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Destabilization of the Si(111) π-bonded chain structure upon Cs adsorption

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Contrary to previous knowledge, we have found an ordered $\sqrt{3}\times\sqrt{3}R30°$ surface reconstruction on the cleaved Si(111) surface after room-temperature deposition of one monolayer of Cs. The preparation and characterization of this surface, and the dispersion of the lowest unoccupied surface-state band as measured with angle-resolved inverse photoemission spectroscopy are presented. The surface is observed at the saturation of the work function and found to be semiconducting.

Alkali-metal overlayers on silicon surfaces have recently attracted considerable interest. A major motivation is the possibility of studying an adsorption system which from the bonding point of view should be rather simple to describe, since only one alkali valence electron is involved. At the same time alkali adsorption has a very large effect on the electronic properties of the surface, e.g., it produces a large decrease of the work function.

In the case of Cs adsorption on the cleaved Si(111)2×1 surface, experimental work in photoelectron spectroscopy and low-energy electron diffraction (LEED) by Tochihara *et al.*[1] indicated that Cs would not form any ordered overlayer, even at saturation coverage, corresponding to one monolayer (ML). Despite this, the authors could present measurements of the development of a new surface state which made the system metallic. They further deduced that (i) Cs adsorption did not destroy the π-bonded chains[2,3] on the Si(111)2×1 surface, (ii) that Cs bonded only weakly ionic to the substrate, and (iii) that Cs produced a two-dimensional metallic overlayer. These findings were put to a theoretical examination by Ishida, Terakura, and Tsukada[4] who, using a first-principles linear combination of atomic orbitals (LCAO) method, could explain and confirm the experimental picture. Later, Ciraci and Batra[5] calculated the surface electronic structure for the K/Si(111) system, which should compare well with Cs/Si(111). They used a self-consistent pseudopotential method and were able to determine the origin of the experimentally observed effects. These authors disagree with the previous work and show the antibonding π^* state, which on the clean surface is unoccupied to become partly filled by the alkali valence electrons. At monolayer coverage, this metallizes the substrate and not the alkali overlayer.

These analyses[1,4,5] all have one basic condition in common: The π-bonded chain is stable upon alkali adsorption. Although Tochihara *et al.*[1] reported no ordered structure for Cs, the calculations both assumed Cs (and K) to go into a 2×1 structure. In a later paper, Batra and Ciraci[6] studied the potassium adsorption on the ideal Si(111)1×1 surface and found, within their adsorption-site model, this adsorption system to have 0.3 eV lower total energy than found for the adsorption on the π-bonded chain structure.

This paper describes the findings from an experiment aimed at shedding more light on the issues of controversy discussed above. With angle-resolved inverse photoemission spectroscopy it should be possible to observe the unoccupied surface states of this adsorption system,[7] and conclude which one of the proposed theoretical models agrees with the experimental results. Our results showed, however, that the above-mentioned basic condition is not valid. Here we are presenting the first observed ordered structure of the Cs/Si(111) system, and we claim that the monolayer coverage of Cs on cleaved Si(111) destabilizes the π-bonded chain structure and induces a $\sqrt{3}\times\sqrt{3}R30°$ reconstruction.

The preparation and characterization of the surface as well as the inverse photoemission measurements were performed in the same vacuum system described elsewhere.[8] Single-crystalline bars of p-doped silicon (resistivity $\rho\approx 0.05$ Ω cm) with a cross-section area of 5×5 mm^2 were cleaved using a knife-and-anvil technique. By cleaving along the [$\bar{2}$11] direction, single-domain 2×1-reconstructed surfaces could be produced and checked with low-energy electron diffraction. Angle-integrated ultraviolet photoelectron spectroscopy (UPS) showed a strong contribution from the occupied dangling-bond surface state. Evaporation of Cs was done by passing current through a well-outgassed dispenser (SAES Getters), with the substrate held at room temperature. During evaporation the pressure never exceeded 1×10^{-10} mbar, while the base pressure was always better than 5×10^{-11} mbar. The evaporation rate was checked with a crystal monitor, but the actual coverage was determined from the change of the secondary electron cutoff energy in UPS. Figure 1 shows the change in the cutoff for a cleaved Si(111) surface exposed to successive evaporations of Cs. After the first evaporation, a downward band bending of 0.15 eV was observed from the shift of the uppermost Si valence states, in agreement with Ref. 1. The cutoff decreases almost linearly until it reaches a saturation value of -3.7 eV. In the saturation region of the cutoff and thus of the work function, a well-ordered $\sqrt{3}\times\sqrt{3}R30°$ LEED pattern (from now on denoted $\sqrt{3}\times\sqrt{3}$) was observed. We interpret this coverage as the completion of the first monolayer. At lower coverages, only a 2×1 pattern of decreasing quality could be observed. It is attributed to a disordered Cs overlayer perturbing the Si(111)2×1 surface. In Fig. 1 the cutoff energy reaches a minimum after 9 min of evaporation and then starts to increase again. From the

