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Development of electronic band structure of the K-adsorbed Si(111)7 × 7 surface

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Abstract. Adsorption of K on the Si(111)7 × 7 surface has been investigated in the submonolayer coverage range at room temperature. The method of threshold photoemission spectroscopy using s- and p-polarized light excitation was employed for studying the evolution of surface electronic structure near the Fermi level, the work function and the ionization energy. A qualitative change in character of band structure has been observed, depending on K coverage. Suppression of metallicity of the Si(111)7 × 7 surface was found at the initial stage of K adsorption. One surface band A_1 below the VBM was revealed at low coverage. Increasing K coverage has led to both the appearance of the K-induced band A_2 and significant movement of the band towards the Fermi level. The K/Si(111)7 × 7 interface was found to be semiconducting-like up to saturation coverage. Near saturation, the Fermi level is seen to cross the K-induced band A_2 . Such surface band structure is identified as being metallic-like. Results indicate metallization via adlayer accompanied by Fermi level pinning.

Alkali-metal/silicon interfaces provide ample information regarding the electrical phase transitions depending on alkali coverage. The systems inherently undergo only a insulator-to-metal transition as a function of alkali coverage. The possibility of studying a metal-to-insulator transition exists, in principle, only for adsorption on the metallic-like Si(111)7 × 7 surface. The electronic structure of the Si(111)7 × 7 surface possesses three filled surface states S_1 , S_2 , S_3 [1–3]. The surface band S_1 originating from the 12 adatoms in the 7 × 7 unit mesh crosses the Fermi level and it is this band S_1 that is the metallic one. The surface band S_2 belongs to the six rest-atoms in the 7 × 7 mesh. This band is well below the Fermi level and its energy position is detected at ~0.2 eV below the valence band maximum (VBM). The photoemission study of the K/Si(111)7 × 7 interface has been carried out in [4] and [5]. Suppression of metallization and shift of surface states have been observed at low coverage. Metallization of the interface was observed at cryogenic temperature during the development of the second adsorption layer. However, development of electronic structure in particular near saturation remains a question to be solved. Moreover, the very low photoemission cross section of the states in the close vicinity of the Fermi energy makes clear determination of the metallicity difficult. The interaction of adsorbed atoms with a surface is still controversial in that the adsorption sites at various coverages have not been determined and the origin of the metal–insulator transition present at low submonolayer coverages is still disputable. For example, a model taking into account vibronic interaction was developed for the quasi-2D system of interacting surface dangling bonds and adsorbed atoms to understand the suppression of the metallic-like properties of the Si(111)7 × 7 surface under Ba adsorption [6]. Theoretical studies of the problem of 2D metallic behaviour have shown that interfacial metallization under

submonolayer adsorption can be of two types: it can arise due to the realization of conductivity either in the top quasi-two-dimensional layer of substrate (substrate metallization) or in the adsorbed metal layer (overlayer metallization) [7, 8]. What type is realized depends crucially on the origin of adsorbate–substrate bonding. It is noteworthy to point out that the fundamental issue of the nature of the chemical bond between alkali-metal atoms and silicon surface has not been settled.

In this publication, we present detailed studies of the occupied electronic bands of the K/Si(111)7 × 7 interface. We use an original method of threshold photoemission spectroscopy (TPS) that possesses a high optical resolution and ultra-high sensibility for probing photoemission from surface states close to the Fermi level and VBM. Moreover, both the work function in the case of metallization and the ionization energy have been obtained as a function of K coverage. The presence of a finite density of surface states at the Fermi level has been determined with high precision. The different electronic structures are found to be semiconducting-like up to saturation coverage. Near saturation, the insulator-to-metal transition has been revealed due to development of K-induced band.

The experiments were performed *in situ* in a vacuum of $P \sim 1 \times 10^{-10}$ Torr at room temperature. A clean Si(111) surface, p-type, $10 \Omega \text{ cm}^{-1}$, was used. The Si(111)7 × 7 reconstructed surface was obtained by the well known annealing procedure [9]. A standard source of atomically pure potassium was employed. The technique of TPS with excitation by s- and p-polarized light was used. The angle of incidence of the light was equal to 45°. The experimental photoemission spectra $I_S(h\nu)$ and $I_P(h\nu)$ excited by the s- and p-polarized light, respectively, were investigated after K deposition. The photoemission signal was stable for hours.

