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Electronic structure of the Rb-adsorbed Si(100)2×1 surface studied by direct and inverse angle-resolved photoemission

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We have studied the development of the surface electronic structure of a rubidium-adsorbed Si(100)2×1 surface for increasing Rb coverages, with angle-resolved direct and inverse photoemission (IPES). At very low coverages, up to 0.2 ML, the 5*s* electrons of the Rb atoms fill the minimum of the normally empty substrate-derived surface band. For higher Rb coverages, the surface electronic structure changes significantly. In the IPES spectra, a new, rubidium-induced peak appears at coverages above 0.3 ML. With increasing Rb coverages, it moves downwards in energy, until it reaches the Fermi level at the 1-ML saturation coverage, causing a metallization of the surface. The dispersion of the empty overlayer state was measured along the main crystallographic directions. A single-domain surface was obtained using vicinal samples, which showed a 2×1 periodicity at the Rb saturation coverage. Large upward paraboliclike dispersions from the minimum at $\bar{\Gamma}$ were observed in both the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-$\bar{J}'$ directions, showing the metallic character of the overlayer and the strong Rb-Rb interaction in both directions. These results provide further evidence for the double-layer model for alkali-metal adsorption on Si(100)2×1, as well as a mainly covalent bonding picture. Our data are compared to previous studies of Li, Na, and K adsorption on the Si(100)2×1 surface. It is shown that although the electronic structures of the different adsorption systems are similar, systematic differences appear that can be attributed to the sizes of the alkali-metal atoms. In particular, a larger alkali-metal atom leads to a stronger alkali-alkali interaction and a weaker alkali-metal–Si interaction. [S0163-1829(98)05131-5]

I. INTRODUCTION

Adsorption of alkali metals on silicon surfaces has been studied extensively in recent years.[1,2] This interest has been motivated by both possible technological applications and by fundamental physics reasons. In the latter case, alkali-metal–Si systems are regarded as model systems for metallization of semiconductor surfaces. Reasons for this are the simple electronic structure of the alkali metals, and the fact that the alkali metals (except for Li) do not intermix with the Si substrates, in contrast to almost all other metals. Much of the recent interest and debate concerns the Si(100)2×1 surface, where the discussion has been focused on such matters as the nature of the alkali-metal–Si bond, the amount of charge transfer from the alkali metals to the substrate, the metallization, the adsorption positions, and the saturation coverage at room temperature (RT).

In early studies of alkali-metal adsorption on Si(100)2×1, Levine's model for Cs adsorption[3] was assumed to be valid for all the alkali-metal-saturated surfaces at RT. In that model, the alkali-metal atoms are placed in the so-called pedestal sites, i.e., in the middle between two neighboring dimers in the same row, which gives a coverage of 0.5 ML of alkali-metal atoms. (1 ML is defined as 6.78×10^{14} atoms per cm^2, i.e., the same density as for a single Si atomic surface layer). Originally, both theoretical[4] and experimental[5] studies of the K/Si(100)2×1 surface supported this model. The room-temperature saturation coverage and the adsorption sites were then hotly debated issues for several years, partly because of the experimental difficulties in determining the alkali-metal coverages. However, in recent years broad agreement (with few exceptions[6]) has developed around the so-called double-layer model for alkali-metal adsorption on Si(100), originally proposed for the K/Si(100) system.[7] In this model, which is illustrated in Fig. 1, the room-temperature alkali-metal saturation coverage is about one ML, and the alkali-metal atoms sit in two different adsorption sites: the pedestal site and the valley-bridge site (in the trough between the dimer rows, straight between two pedestal sites). A large body of experimental evidence has been obtained, which wholly or partially supports this model, e.g., with x-ray photoelectron diffraction,[7] angle-resolved photoemission[8,9] (ARUPS), inverse photoemission[10,11,12] (IPES), core-level spectroscopy,[13,14] and ion scattering.[15]

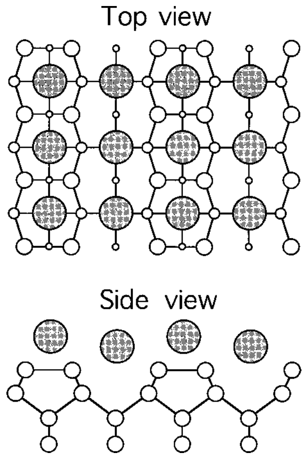

FIG. 1. Schematic illustration of the double-layer model originally proposed for the Si(100)2×1-K surface in Ref. 7. The alkali-metal atoms (large shaded circles) are located both between and on top of the dimer rows right above the third Si layer.

