

Development of the surface electronic structure of K and Cs overlayers on Si(111)7×7

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The interaction between the metallic Si(111)7×7 surface and evaporated alkali metals, K and Cs, has been studied by angle-integrated ultraviolet photoelectron spectroscopy and angle-resolved inverse photoemission. Changes observed in both the occupied and unoccupied surface electronic states show a transition from metallic to semiconducting surfaces taking place in both systems after submonolayer coverages. Both metals are found to interact preferentially with the silicon adatom dangling bonds, filling the empty state and lowering the energy of the filled one. At saturation of the work function both the K- and Cs-covered surfaces exhibit a 7×7 structure in low-energy electron diffraction and a narrow semiconducting gap. One K-induced and two Cs-induced empty surface states have developed at this stage. Further evaporation beyond the saturation coverage yields a metallic surface in the case of cesium, while the K-covered surface remains semiconducting.

I. INTRODUCTION

Studies of the electronic structure of alkali-metal overlayers on semiconductor surfaces have in the past focussed on the question of surface metallization and the role of the alkali-metal valence electrons.¹ The transition from semiconducting to metallic surface structure with increasing alkali-metal coverage has been proposed from calculations and experimentally observed in some cases, e.g., K/Si(100), although these results have recently been questioned.²

The possibility of studying the reverse transition from a metallic to a semiconducting surface exists, in principle, only in one system. It is well known that at room temperature the Si(111)7×7 surface exhibits a surface state which renders this surface metallic, i.e., it has a Fermi-level cutoff in ultraviolet photoelectron spectroscopy (UPS).³⁻⁵ This surface has been extensively studied with different techniques including scanning tunneling microscopy (STM). Hamers *et al.*⁶ have used the STM in the spectroscopic mode and thereby localized and identified the surface states of the Si(111)7×7 surface previously observed in direct³⁻⁵ and inverse photoemission.^{7,8} For the discussion to follow we note that Hamers *et al.*⁶ identified the surface state at the Fermi level and the lowest empty surface state as originating from the adatom dangling bonds in the dimer-adatom-stacking-fault (DAS) model of Takayanagi *et al.*⁹

We have applied the techniques of angle-integrated UPS and angle-resolved inverse photoemission to the problem of K and Cs adsorption on the annealed Si(111)7×7 surface. Our results show that both metals interact preferentially with the Si adatom dangling bonds, induce new empty states, and that the just saturated surfaces are semiconducting. Continued exposure to alkali metal has no effect in the case of K, while the Cs-covered surface reenters a metallic state.

II. EXPERIMENT

The experiments were performed in a two-chamber vacuum system.¹⁰ The preparation and subsequent characterization of the surfaces and the actual measurements were done in separate, interconnected chambers, respectively. Clean Si(111)7×7 surfaces were prepared by resistive heating of a silicon wafer (*p*-type doped, 0.03 Ω cm) up to ≈1100°C followed by annealing to obtain well-ordered surfaces, as checked by low-energy electron diffraction (LEED). The evaporations of potassium and cesium were done from resistively heated, well-outgassed dispenser ovens (SAES Getters/Italy) with the Si crystal held at room temperature. The base pressure in the entire system was below 5×10⁻¹¹ mbar and never rose above 1×10⁻¹⁰ mbar in the preparation chamber during evaporation. The calibration of the alkali-metal sources was performed by monitoring the change in the secondary-electron cutoff energy in UPS, which is related to the change in work function and has a characteristic dependence on coverage. UPS utilized an angle-integrating hemispherical electron-energy analyzer and a He resonance lamp. Angle-resolved inverse-photoemission spectra were recorded using an electron gun with a beam divergence of less than 3° and a Geiger-Müller-type detector working at a photon energy of $h\nu=9.5$ eV. The *k*-space resolution was better than 0.1 Å⁻¹, and the total-energy resolution was 0.35 eV. The latter was derived from the width of the Fermi-level onset for a tantalum foil which was periodically interchanged with the Si crystal. The position of the onset was used as reference energy $E_F=0$.

III. RESULTS AND DISCUSSION

A. Potassium on Si(111)7×7

The change in the secondary-electron cutoff energy in UPS as a function of K evaporation time is shown in Fig.

