample. The angle of incidence of the light was 45° and the electric-field vector was always parallel to the probed crystal direction. The base pressure in the chamber was $\approx 1 \times 10^{-10}$ Torr.

Prior to insertion into the spectrometer, the samples were implanted with B ions of 90 keV energy to a coverage of $5 \times 10^{15} \text{ cm}^{-2}$ using a commercial process. Outgassing of the sample and preparation of the $\text{Si}(111)\sqrt{3} \times \sqrt{3}R30^\circ\text{:B}$ surface were performed *in situ* by resistive heating to 600°C and 1050°C , respectively.

Potassium was evaporated from thoroughly outgassed dispenser ovens (SAES Getters S.p.A.). The relative coverage of K on the surface was estimated by the integrated intensity of the K $3p$ level and also by the change in work function ($\Delta\phi$), monitored by the change in the low-energy electron cutoff. Saturation of alkali-metal atoms on the surface is here defined as the coverage where the work function has its lowest value.

Azimuthal alignment and identification of surface reconstructions were performed by low-energy electron diffraction (LEED). In order to avoid surface contamination, the investigated K-deposited surfaces were never older than 20 min.

In Fig. 1 the change in work function is plotted as a function of deposition time. Initially, the work function decreases linearly with deposition time. After 1 min of deposition, the curve starts to level out, and a clear break in the curve is seen at 1.5 min. Further deposition, beyond 5 min and $\Delta\phi = -2.7$ eV, gave no further change of the work function. Saturation was also observed in the

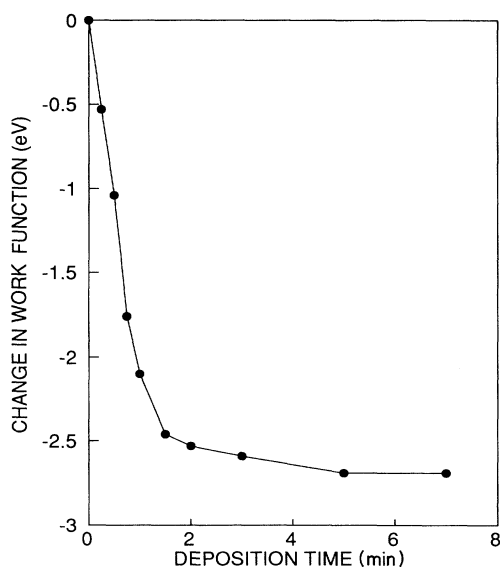


FIG. 1. The change in work function for the $\text{Si}(111)\sqrt{3} \times \sqrt{3}R30^\circ\text{:B-K}$ surface as a function of deposit time, derived from the secondary electron cutoff.

integrated intensity of the K $3p$ core level (not shown) after 5-min deposition time. The relation between work-function changes and deposition time was for low coverage qualitatively similar to earlier alkali metals on semiconductor-surface adsorption studies.^{19–22} After passing the saturation coverage, no increase in the work function was observed in contrast to results from some earlier alkali adsorption studies on Si surfaces.^{19,20,22} It is noticeable that the LEED pattern remained the same, a sharp $\sqrt{3} \times \sqrt{3}R30^\circ$ for all potassium coverages.

Valence-band spectra, collected at an emission angle of -6° relative to the surface normal, for different potassium coverage, are plotted in Fig. 2. Initially, the clean surface shows no density of states at the Fermi level. Low doses of potassium led to the formation of a new state, denoted *S*, 0.7 eV below the Fermi level. This state reached a maximum in intensity after 1.5 min of K-deposition time which corresponds to the break point in the work-function curve (see Fig. 1). Further potassium deposition led to a somewhat less pronounced *S* state. It can also be seen in Fig. 2 that the bulk structures at high coverage became less distinct. This is mainly an effect of the decrease in the work function, giving an increase in the number of scattered secondary electrons at higher energies. After 7 min of K deposition, a Fermi edge is de-

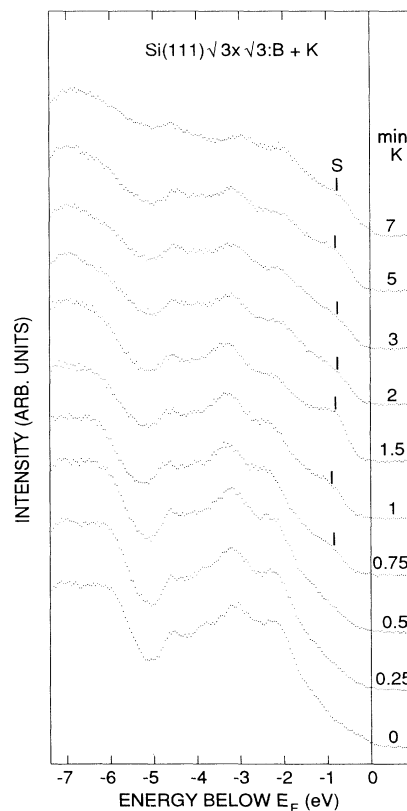


FIG. 2. Energy distribution curves from the $\text{Si}(111)\sqrt{3} \times \sqrt{3}R30^\circ\text{:B-K}$ surface for different K deposit times. Measured at an emission angle of -6° and with an incident photon energy of 21 eV.