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Similarly, recent theoretical total-energy calculations also support this model.[16,17]

The nature of the alkali-metal–Si bond and the surface metallization are two other widely debated topics, in particular after the early proposal by Ciraci and Batra[4,18] that the alkali-metal–Si bond is strongly ionic at saturation coverages, and consequently that metallization occurs by simple charge transfer from the alkali metal to the substrate surface states. More recent theoretical studies[16,17] have come to a different conclusion, describing the bond as a hybridization of Si dangling bonds and alkali-metal ns-np orbitals, which is then called a polarized covalent bond. Many experimental studies have confirmed the covalent-bond picture, in particular photoemission[6,8,9,13,19] and inverse-photoemission studies.[10,11,12] ARUPS studies have shown a transformation of the dangling-bond band into at least two new bands at alkali-metal saturation coverages, whereas the IPES results have shown the emergence of new dispersing overlayer-derived bands.

The onset of metallization of the RT-saturated K/Si(100)2×1 surface was demonstrated experimentally in our earlier combined IPES/ARUPS study,[10] where it was shown that metallization occurs through occupation of the minimum of a strongly dispersing empty overlayer-derived band at saturation. The combination of IPES and ARUPS in the same spectrometer provides a particularly powerful tool for such studies. Later photoemission[9,20] and scanning tunneling microscopy[21] studies confirmed these results. Our later IPES/ARUPS investigations of Na (Ref. 11) and Li (Ref. 12) adsorption on Si(100)2×1 have shown general similarities to the K/Si(100)2×1 results, but also significant differences in the electronic structure, in particular the lack of metallization in the Li and Na cases.

In the present work we continue our alkali-metal adsorption studies with the investigation of rubidium adsorption on Si(100)2×1. It is shown that saturation coverage of Rb leads to a metallization, similar to K/Si(100), caused by a Rb-induced dispersing empty band, that reaches down to the Fermi level. The combined data from our studies of Li, Na, K, and Rb adsorption on Si(100)2×1 allows us to identify systematic changes in the electronic structure of the alkali-metal-saturated surfaces (at RT) that can be qualitatively related to the size of the alkali-metal adsorbate atoms.

II. EXPERIMENT

The experiments reported here were performed in a two-chamber ultrahigh-vacuum system described elsewhere.[22] The base pressures in the chambers were in the 10^{-11}-mbar range. 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 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 Fermi-level position of a tantalum foil was taken as the energy reference, $E_F=0$. The samples were highly n-doped Si(100) single crystals (ρ=4–8 mΩ cm, arsenic, from Wacker-Chemitronic), cut 4° off the [100] direction, tilting toward [011]. The use of such vicinal samples is a well-known method for obtaining Si(100) surfaces with a single-domain 2×1 reconstruction.[23] On-axis cut, p-doped substrates (ρ=0.02–0.03 Ω cm, boron, from Virginia Semiconductor) were also used, giving a two-domain 2×1 reconstruction. Before insertion into UHV, the samples were cleaned with the Shiraki etching method.[24] Then *in vacuo*, the samples were outgassed at about 600 °C and cleaned by resistive heating at 900 °C for several minutes. Subsequently, good single-domain low-energy electron-diffraction (LEED) patterns for the vicinal samples, and good two-domain 2×1 LEED patterns for the on-axis cut samples, were observed. The surface cleanliness was checked by studying the emission intensity of the contamination-sensitive dangling-bond surface state in ARUPS.