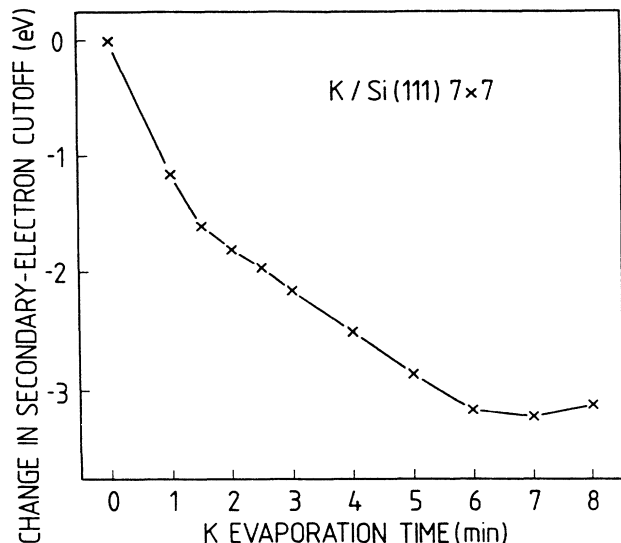


FIG. 1. The change in the secondary-electron cutoff energy in UPS from the K/Si(111)7 \times 7 surface as a function of K evaporation time.

1. After a strong initial drop the decrease is almost linear until a shallow minimum of -3.2 eV is reached after 6 min of evaporation time. We define this minimum of the work function as the completion of the saturated, monolayer-covered surface. LEED still shows a 7 \times 7 pattern at saturation coverage, the reduced quality of which, however, indicates a reduction of the long-range order. The K 3*p* intensity, as measured with UPS at $h\nu=40.8$ eV (He II), saturates simultaneously (not shown) and hence supports this definition. This emission appears in the He I spectra just above the Fermi level as can be seen in Fig. 2. For the discussion of metallicity at higher coverages (see below) we show the 7-min-K spectrum also with the He II emission suppressed (dashed line).

The development of the electronic structure from the clean to the K-saturated surface is presented in Fig. 2. Note the different scales for UPS (left scale) and inverse photoemission (right scale). The spectra of the clean Si(111)7 \times 7 surface show the well-known³⁻⁵ filled surface states labeled S_1 , S_2 , and S_3 as well as the empty adatom-derived surface state U_1 (Refs. 7 and 8). Considerable changes in the surface electronic structure are observed upon evaporation of K: The metallic S_1 state moves down in energy away from the Fermi level rendering a semiconducting surface already in the submonolayer regime and becomes the dominant surface-state feature. States S_2 and S_3 are also shifting to lower energies, but after 3 min of K evaporation S_3 has weakened considerably and S_2 is merging with S_1 , obscuring further detailed information on the filled surface states.

The empty surface state U_1 is observed to decrease drastically in intensity and has totally vanished after 5 min of evaporation time (cf. Fig. 2). According to Fig. 1 this corresponds to almost the saturation-monolayer coverage. Instead a new state denoted U'_1 has developed at

$E_F + 1.0$ eV, moving down in energy with increasing coverage. At saturation it is found very close to the energy position of U_1 .

We interpret these experimental findings as effects of the bonding of K atoms to the Si adatoms in the 7 \times 7 surface unit cell. The changes observed in the spectral appearance of S_1 and U_1 are indicative of a filling of the Si adatom dangling bond states presenting a typical charge-transfer behavior. The attributed⁸ localized character of S_1 and bandlike character of U_1 explain the different behavior of these states upon K evaporation. The additional charge transferred from the K atom to the Si adatom dangling bond causes a 0.7 eV shift of S_1 , which reflects the effective Coulomb repulsion energy involved. On the other hand, no shift is observed for U_1 (cf. Fig. 2), its spectral intensity merely decreasing in accordance with a bandlike behavior.

The potassium-induced surface state U'_1 appears after evaporation of about 0.8 monolayer and grows in intensity with coverage. It reaches its maximum at the completion of the full monolayer (6 min of K evaporation in Fig. 2). The energy of U'_1 is at the same time reduced from $E_F + 1.0$ to $E_F + 0.4$ eV at 7 min of evaporation time. This energy shift reflects the reduction of the bonding strength between the K overlayer and the silicon surface along with the increase in coverage. Hence, surface state U'_1 exhibits a very similar behavior¹¹ as the empty potassium surface state on GaAs(110).