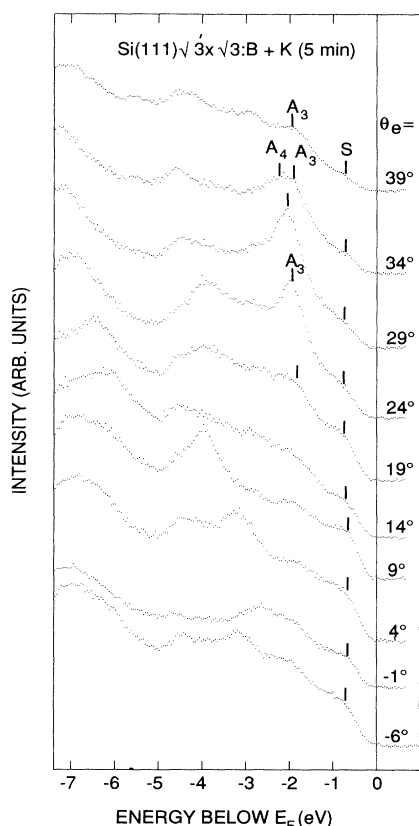


FIG. 3. Energy distribution curves measured along the $\bar{\Gamma}$ - \bar{M}' direction in the $\sqrt{3} \times \sqrt{3} R 30^\circ$ SBZ after 5 min of K deposition.

veloping in the spectra. At lower coverage, no significant density of states was observed at E_F .

Figure 3 shows the valence-band spectra, recorded after 5 min of potassium deposition, along the $\bar{\Gamma}$ - \bar{M}' direction in the $\sqrt{3} \times \sqrt{3} R 30^\circ$ SBZ. The S state is positioned mainly 0.7 eV below the Fermi level and shows a very small dispersion of ~ 0.1 eV. The nondispersive behavior of the S state indicates that it is a localized state, similar to the S_1 and S_2 surface states on the $\text{Si}(111)7 \times 7$ surface.²³ In the spectra of Fig. 3, for polar angles $\geq 19^\circ$, the surface states A_3 and A_4 , earlier identified on the clean $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface,¹⁷ appear. By comparing to ARPES data from the clean $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface,¹⁷ it can be concluded that the A_3 and A_4 states are mainly unaffected by the presence of potassium on the surface.

It is possible to rule out a binding mechanism involving purely electrostatic interaction between the potassium atom and the Si surface. In such a picture, it is expected that the K $4s$ electrons occupy the empty surface-state band of the $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface. This would result in a Fermi-level crossing for a wide coverage range and an energy position of the band that should be depen-

dent on the coverage. However, it is clear, from the spectra in Figs. 2 and 3, that within the experimental sensitivity no density of states is observed at the Fermi level for the K-unsaturated surface. Instead, a new state is developing 0.7 eV below the Fermi level, indicating a large degree of covalence in the binding mechanism.

The A_3 state earlier identified as the adatom backbond state on the clean $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface was not affected by the K adsorption. A similar observation was made for the $\text{Si}(111)7 \times 7$:Cs surface where Cs deposition did not alter the relative energy position of the backbond state.²⁰ Instead, it was observed that the Cs mainly interacted with the dangling-bond bands S_1 and S_2 , known as the dangling bonds of the adatom and the rest atom, respectively, forming a new state S' . In contrast to the $\text{Si}(111)7 \times 7$ surface, the clean $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface has no occupied state near the Fermi level.

In Ref. 18 it is argued, based on the large K-induced core-level shifts in the Si $2p$ and B $1s$ levels of the $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B-K surface, that a large amount of charge is transferred from the K atom to the $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface. As a consequence, it was argued that the charge transfer is determined by the occupation of band-gap states at the clean surface. This would imply² a mainly ionic bond between the K atom and the substrate. The valence data presented here, where no occupied states are observed in the vicinity of the Fermi level, instead support a covalent picture, in which the p_z orbitals of Si adatoms hybridize with the K $4s$ levels. Since the occupied Si-B bands are mainly unaffected by the potassium adsorption, we conclude, in agreement with Ref. 18, that the empty band of the substrate is involved in the Si-K bond. We emphasize that the interaction is not just a charge transfer into the empty band (ionic picture), but consists of a covalent bond, giving rise to a new occupied state. We argue, consistent with the covalent binding model, that the lack of dispersion of the S state is a result of the localized nature, with little overlap of the orbitals parallel to the surface, of this bond.

In summary, adsorption of potassium on the $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface has been studied with LEED and ARPES. A new state labeled S was observed developing 0.7 eV below the Fermi level. The energy position of the S state shows only minor dependence on the actual K coverage. When the S state was probed at saturation coverage along the $\bar{\Gamma}$ - \bar{M}' direction in the $\sqrt{3} \times \sqrt{3} R 30^\circ$ SBZ, only a small dispersion of 0.1 eV was observed, indicating a localized state. The spectra from the $\text{Si}(111)\sqrt{3} \times \sqrt{3} R 30^\circ$:B surface with submonolayer coverage of potassium showed no intensity at the Fermi level. The deposited potassium did not alter the LEED pattern; instead the $\sqrt{3} \times \sqrt{3} R 30^\circ$ pattern stayed the same, independent of coverage.

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