Rubidium was evaporated from a well-outgassed getter source (SAES Getters) onto the samples at RT. The amount of evaporated Rb was indirectly controlled by measuring the change in work function ($\Delta\phi$) as a function of evaporation time.[25] This was done by monitoring the absorption onset of the electron current from the IPES electron gun on the negatively biased sample (diode method). The degree of oxidation due to rest-gas oxygen was monitored with ARUPS. The data presented here were recorded on freshly Rb-covered surfaces without any significant oxidation. The samples were cleaned, and new evaporations were made several times, with excellent reproducibility of the data.

III. RESULTS

The changes in the surface states at $\bar{\Gamma}$ in the surface Brillouin zone with increasing Rb coverage are illustrated in Fig. 2, where IPES and ARUPS spectra recorded at normal incidence and normal emission, respectively, are shown. The data were measured on an on-axis cut Si(100) wafer, with the clean surface showing a good two-domain 2×1 LEED pattern. The Rb coverage was monitored by measuring the change in work function ($\Delta\phi$). The $\Delta\phi$ curve as function of evaporation time is shown in Fig. 3, going down to a shallow minimum at $\Delta\phi=-3.5$ eV and saturating at -3.4 eV. By this coverage a good 2×1 LEED pattern was observed. Our curve is very similar to the one in the earlier photoemission study in Ref. 26 of Rb/Si(100). We expect the saturation coverage to be about 1 ML, similar to K, which is the next smaller alkali metal, and Cs, which is the next larger alkali metal (see, e.g., Ref. 15). As shown below, the similarity to K/Si(100) in the electronic structure gives further strong evidence for this conclusion. With this assumption, the coverages for the different spectra in Fig. 2 may be extracted from Fig. 3 with an uncertainty of about ±0.1 ML.

In the spectra from the clean surface in Fig. 2 (the bottom spectra, $\Delta\phi$=0), contributions from the well-known filled (S_1) and empty[27] (U_1) dangling-bond states are visible at energies -0.5 and 0.4 eV, respectively. The structures above 3 eV and below -2 eV are attributed to Si conduction-band and valence-band emission, respectively. At low Rb coverages, a peak, denoted U_1', appears at the Fermi level in the ARUPS spectra, reaching a maximum for $\Delta\phi=-1.20$ eV. In addition, the whole valence-band spectrum shifts abruptly downwards in energy by 0.3 eV, indicating a band-bending shift. Similar peaks have been seen for low coverages of Li,[28] Na,[13] K,[8,13] and Cs[14] on Si(100). This Fermi peak corresponds to the partial occupation of the previously empty U_1 dangling-bond state, by charge transfer from the alkali-