Similar inverse-photoemission features have been observed for alkali-metal deposition on metal surfaces like silver¹² and aluminum.¹³ There, they were attributed to the lowest unoccupied alkali-metal level, corresponding

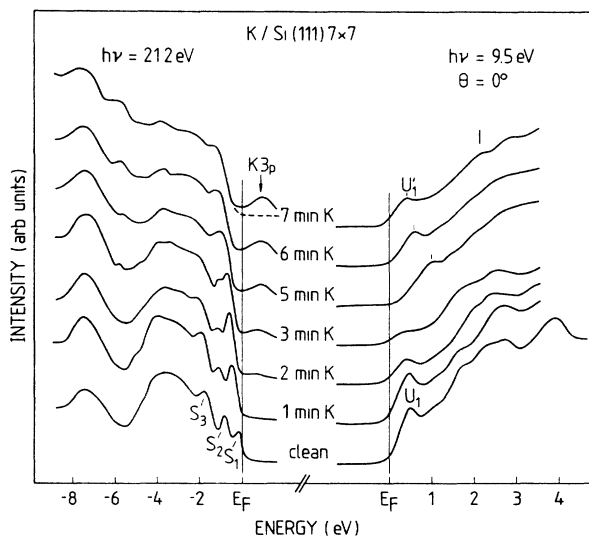


FIG. 2. Angle-integrated photoelectron spectra recorded at $h\nu=21.2$ eV in normal emission (left panel) and angle-resolved inverse-photoemission spectra recorded at $h\nu=9.5$ eV in normal incidence (right panel) after various evaporation times of K on the Si(111)7 \times 7 surface. The dashed line of the 7-min spectrum represents the He I UPS curve with the He II emission suppressed.

to K $4p$ in our case. The energetic shift as a function of coverage is then caused by the depolarization effect as it was also discussed in connection with electron-energy-loss measurements of cesium on transition metals.¹⁴ The bonding in that case occurs via the alkali-metal s electron to substrate surface states which project far out into vacuum facilitating the formation of a covalent bond. We believe that the Si adatom states on the Si(111)7 \times 7 surface behave in an analogous way, as both the filled Si surface S_1 and the U_1' surface state shift down in energy with increasing coverage.

Further elucidation of the nature of the filled surface states requires angle-resolved UPS techniques and this work is in progress. The question of band bending in this system cannot be solved in the present work because this would require studies of, e.g., the Si $2p$ level.

B. Cesium on Si(111)7 \times 7

Figure 3 shows the shift of the secondary-electron cutoff energy in UPS after successive exposures of cesium onto the Si(111)7 \times 7 surface. As in the case of potassium a shallow minimum of -3.25 eV is found which we define as the completion of the saturated-monolayer covered surface. UPS measurements of the Cs $5p$ emission (not shown) support this definition. Simultaneous LEED observations suggest a slight disturbance of the surface order after Cs evaporation, but the 7 \times 7 pattern persists.

The changes of the surface electronic structure as observed by UPS and inverse photoemission after successive evaporations of Cs are initially analogous to the K case. In Fig. 4 we note the downward shift of the S_1 state with increasing coverage, which then becomes the dominant feature in the occupied part of the spectra. The very early development of the three filled surface states is present-

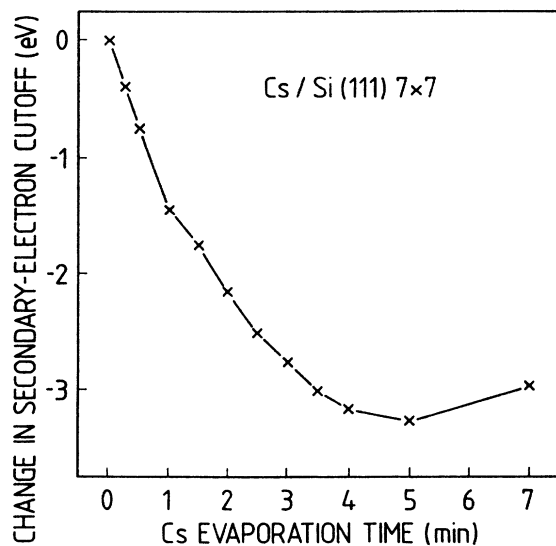


FIG. 3. The change in the secondary-electron cutoff energy in UPS from the CsSi(111)7 \times 7 surface as a function of Cs evaporation time.

