Empty Surface States on the Si(100)2×1-K Surface: Evidence for Overlayer Metallization

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The electronic structure of potassium-covered single-domain Si(100)2×1 surfaces has been studied with angle-resolved direct (ultraviolet) and inverse photoemission at room temperature. At saturation coverage, the surface is metallic due to the filling of the minimum of a strongly dispersive empty surface state of mainly K $4p_z$ character. Paraboliclike dispersions are observed for this state in the $\bar{\Gamma}$-$\bar{J}'$ and the $\bar{\Gamma}$-$\bar{J}$ directions (i.e., both along and perpendicular to the dimer rows), showing the metallic bonding in the overlayer and a strong K-K interaction in both directions.

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In recent years, there has been a great interest in alkali-metal adsorption on semiconductor surfaces [1,2]. This interest is motivated both by possible technological applications and by fundamental physics reasons. In the latter case, alkali metals on semiconductors are regarded as model systems for metal-semiconductor interfaces. In particular, the Si(100)2×1-K surface has been the subject of considerable research efforts [3-22]. However, substantial disagreement exists as to most of the major properties of this system, e.g., the room-temperature (RT) saturation coverage, the metallization of the substrate and/or the overlayer, the nature of the Si-K bonding, the adsorption sites(s), and the surface electronic structure. The literature concerning these questions is quite extensive and we refer to Refs. [1] and [2] for reviews.

In the present work, the Si(100)2×1-K surface has been studied with angle-resolved inverse and ultraviolet (direct) photoemission (IPES and ARUPS, respectively). By use of vicinal Si(100) samples, single-domain 2×1-reconstructed surfaces were obtained. As a result, the surface-state dispersions were measured along the main symmetry directions of the surface, i.e., along and perpendicular to the dimer rows, in contrast to a previous IPES study of this surface [3]. In this work, we show conclusively that at saturation coverage at RT, the surface is metallic due to the filling of the minimum of a surface band with paraboliclike dispersion, associated with the K overlayer. Our results support a mainly covalent K-Si bonding at saturation and atomic models based on a full monolayer (ML) coverage (1 ML being defined to be 6.78×10^{14} atoms per cm^2, i.e., the same density as for one atomic Si layer).

The experiments reported here were performed in a previously described [23] two-chamber ultrahigh vacuum (UHV) system. The IPES experiments were carried out in the isochromat mode, detecting 9.5-eV photons with an overall energy resolution of 0.35 eV and a wave-vector resolution of $\Delta k_{\parallel}=0.08$ Å^{-1}. The ARUPS experiments were performed with unpolarized He I light ($h\nu=21.2$ eV) and an overall energy resolution of 0.1 eV.

The samples were highly n-doped Si(100) single crystals ($\rho=4$-8 mΩ cm, arsenic, from Wacker-Chemitronic). In order to obtain single-domain 2×1 reconstructions, vicinal samples were used [24,25], cut 4° off the [100] direction, tilting towards [011]. On-axis-cut samples (giving two-domain reconstructions) were also used in the experiments.

Before insertion into the UHV system, the samples were cleaned with an etching method [26], and in UHV they were outgassed and finally cleaned by resistive heating at 600 and 850 °C, respectively.

Potassium was evaporated from a well outgassed getter source (SAES Getters) onto the samples at RT (~22 °C) at a pressure below 1×10^{-10} mbar. The amount of evaporated potassium was indirectly controlled by measuring the change in work function ($\Delta\phi$) as a function of evaporation time. This was done by measuring the absorption onset of the electron current from the IPES electron gun on the negatively biased sample. The degree of oxidation due to rest-gas oxygen was monitored with ARUPS. The data presented here were recorded within 90 min after K evaporation at a pressure of 5×10^{-11} mbar.

In order to calibrate the K source we measured the relation between $\Delta\phi$ and the evaporation time. The general shape of that curve (not shown), as well as its minimum and saturation values ($\Delta\phi=-3.38$ and -3.2 eV, respectively), is similar to those found in several other studies [8,9,12,17-19].