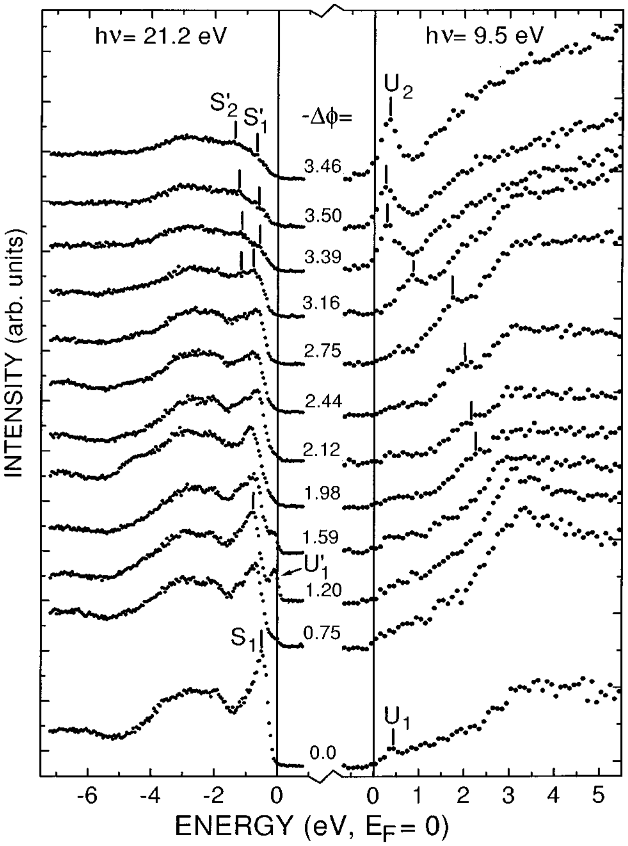

FIG. 2. ARUPS normal-emission and IPES normal-incidence spectra recorded on the Si(100)2×1-Rb surface for increasing Rb coverage. The coverage was indirectly controlled by measuring the work-function shift. The labels are explained in the text.

metal adsorbate's outer *s* level to the substrate. This simple charge transfer effect suggests a mainly ionic bonding at this low coverage (up to 0.2 ML), a conclusion that is also supported by low-energy ion scattering studies of K and Cs adsorption on Si(100).[29] For further increasing coverages, the U_1' peak in the ARUPS spectra fades away, and at high coverages the dangling-bond peak is split into two faint structures S_1' and S_2', which at saturation appear at energies of -0.6 and -1.4 eV, respectively.

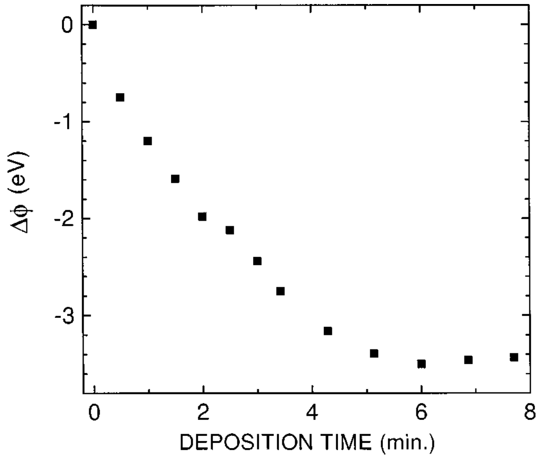

FIG. 3. Measured shifts in the work function, $\Delta\phi$, for the Si(100)2×1 surface as a function of Rb evaporation time.

The band-bending shifts could not be further monitored in this experiment, due to the absence of sharp bulk features in the spectra in Fig. 2. However, the band-bending changes upon increasing Rb coverages on Si(100) were previously measured with core-level spectroscopy in Ref. 30. Similar to the present work,[31] the authors of Ref. 30 found an initial abrupt upward shift by 0.3 eV for the Fermi level (a downward shift for the Si $2p$ core level) at low Rb coverages. For increasing Rb coverages, the Fermi level shifted gradually downward in the band gap, and at room-temperature saturation coverage its energy position was 0.16 eV above the valence-band maximum (VBM).

In the IPES spectra, a new surface-related structure, denoted U_2, appears at an energy of 1.5 eV at a coverage corresponding to $\Delta\phi = -1.98$ eV, i.e., about one-third of the saturation coverage. With further increasing coverage its energy position is shifted downwards, until it reaches the Fermi level at saturation coverage. Due to the limited energy resolution the apparent peak position is about 0.25 eV above E_F. Simple simulations of a Lorentzian peak close to the Fermi edge convoluted with the experimental resolution indicate that the precise peak position within 0.0–0.25 eV above E_F cannot be determined with higher accuracy. However, the fact that a slight emission increase appears at the Fermi level in the corresponding ARUPS spectra indicates a metallization of the surface. This is very similar to the IPES/ARUPS results from the K/Si(100)2×1 surface,[10] although the metallization is not so clearly visible in this case as for K/Si(100). For Cs adsorption on Si(100) at RT, the metallization at saturation coverage is also obvious in the ARUPS spectra of Ref. 14, with a clearly visible Fermi edge.

It is also notable that the emission from the empty dangling-bond state U_1 is still visible at relatively large Rb coverages, up to $\Delta\phi = -2.75$ eV. Similarly, the filled dangling bond S_1 also has a significant intensity up to this coverage.