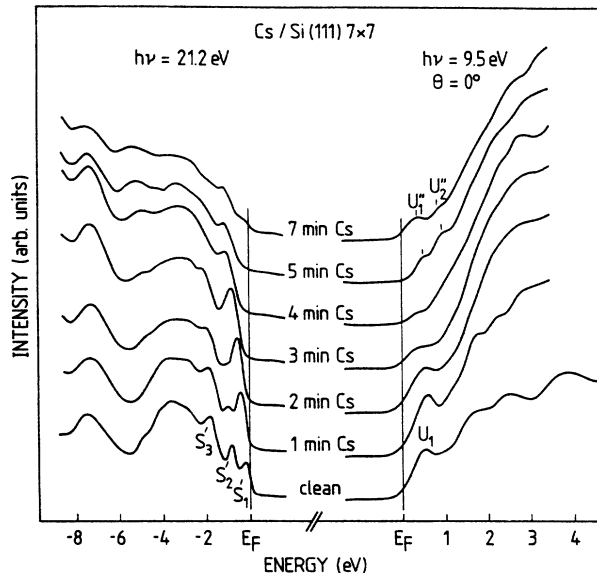


FIG. 4. Angle-integrated photoelectron spectra recorded at $h\nu=21.2$ eV in normal emission (left panel) and angle-resolved inverse-photoemission spectra recorded at $h\nu=9.5$ eV in normal incidence (right panel) after various evaporation times of Cs on the Si(111)7 \times 7 surface.

ed in detail in Fig. 5. The shift away from E_F occurs already after small amounts of Cs deposition, and after 1 min of evaporation the surface appears to be semiconducting. Simultaneously we observe the reduction in intensity of the unoccupied U_1 state, indicating, as in the case of K a filling of the empty adatom dangling-bond states. In this context we note the changes in slope of the work-function plots for K and Cs around 1-min evaporation time (see Figs. 1 and 3). They could be connected to

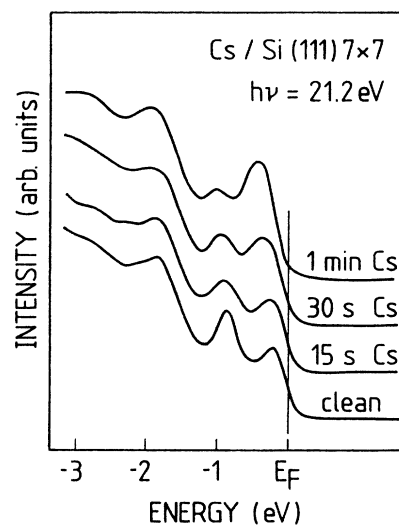


FIG. 5. Angle-integrated UPS data recorded at $h\nu=21.2$ eV in normal emission for small (<0.2 monolayer) coverages of Cs on Si(111)7 \times 7.

the disappearance of metallicity at this coverage, but a present we cannot offer a more detailed understanding. At the minimum of the work function after 5 min of Cs evaporation the surface is clearly nonmetallic in agreement with the results for K. However, a major difference is found in the development of *two* new empty surface states, denoted U'_1 and U'_2 in Fig. 4. As with potassium we interpret these states as the lowest unoccupied cesium levels. The appearance of *two* empty Cs-induced surface states at saturation coverage may suggest the existence of two inequivalent adsorption sites for the Cs atoms on the Si(111)7×7 surface. A similar observation¹¹ of two empty surface states for Cs on GaAs(110) was interpreted in support of two adsorption sites as derived¹⁵ from the coverage-dependent splitting of the Cs 4*d* core level. Finding two Cs-induced empty surface states on such different surfaces as Si(111)7×7 and GaAs(110) may, however, point towards an intrinsic property of the bonding of Cs to covalent dangling bonds. Studies of the adsorption of Cs on the cleaved Si(111)2×1 surface have shown¹⁶ that large effects on the surface reconstruction can be induced, in that special case yielding a $(\sqrt{3} \times \sqrt{3})R 30^\circ$ -Cs overlayer structure.

Aside from the occurrence of two Cs states we find another difference with respect to potassium. Upon further evaporation of Cs, beyond the minimum of the work function and without noticeable increment of the Cs 5*p* core-level intensity, a procedure which can be called "over-cesiation," the electronic structure changes. The Cs-induced empty surface states U'_1 and U'_2 shift down in energy, U'_1 even enough to yield considerable intensity at the Fermi level after 7 min of Cs evaporation (cf. Fig. 4). At the same time UPS also shows enhanced intensity at E_F . Figure 6 combines the UPS and inverse-photoemission results close to the Fermi level for this