The technique of TPS has been employed for probing a surface band structure near both the Fermi level and VBM. TPS allows us to ascertain a finite density of surface states at the Fermi level and to measure the ionization energy and work function. TPS is based on the separation of surface photoemission and bulk photoemission and on the near-threshold enhancement in photoemission from surface states. Experimental and theoretical aspects of TPS have been described previously [10–12]. Threshold photoemission is operated in constant final state mode. Thus, the photoemission signal is directly proportional to the density of occupied surface states or bulk ones. The s-polarized light can excite photoemission $I_S(h\nu)$ only from bulk states. The p-polarized light can excite the photoemission $I_P(h\nu)$ from both the bulk states and surface ones in the energy region $h\nu > h\nu_S$, where $h\nu_S$ is the photoemission threshold for the s-polarized light. $h\nu_S$ determines the energy position of the VBM relative to the vacuum level; it is $h\nu_S$ that is the ionization energy $\phi = h\nu_S$. The surface photoemission can be separated as the ratio $I_P(h\nu)/I_S(h\nu)$ that is directly proportional to the density of occupied surface states. In the energy region above VBM ($h\nu_S > h\nu > h\nu_P$), the p-polarized light can excite photoemission only from surface states. This fact can be indeed used to analyse the character of the surface band above VBM. In the case of photoemission from the metallic-like surface band at E_F , the main feature of the spectra $I_P(h\nu)$ is quadratic behaviour, which corresponds to Fowler's law $I_P(h\nu) = k(h\nu - h\nu_P)^2$. In this case $h\nu_P$ is the work function ϕ and the parameter k is directly proportional to the surface state density at E_F .

The photoemission spectra $I_S(h\nu)$ and $I_P(h\nu)$ obtained with excitation by the s- and p-polarized light, respectively, were studied at different K coverage. The thresholds $h\nu_S$ and $h\nu_P$ were determined by approximating the spectra. Figure 1 shows a change in the photoemission thresholds as a function of K deposition time. An essential difference in behaviour of the thresholds has been observed. The threshold $h\nu_S$ determines the ionization energy $\phi = h\nu_S$. Upon K adsorption, a sharp decrease of ϕ has been revealed up to 1.75 eV.

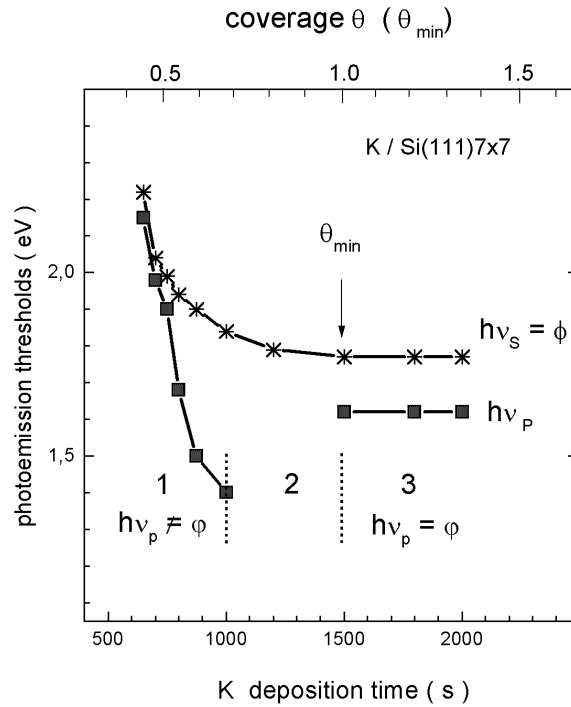


Figure 1. Photoemission thresholds $h\nu_S$ and $h\nu_P$ for the s- and p-polarized light, respectively, for the K/Si(111) 7×7 interface as a function of K deposition time.

After K coverage corresponding to the deposition time of ~ 1500 s, increase of coverage does not change ϕ , i.e., ϕ reaches saturation. We shall mark the K coverage corresponding to the saturation one as $\theta = \theta_{min}$. The threshold $h\nu_P$ determines either the position of the edge of surface band below the Fermi level in the case of a semiconducting gap or the position of the Fermi level in the case of metallization [11, 12]. Three different ranges of coverages can be selected taking into account variation of the threshold $h\nu_P$. In range (1), the difference between the thresholds sharply increases from 0.05 eV at $\theta \sim 0.4\theta_{min}$ to 0.45 eV at $\theta \sim 0.7\theta_{min}$. The result indicates a shift of surface band toward the energy gap. However, there is no local density of surface states at the Fermi level. Therefore, the suppression of metallization of the Si(111) 7×7 surface occurs at low K coverage $\theta < 0.4\theta_{min}$. An important point is that the energy positions of the thresholds are found to almost coincide at $\theta \sim 0.4\theta_{min}$. According to this phenomenon we may conclude that the initial stage of the K adsorption leads to disappearance of the surface states above the VBM. In range (2), signal instability makes it impossible to obtain the position of $h\nu_P$ and consequently to determine whether the interface is metallic or semiconducting-like. In range (3), the analysis of surface photoemission spectra $I_P(h\nu)$ near the threshold $h\nu_P$ exhibits a finite density of surface states at the Fermi level, which is a sign of metallicity. In this case the threshold $h\nu_P$ is the work function ϕ . Thus, a transition to metallic-like surface structure has been found to be near saturation. The insulator-to-metal transition is accompanied by the Fermi level pinning which is derived from constancy of the energy positions of the thresholds.