Figure 4 shows a collection of IPES spectra recorded in the [010] direction on a two-domain surface at the Rb saturation coverage. This direction corresponds to the diagonal $\overline{\Gamma}$-$\overline{J}'$ direction in the surface Brillouin zone (SBZ), which is equivalent for the two domains; see Fig. 5(a). The strong dispersion of the U_2 state is clearly visible, going from 0.2 eV at $\theta = 0°$ to 1.2 eV at $\theta = +28°$. Another striking effect in the spectra is the large difference in the emission intensity of U_2 for large positive and negative incidence angles. This can be explained by considering the experimental geometry, as illustrated in Fig. 5(b). For large negative θ the recorded photons have small emission angles, i.e., close to normal emission, and the polarization vector of the photons is mainly parallel to the surface. Similarly, for large positive θ the recorded photons have large emission angles and the polarization is mixed parallel and perpendicular to the surface. Therefore the higher intensity of U_2 for positive θ indicates a strong p_z character for the state, as explained by calculations of photoionization cross sections for atomic orbitals.[32] The same result was found for the empty state of the K/Si(100)2×1 surface,[10] and was supported by theoretical calculations,[16] which described an empty band corresponding to the U_2 band as having mixed K $4s$-$4p_z$ character.

IPES spectra were also recorded in the [011] and [011]

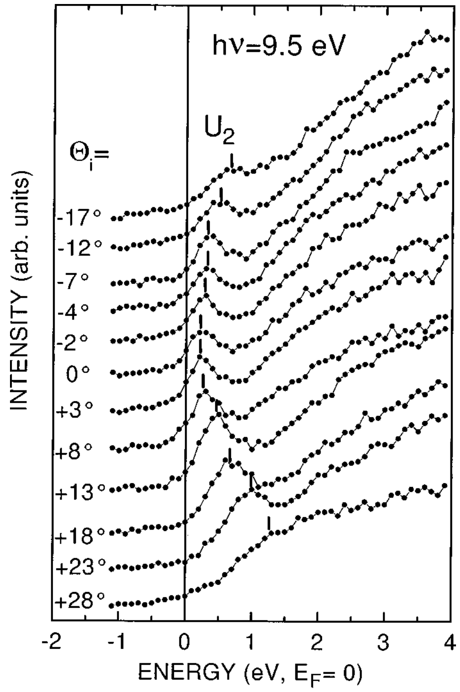

FIG. 4. Inverse-photoemission spectra recorded on the saturated two-domain Si(100)2×1-Rb surface for different incidence angles θ_i along the diagonal [010] direction, i.e., the $\bar{\Gamma}$-$\bar{J}'$ direction of the SBZ. The 2×1 SBZ is shown in Fig. 5(a).

directions, corresponding to $\bar{\Gamma}$-$\bar{J}'$ and $\bar{\Gamma}$-$\bar{J}$ in the SBZ, on a single-domain 2×1-reconstructed surface at a saturation coverage of Rb (data not shown).[33] The dispersion of the U_2 band obtained from these data is plotted in Fig. 6. Remarkably large dispersions, up to 1.4 eV, are observed in both directions, with a paraboliclike shape. This is evidence for a similarly strong interaction between the alkali-metal atoms in both directions, thus supporting the double-layer model for Rb/Si(100)2×1. The paraboliclike shape is also consistent with a Rb $5s$ or Rb $5p_z$ character.[34] The absence of any umklapp-scattered branch in the $\bar{\Gamma}$-$\bar{J}$ direction suggests a weak interaction with the 2×1-reconstructed substrate.

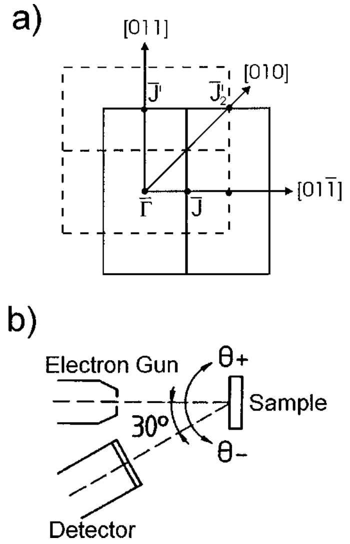

FIG. 5. (a) The surface Brillouin zones (SBZ) for a two-domain 2×1-reconstructed Si(100) surface. (b) The measurement geometry for the IPES experiment.