The evolution of the surface states at $\bar{\Gamma}$ in the surface Brillouin zone (SBZ) for increasing K coverage is shown in Fig. 1. In the spectra from the clean surface ($\Delta\phi=0.0$), contributions can be seen from the filled and empty dangling-bond surface states [25], denoted by S_1 and U_1, respectively. A small contribution from the U_1 state can also be seen in the ARUPS spectrum, due to the high n doping of the crystal [25]. Prominent bulk structures, denoted A and B, exist above 3 eV in the IPES spectrum. At low K coverages no major changes occur in the spectra. However, at a coverage corresponding to $\Delta\phi=-2.0$ eV an empty surface state appears at 2.4 eV energy, denoted U_2. With further increasing coverage it shifts downwards in energy until it reaches the Fermi level at the same coverage where the work function reaches its minimum at $\Delta\phi=-3.38$ eV. Then the U_2 state also becomes visible in the ARUPS spectra (denoted U_2'). Above this coverage, a second, weak empty feature ap-

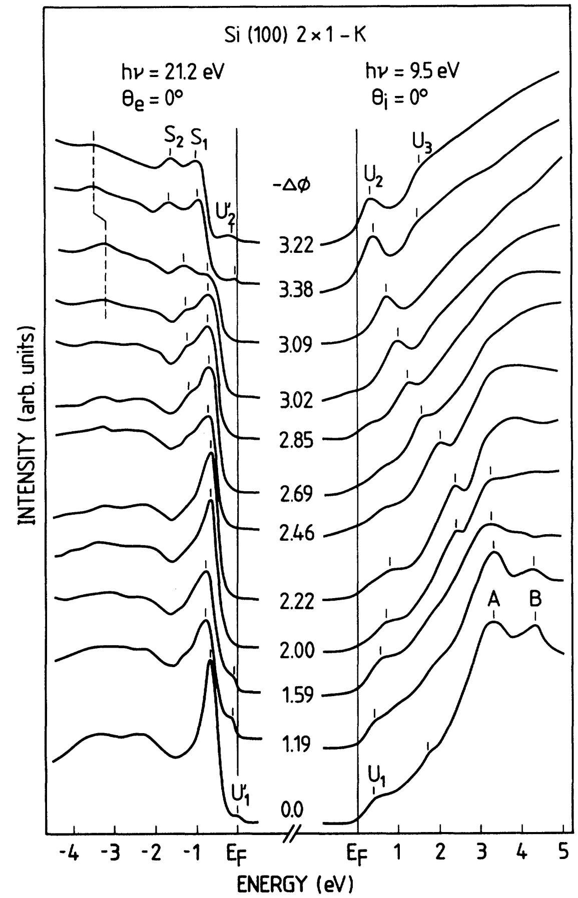

FIG. 1. ARUPS normal-emission and IPES normal-incidence spectra recorded on the Si(100)2×1-K surface for increasing K coverage. The coverage was indirectly controlled by the measured work-function shift ($\Delta\phi$). The symbols are explained in the text.

pears at ~1.6 eV, labeled U_3.

In the ARUPS spectra, a second surface state, denoted by S_2, appears to split off from the S_1 peak for $\Delta\phi = -2.85$ eV and to move to lower energies for increasing coverage. Between $\Delta\phi = -3.09$ and -3.38 eV, all ARUPS features shift downwards by ~0.3 eV, as indicated in Fig. 1. This energy shift thus coincides with the reaching of the minimum in the $\Delta\phi$ curve and occurs quite abruptly with respect to the evaporation time (within the last 10% of the time needed to reach the minimum). The observation of this energy shift is in good agreement with the earlier ARUPS valence-band and K 3*p* core-level results of Enta *et al.* [9] on the two-domain Si(100)2×1-K surface. In accordance with their conclusions, we interpret it to be a band-bending shift caused by the onset of the filling of the previously empty surface state U_2. The same band-bending shift was also observed by Pervan *et al.* [17], although it was less abrupt in their case.

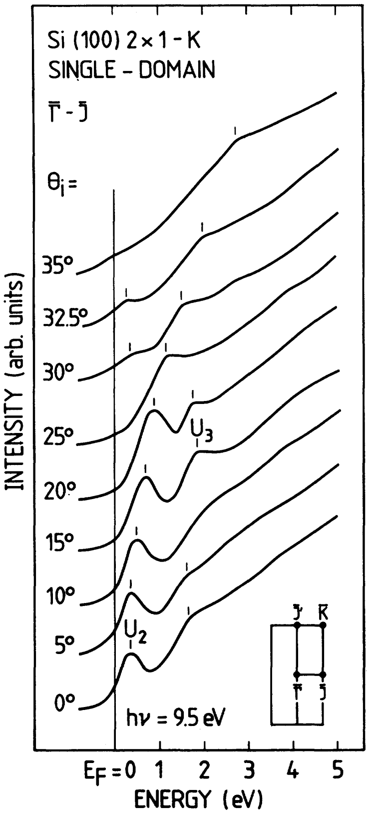

FIG. 2. IPES spectra recorded on the single-domain Si(100)2×1-K surface for different incidence angles θ_i in the $\bar{\Gamma}$-$\bar{J}$ direction in the SBZ. The 2×1 SBZ is shown in the inset. The K coverage for these spectra corresponds to the minimum of the $\Delta\phi$ curve, i.e., -3.38 eV.