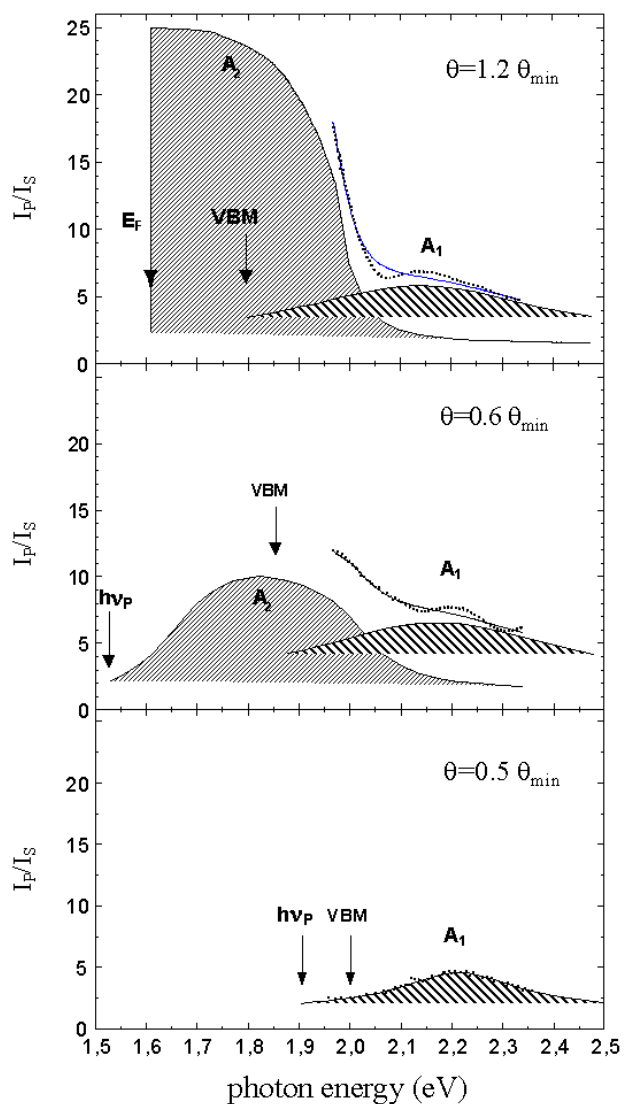


Figure 2. Surface photoemission spectra $I_p(h\nu)/I_S(h\nu)$ (solid lines) and results of decomposition of the spectra (shaded contours) at various K coverage. Arrows indicate the energy position of the VBM and photoemission threshold $h\nu_p$. In the case of metallization at $\theta \sim 1.2\theta_{min}$ the arrow indicates the Fermi level position.

Figure 2 represents a series of surface photoemission spectra $I_p(h\nu)/I_S(h\nu)$ for the K/Si(111) interface and the results of decomposition of the spectra. The surface band A_1 has been observed below the VBM at all K coverages. Parameters of the band are very stable. The band A_1 has energy characteristics similar to those of the surface-state band S_2 originating from the rest-atom dangling bonds of the 7×7 unit mesh. Recent studies have shown that the surface band S_2 changes weakly upon alkali-metal adsorption [4, 5]. Therefore, we may predict that the origin of the band A_1 is connected with the rest-atom dangling bonds. At $\theta = 0.5\theta_{min}$ the spectrum reveals only one band A_1 below the VBM with weak surface state density in the