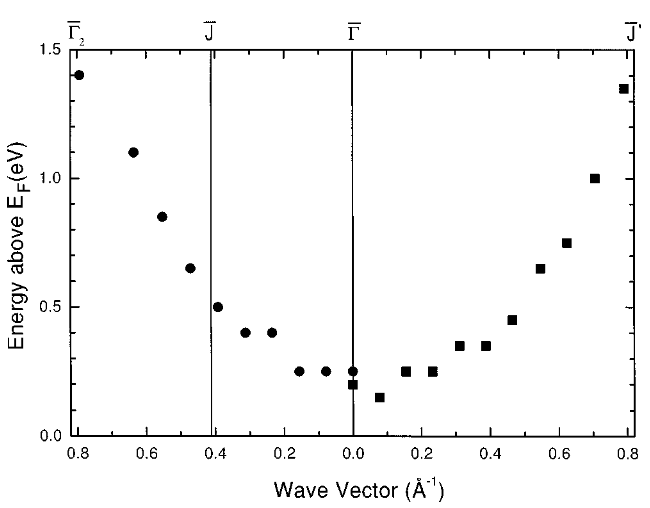

FIG. 6. The measured dispersions of the U_2 state in the [011] and [01$\bar{1}$] directions [see the SBZ in Fig. 5(a)] on a single-domain saturated Si(100)2×1-Rb surface.

IV. DISCUSSION

We first note that the results presented above for the Rb-saturated Si(100)2×1 surface strongly resemble our previous IPES/ARUPS results from the K-saturated Si(100)2×1 surface,[10] as already discussed above. In particular, the appearance and behavior of the empty band U_2 is quite similar, and we therefore make a similar interpretation of this state: i.e., U_2 is a Rb-overlayer-derived state with a strong Rb $5p_z$ character. Its large isotropic dispersion reveals the strong Rb-Rb interaction within the metallic overlayer in both the [011] and [01$\bar{1}$] directions, thereby excluding Levine's 0.5-ML model[3] at the rubidium RT saturation coverage. We also note that although the U_2 state appears to cause a metallization at saturation coverage, the surface electronic structure at 1-ML Rb coverage is expected to be semiconducting (by counting the valence electrons in the 2×1 unit cell), with a surface band gap of about 0.6 eV, as measured in this work. The occupation of the minimum of U_2 is then explained by small amounts of excess charge on the surface, as well as by the deep energy position of the band minimum in the bulk band gap: ~0.2 eV above the VBM.

Very few theoretical and experimental studies of Rb adsorption on Si(100) have been published, in surprising contrast to K and Cs adsorption. However, our ARUPS results presented here agree well with the recent ARUPS study of Rb/Si(100)2×1 in Ref. 26. At the Rb saturation coverage, these authors found, in normal emission, two weak structures at −0.6 and −1.5 eV. For increasing emission angles these structures dispersed toward each other, and when they entered the projected bulk band gap, their intensities became quite strong. The measured dispersions were found to be in qualitative agreement with the surface-state dispersions of K- and Cs-saturated Si(100) surfaces.