Figure 2 shows IPES spectra recorded for different incidence angles θ_i in the $\bar{\Gamma}$-$\bar{J}$ direction in the SBZ (see inset of Fig. 2). (All incidence and emission angles in this study refer to the [100] direction and *not* to the surface normal for the vicinal samples.) The spectra were recorded at the coverage corresponding to the minimum of the $\Delta\phi$ curve ($\Delta\phi_{\min} = -3.38$ eV). The U_2 state shows a strong upward dispersion from $\bar{\Gamma}$, which is plotted in Fig. 3. The observable bandwidth is ~2.5 eV. A similar, although slightly less steep, dispersion was recorded in the perpendicular $\bar{\Gamma}$-$\bar{J}'$ direction. These dispersions were fully developed already at the coverage corresponding to $\Delta\phi = -3.0$ eV. A strong peak is also seen at 1.8 eV in the $\theta_i = 15°$ spectrum in Fig. 2, which corresponds to a $k_{\parallel}$ value near the $\bar{J}$ point. This peak is most likely the same U_3 state as that seen in normal emission.

A surprising result is that the U_2 dispersion does not follow the periodicity of the substrate reconstruction in the $\bar{\Gamma}$-$\bar{J}$ direction (perpendicular to the dimer rows), as clearly seen in Figs. 2 and 3. Only a faint umklapp-scattered U_2 peak is observed at $\bar{\Gamma}$ in the second SBZ (see the $\theta_i = 32.5°$ spectrum in Fig. 2). It should be noted that the surface reconstruction was clearly single-domain 2×1. That fact was evidenced by (a) the observation of a

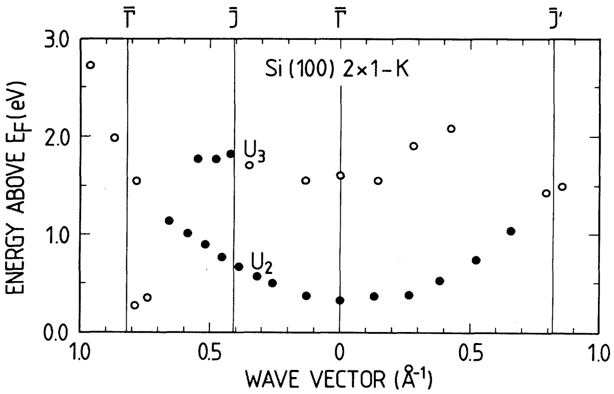

FIG. 3. The measured dispersions of the surface-related peaks in the IPES spectra from the Si(100)2×1-K surface. The K coverage is the same as for the spectra in Fig. 2. The solid and open symbols denote strong and weak features, respectively, in the IPES spectra.

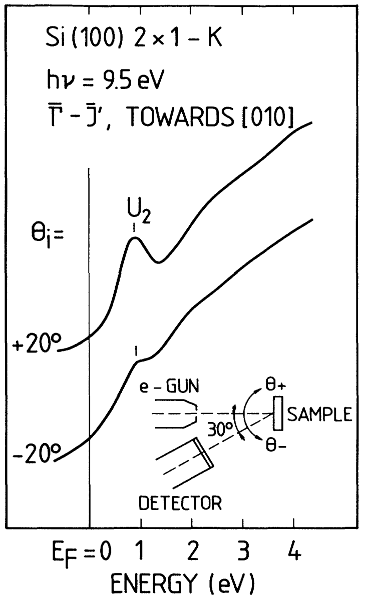

FIG. 4. Two IPES spectra recorded on a two-domain Si(100)2×1-K surface in the diagonal [010] direction (Γ̄-J̄'), with the same magnitude for the electron incidence angle, but with different photon collection geometries, as illustrated in the inset. For the +20° spectrum the sample was rotated upwards (away from the detector) and photons emerging at a high emission angle were collected, while for the −20° spectrum the sample was rotated downwards (towards the detector) and photons emerging in near-normal emission were collected. The angle between the electron beam and the detector axis was kept fixed. The K coverage is the same as for the spectra in Figs. 2 and 3. The same result was also found on single-domain surfaces.

good, single-domain low-energy electron-diffraction pattern, (b) the strong U_3 peak at $\theta_i = 15°$ in Fig. 2, which was not found in the perpendicular direction, and (c) significant differences in ARUPS spectra recorded at the same emission angles in the two perpendicular azimuthal directions (data not shown).