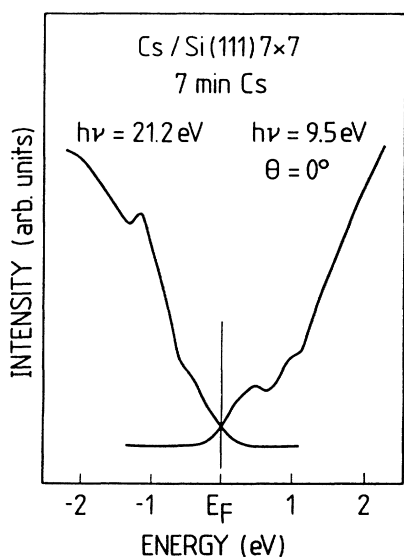


FIG. 6. Combined UPS and inverse-photoemission spectra of the over-cesiated Si(111)7×7 surface in the vicinity of the Fermi level.

over-cesiated surface. The conclusion we draw from this is that over cesiation, in contrast to overexposure of potassium, drives the semiconducting surface towards metallicity again. We suggest the driving force to be the Cs-Cs interaction which at a continued flow of Cs atoms onto the already saturated surface can change the surface ordering and thereby the direction of charge transfer between Cs and Si. An important parameter is the size of the Cs atom in relation to the distance between Cs adsorption sites. This finding is in perfect agreement with previous results for the GaAs(110) surface¹¹ where over cesiation also makes the surface metallic, while K does not show this effect. This apparently substrate-independent behavior supports a model where the alkali-metal-alkali-metal interaction determines the electronic structure in the high-coverage (monolayer) regime. Detailed theoretical considerations are needed to explain the difference between adsorption of Cs and K on the above discussed surfaces.

Finally, we compare our inverse-photoemission results to calculations of Wimmer¹⁷ for free-standing hexagonal monolayers of K and Cs. At the center of the surface Brillouin zone, $\bar{\Gamma}$, where we probe in our experiments, Wimmer¹⁷ calculated an energy difference between the unoccupied Cs 6*p*- and Cs 5*d*-derived bands of 0.68 eV. This compares fairly well with our measured value for the energy separation of U'_1 and U'_2 of 0.5 eV in Fig. 4. If this interpretation were valid and could also be applied to K, we should see spectral intensity about 1.4 eV above U'_1 according to the calculations.¹⁷ A weak feature is indeed observed in Fig. 2 in the spectrum for 7 min of K evaporation (see tickmark at +2.3 eV). A similar picture for alkali-metal adsorption on GaAs(110) seems also possible. In that case, however, the dispersion of the empty K-induced band was measured¹¹ to be downward in disagreement with the calculated¹⁷ band dispersion. A theoretical investigation may clarify the importance of this comparison which has the immediate consequence of a nearly-free alkali-metal monolayer loosely bound to the substrate as the coverage approaches saturation.

IV. CONCLUSIONS

By combining UPS and inverse photoemission we have studied the development of the electronic structure of submonolayer to monolayer coverages of Cs and K on the initially metallic Si(111)7×7 surface. Both metals are found to interact preferentially with the adatom dangling bonds. This interaction lowers the energy of the filled, metallic surface state S_1 , making it the dominant surface feature, and the surface becomes semiconducting. At the same time the empty surface state U_1 becomes weaker and has totally vanished at saturation coverage. We interpret this as the filling of the adatom empty dangling bonds by the alkali-metal valence *s* electrons. The characteristic behavior of S_1 and U_1 , i.e., energetic shift versus vanishing reflects their localized and bandlike nature, respectively.

For coverages just below saturation coverage, new alkali-induced empty surface states appear. They move towards the Fermi level with increasing coverage, but

leave both K and Cs surfaces semiconducting at saturation coverage. Overexposure of K does not change the electronic structure of the resulting surface, while overcesiation is found to increase the spectral intensity on both sides of the Fermi level, making the surface metallic again. The latter is proposed to be due to a non equilibrium process with possible energy transfer to the surface, where the Cs-Cs interaction forces the surface atoms to rearrange, similar to surface annealing.

In the cesium case two empty surface states are clearly observed, while potassium exhibits only one. We suggest

it to be an indication for two different adsorption sites for Cs on Si(111)7×7. It might also reflect the electronic structure of Cs adsorbed on a semiconductor surface, i.e., the interaction with the dangling bond states. The interpretation in terms of a metallic Cs film is one possibility. Finally we note the large similarities with our previous work¹¹ with K and Cs on GaAs(110).

ACKNOWLEDGMENTS

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