Our results fit very nicely into the overall picture that has emerged for RT saturation coverage of alkali metals on Si(100)2×1, i.e., about a full monolayer coverage, arranged

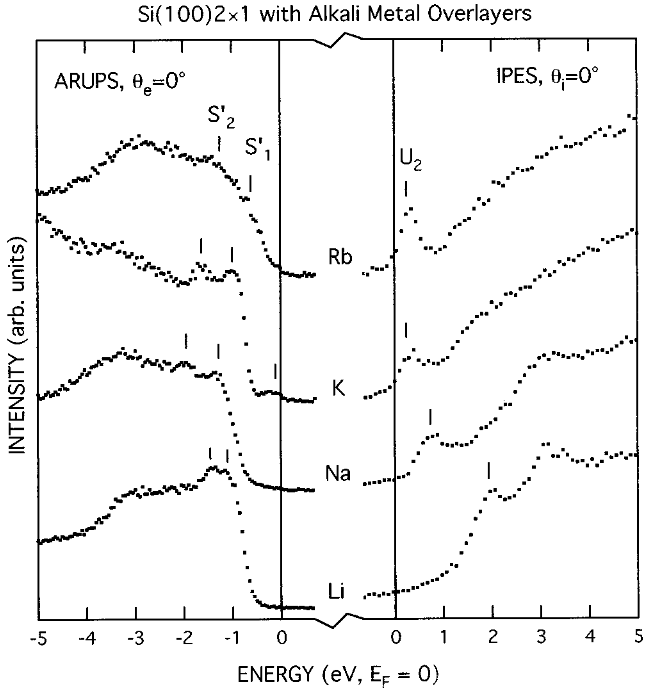

FIG. 7. Comparison of ARUPS normal-emission and IPES normal-incidence spectra recorded from alkali-metal-saturated Si(100)2×1 surfaces for Li, Na, K, and Rb adsorbates. The Li, Na, and K data are taken from Refs. 12, 11, and 10, respectively.

into a double layer above the still dimerized 2×1-reconstructed substrate, a relatively weak polarized covalent Si–alkali-metal bond, and a semiconducting surface band structure (in the ideal 1-ML case; see discussion above). However, within this overall picture there are significant differences between the different alkali-metal adsorbates, and exceptions, as discussed below.

The present results, together with our previous results for Li,[12] Na,[11] and K[10] adsorption on Si(100)2×1, provide a database that allows us to investigate systematically the effects of the size of the alkali-metal adsorbate atoms. The combination of ARUPS and IPES in one spectrometer made it possible to determine unambiguously important parameters of the surface electronic band structure. In particular, the maximum energy of the topmost occupied band at $\bar{\Gamma}$ and the minimum energy of the unoccupied band could be determined by recording an IPES spectrum and an ARUPS spectrum directly after each other on the same surface preparation. Thereby the surface band gap could be (almost) unambiguously determined. This parameter provides information about the strength of the Si–alkali-metal bond. A strong bond leads to a smaller Si–alkali-metal bond length and a larger band gap, whereas a weak bond leads to the opposite.[16] In addition, the bandwidth of the empty overlayer-derived U_2 band gives qualitative information about the strength of the alkali-alkali interaction in the overlayer.

Figure 7 illustrates the differences in surface-state energy positions at $\bar{\Gamma}$ for saturation coverage of the different alkali-metal adsorbates. One can clearly see how the surface band gap monotonically changes from a quite large gap for Li, down to a quite small gap for Rb. This is mainly caused by the movement of the U_2 band minimum downward toward the Fermi level for increasing alkali-metal-atom size. However, the occupied states also move slightly toward the Fermi level for increasing alkali-metal atom size. The energy positions are also influenced by band-bending shifts, as discussed below.

TABLE I. Metallic atomic radii for the alkali atoms and measured surface electronic-structure parameters for saturation coverages of Li, Na, K, and Rb on Si(100)2×1. The data for Rb are from this work and the data for Li, Na, and K are from Refs. 12, 11, and 10, respectively. The absolute U_2 minimum positions are based on measured E_F positions from Refs. 14 and 35. The uncertainties in determining the energy positions are given by the energy resolution of the experimental techniques and the resulting cutoff effects by the Fermi level. The resulting errors for the surface band-gap values are estimated to be ±0.2 eV.