The photon emission intensity from transitions to the U_2 state was strongly dependent on the emission direction. This is shown in Fig. 4. The essential difference between the two spectra is the emission angle of the collected photons. Thus for a high emission angle, a strong U_2 peak was obtained, while for near-normal emission the peak was faint. The paraboliclike dispersion of U_2 is consistent with a K 4s and/or K 4p_z character [27], whereas the strong angular dependence of the photon emission implies a dominant p_z character. This is supported by the calculated angular dependence of the photoionization cross section for atomic orbitals [28]. Solid-state effects may complicate the picture, but we can exclude that since we found the same angular dependence for all three main azimuths (as well as on single-domain and two-domain surfaces). A similar K 4p_z-derived band with parabolic dispersions has previously been observed for K adsorbed on Ag(110) [29]. A minor K 4s contribution cannot be ruled out in our case, but a major 4s character is very unlikely. Furthermore, metastable deexcitation spectroscopy by Nishigaki *et al.* [18] on the Si(100)2×1-K surface locates the K 4s-derived peak ~1 eV below the Fermi level, suggesting that the 4s level is occupied and mainly hybridized with the dangling-bond states of the Si substrate.

Metallization of the K overlayer has previously been reported employing indirect experimental techniques like energy loss [4,5] and core-level [12] spectroscopy, as well as oxygen-dosing studies [17]. The data presented above however, are direct and conclusive evidence for overlayer metallization, since in the IPES and ARUPS spectra we directly observe the crossing of the Fermi level of the overlayer-derived U_2 band. This metallization occurs at the coverage corresponding to $\Delta\phi_{\min}$, whereas at a slightly lower K coverage, at $\Delta\phi = -3.09$ eV, the surface is still semiconducting. Further evidence for a metallic overlayer is given by the paraboliclike dispersion of the U_2 band, which indicates a metallic bonding within the overlayer with strong K-K interaction both parallel and perpendicular to the dimer rows. The partial independence of the substrate periodicity for the U_2 band can be understood in the context of a weak substrate-overlayer interaction, which is consistent with a metallic overlayer. We simply observe the continuation of a mainly parabolic free-electron-like dispersion in the second SBZ, whereas the umpklapp-scattered branch of the parabola is observed only as a faint structure around Γ̄ in the second SBZ. This suggests that the atomic positions in the K overlayer may be close to a 1×1 periodicity.

By comparing to calculated band structures for Si(100)2×1-K [7,15,16], it is clear that our results are consistent with atomic models based on 1-ML coverage, e.g., the double-layer model [11], but not with $\frac{1}{2}$-ML models, e.g., the one-dimensional alkali chain (ODAC) model [4]. The main features of the $\frac{1}{2}$-ML models (one filled surface band and one half filled, with the empty part dispersing downwards from $\bar{\Gamma}$) are widely different from the experimental results presented here and in Refs. [9] and [14] (two filled surface bands well below the Fermi level, a semiconducting surface just before saturation, and a mainly empty surface band dispersing upwards from $\bar{\Gamma}$). The steep dispersion of U_2 in the direction perpendicular to the dimer rows is also clearly inconsistent with the ODAC model, since it indicates a strong K-K interaction in this direction.

In contrast, our results are qualitatively in good agreement with the recent detailed theoretical study of Ishida and Terakura [16]. For the double-layer model (1 ML) they found a semiconducting surface band structure with two filled bands derived from the Si dangling bonds and K 4*s* and $4p_{x,y}$ orbitals, and one empty band with mixed K $4p_z$ and 4*s* orbital content. The character of the empty band agrees well with the U_2 band in the present work. Our results thus give strong support to the polarized covalent Si-K bonding picture proposed in Ref. [16]. There is good quantitative agreement between the dispersions of the empty state in the $\bar{\Gamma}$-$\bar{J}$ direction, but less good along $\bar{\Gamma}$-$\bar{J}'$. The band gap at $\bar{\Gamma}$ between the filled and empty bands is about half of the experimentally determined gap (~ 1.0 eV) between the U_2 and S_1 bands. However, this difference may be attributed to the local-density approximation.

Ciraci and Batra have also studied the double-layer model theoretically [15]. However, no empty overlayer-derived bands were identified in those calculations, and it was concluded that overlayer metallization does not occur at 1-ML coverage, due to the mainly ionic Si-K bonding. As shown above, this does not agree with our experimental results. A previous IPES study [3] for a two-domain surface is in agreement with our present findings for a K coverage near saturation, but an actual coverage calibration was missing. The theoretical agreement claimed in that paper existed only at the $\bar{\Gamma}$ point.

In conclusion, we have studied the single-domain Si(100)2×1-K surface with angle-resolved inverse and direct photoemission. Evidence for overlayer metallization above 1-ML coverage has been obtained. The metallization occurs through the formation and partial filling of a mainly empty overlayer band of dominant K $4p_z$ character. These results support a covalent Si-K bonding at saturation and structural models based on 1-ML coverage.

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