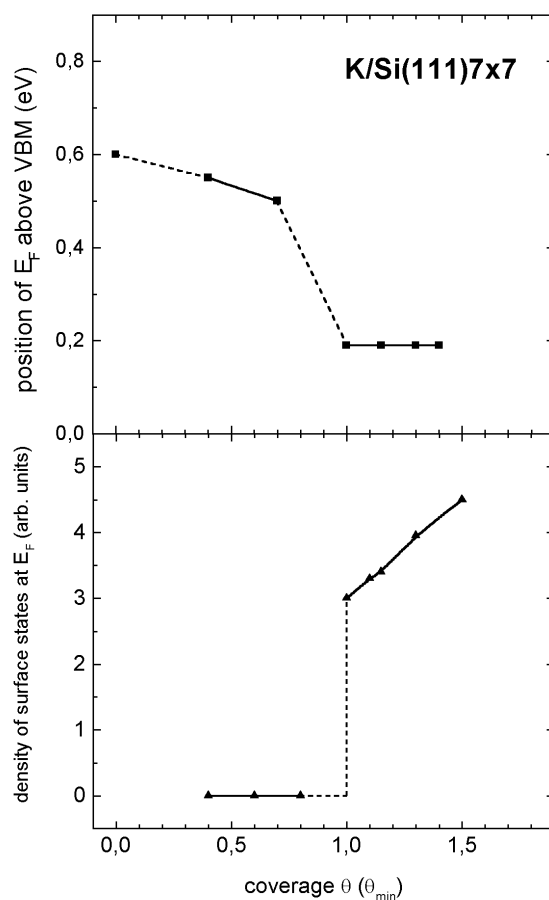


Figure 3. The Fermi level position with respect to the VBM and density of surface states at the Fermi level as a function of K coverage.

energy gap. The K/Si(111) 7×7 interface is semiconducting-like. This result testifies that there is suppression of metallicity of the Si(111) 7×7 surface due to the initial stage of K adsorption at $\theta < 0.5\theta_{min}$.

At $\theta > 0.5\theta_{min}$, the spectra clearly exhibit the appearance of the band A_2 induced by K adsorption. In contrast to the band A_1 , an essential change in behaviour of the band A_2 is revealed upon K adsorption. The peak A_2 tends to shift towards the Fermi level side. Near the saturation at $\theta \sim \theta_{min}$, the K-induced band A_2 crosses the Fermi level. This surface band structure is identified as being metallic-like. The semiconductor interface becomes metallic again. The insulator-to-metal transition at a coverage in the range from $\theta = 0.6\theta_{min}$ to $\theta = 1.2\theta_{min}$ (see figure 2) is in accordance with the presence of some density of surface states at the Fermi energy at $\theta > \theta_{min}$ as we found above under consideration of figure 1, range (3). Thus, two types of transition are revealed for the K/Si(111) 7×7 interface. The metal-to-insulator transition occurs at low coverage and the insulator-to-metal transition takes place in the close vicinity of saturation coverage θ_{min} .

Figure 3 shows both the E_F position with respect to the VBM and the change in surface state density at E_F for different K coverages. The E_F position for the clean Si(111) 7×7 surface is

borrowed from [5]. For $\theta = 0.4\theta_{min}$ and for $\theta = 0.7\theta_{min}$, the E_F positions have been obtained from surface photoemission spectra as values exceeding the edges of the K-induced band A_2 . For $\theta \geq \theta_{min}$, the E_F pinning position can be deduced from figure 1 as the difference between the thresholds. In the case of interface metallization the surface state density at the E_F has been derived from approximation of the spectra $I_P(h\nu)$ taking into account variation of the parameter k in Fowler's law. It is evident that anomalous behaviour of both dependencies is observed near saturation coverage θ_{min} .

To summarize, upon K adsorption a pronounced modification of electronic structure of the Si(111) 7×7 surface is observed. Results show that there are two critical coverages for which a drastic change in electronic properties of the K/Si(111) 7×7 interface takes place. At the initial stage of K adsorption, suppression of metallicity of the clean Si(111) 7×7 surface occurs. At saturation coverage the interface undergoes the insulator-to-metal transition. The latter seem to be most probable as a result of K–K interaction. To date the K adatom concentration corresponding to the saturation coverage not known. Therefore, according to [4] we can assume $\theta_{min} \leq 1$ ML. Suppression of metallicity of the Si(111) 7×7 surface can be provided by interaction of the K atoms with the adatom dangling bonds and corner-hole dangling bond. Before occupying 12 adatom sites, i.e. at coverage $\sim \frac{1}{4}$ ML, probability exists for the K atom on the corner-hole dangling bond to be found. In fact, the above mentioned effect means suppression of the metallicity of the Si(111) 7×7 surface. That is why we may predict that adsorption causes mainly a charge localization in the K–Si bond at low K coverage. The process is accompanied by interaction of the K atoms with the adatom dangling bonds. This interaction leads to filling the dangling bonds and increasing the binding energy. Electronic surface structure exhibits only the band A_1 below the VBM revealing the energy gap. The band A_1 may be compared with the band S_2 originating from the rest-atom dangling bonds of the clean (7×7) surface. Further, at saturation coverage the semiconducting-like interface becomes metallic again. Electronic structure development shows the band A_2 to be related to the K–K interaction in the overlayer. The K-induced band A_2 extends up to the Fermi level at saturation coverage and it is this metallic band which pins the Fermi level at ~ 0.2 eV above VBM. Results indicate that metallization occurs via an adlayer, accompanied by increasing local density of surface states at the Fermi level. Therefore the actual transition to a metallic-like interface takes place at least before the first K monolayer formation.

Acknowledgments

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