Alkali-metal atom	Metallic atom radius (Å)	Surface band gap (eV)	U_2 min. ref. to E_F (eV)	U_2 min. ref. to VBM (eV)	U_2 bandwidth (eV)
Li	1.52	3.0	2.0	2.3	0
Na	1.86	2.1	0.7	1.25	0.3
K	2.27	1.0	0	0.3	1.4
Rb	2.48	0.6	0	0.2	1.4

One interesting parameter is the absolute energy position of the U_2 band minimum, as it refers to the bulk band structure, for the different alkali-metal adsorbates. This parameter can be obtained if the Fermi-level position at the surface is known. The E_F energy positions for the alkali-metal-saturated Si(100)2×1 surfaces have been determined with core-level spectroscopy[30] to be 0.55, 0.29, 0.16, and 0.06 eV above the valence-band maximum for Na, K, Rb and Cs, respectively. For Li, the E_F position at 1-ML Li coverage is 0.30 eV above the VBM.[35] Hence, the energy of the U_2 band minimum changes monotonically with increasing alkali-metal-atom size from 2.3 eV above the VBM for Li down to 0.2 eV above the VBM for Rb. Following this trend, one expects that for Cs the U_2 minimum lies even further down. Considering that the E_F position is only 0.06 eV above the VBM, and that a clear Fermi edge is seen in ARUPS spectra,[14] we suggest that the U_2 minimum in the Cs case lies below the VBM, thus closing the bulk band gap completely.

The values of the band gaps and U_2 minimum positions, as well as the covalent and ionic radii and the U_2 bandwidths, are shown in Table I. The U_2 bandwidths display the opposite trend, as did the band gaps. For Li the U_2 dispersion is flat, and, for increasing alkali-metal atom size, the bandwidth increases up to about 1.4 eV for K and Rb. The reason for this change can be found by considering the adsorption positions on the Si(100)2×1 surface. In the double-layer model (see Fig. 1), the nearest-neighbor distances for the alkali-metal atoms are 3.84–4.0 Å, giving an atomic radius of about 1.9–2.0 Å. This can be compared to the atomic radii for the alkali-metal atoms in the metallic phase (see Table I). One observes that the larger alkali metals (K, Rb) sit considerably closer to each other on the Si(100)2×1 surface compared to in K and Rb metals, respectively, leading to a strong alkali-alkali interaction and thereby a large U_2 dispersion. The atomic radius of Li, however, is considerably smaller than the Li-Li distance on the Si(100)2×1 surface, leading to small wave-function overlap, i.e., small Li-Li interaction, and thus no dispersion for U_2. In general the wave-function overlap and thereby interaction should thus be larger for increasing alkali-metal-atom size. This is precisely what the U_2 bandwidth differences indicate.

V. CONCLUSION

We have studied rubidium adsorption on the Si(100)2×1 surface with angle-resolved inverse and direct photoemission, LEED, and work-function measurements. The changes in the surface electronic structure for increasing Rb coverages follow the same general pattern as for other alkali-metal adsorbates. The filled dangling-bond state is split into two states, and a new, overlayer-derived empty state appears, which moves downwards toward the Fermi level for increasing Rb coverage. At saturation coverage a metallization is observed, due to the occupation of the minimum at $\bar{\Gamma}$ of this strongly dispersing state. These results fit well into the general picture of alkali-metal adsorption on Si(100)2×1: about 1-ML saturation coverage, with the adsorbate atoms arranged into the so-called double-layer model, a polarized covalent Si–alkali-metal bond, and a semiconducting surface band structure (ideally) at 1-ML coverage.

Our results are compared to the results of our previous ARUPS/IPES studies of Li, Na, and K adsorption on Si(100)2×1. We find that important parameters of the surface electronic structure change systematically with changing alkali-metal-atom size. In particular, the surface band gap decreases for increasing alkali-metal size, indicating a decreasing alkali-metal–Si interaction. On the other hand, the bandwidth of the overlayer-derived empty band increases for increasing alkali-metal size, showing an increased alkali-alkali interaction. This is explained by the fixed alkali-metal-atom nearest-neighbor distance of 3.84–4.0 Å due to the Si(100)2×1 substrate reconstruction. Therefore the larger alkali-metal atoms have a larger wave-function overlap, leading to a larger interaction and thus larger bandwidths.

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