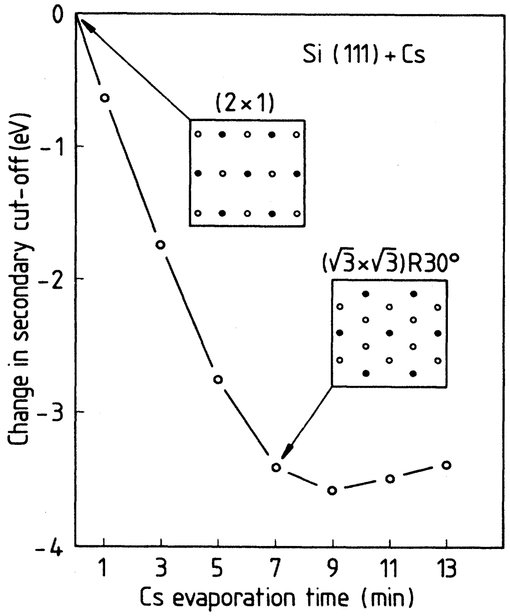

FIG. 1. The change in the cutoff energy for secondary electrons in UPS from the Cs/Si(111) surface as a function of Cs evaporation time. The LEED patterns observed at zero coverage and after 7 min are shown as insets. The latter is attributed to the full-monolayer coverage.

change in the valence-band emission we believe this to be an effect of oxidation. The apparent lifetime of the monolayer Cs-covered surface was ~2 h during measurements.

The angle-resolved inverse photoemission measurements were performed using an electron gun with a beam divergence of less than 3° and a Geiger-Müller–type detector counting photons of energy $h\nu = 9.5$ 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 could be interchanged with the silicon crystal. The position of the tantalum Fermi level E_F was used as reference energy.

In Fig. 2 we present a series of inverse photoemission spectra for different angles of incidence θ probing states along the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ line in the $\sqrt{3}\times\sqrt{3}$ surface Brillouin zone (SBZ). The tick-marked structures fall into an energy range where no Si bulk features appear as known from previous work,[9] and are thus identified as emission from a surface state. The peak moves to higher final-state energies with increasing angles, reaching a maximum between $\theta = 20°$ and 25°. This corresponds to the $\bar{K}'$ point in the SBZ at $k_{\parallel} = 0.63$ Å^{-1}. For higher incidence angles, probing the $\bar{K}'$-$\bar{M}'$-$\bar{K}'$ line, the peak moves down through a minimum before it turns up again, with an apparent symmetry around $\theta = 35°$ corresponding to the $\bar{M}'$ point in the SBZ. Figure 3 shows a similar series of spectra along the $\bar{\Gamma}$-$\bar{M}'$ line in the SBZ. Here the surface structure shows hardly any movement in final-state energy within our experimental accuracy.

The data have been analyzed in the usual way, taking into account the lowering of the work function [from 4.85 eV for the clean Si(111) (Ref. 10) to 1.15 eV for the $\sqrt{3}\times\sqrt{3}$-Cs surface]. They are presented in Fig. 4, converted into measured points of the $E_f(k_{\parallel})$ dispersion for the lowest unoccupied surface state on the Si(111)$\sqrt{3}\times\sqrt{3}$-Cs surface. The crosses represent the experimental accuracy in determining peak energy positions and the uncertainty in incidence angle. The inset shows the irreducible part of the SBZ in relation to the projected bulk BZ and the corresponding crystal directions. Energies are referenced to the valence-band maximum, $E_V = E_F - 0.55$ eV.[11] Note the symmetric dispersion around the $\bar{M}'$ point in both directions. Since the dispersion for the surface state is more pronounced along the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ than along the $\bar{\Gamma}$-$\bar{M}'$ direction, there must be a larger interaction between the involved electronic states on neighboring atoms along a $\langle 11\bar{2}\rangle$ than along a $\langle 10\bar{1}\rangle$ direction.

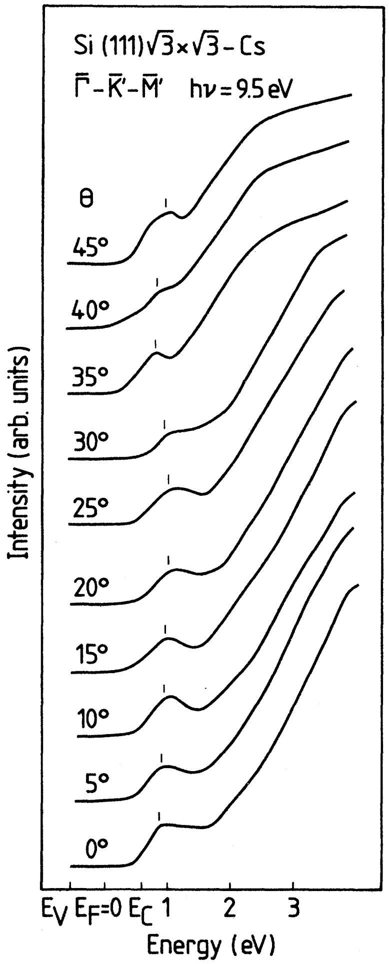

FIG. 2. Angle-resolved inverse photoemission spectra at $h\nu = 9.5$ eV for different incidence angles θ, probing states along the $\bar{\Gamma}$-$\bar{K}'$-$\bar{M}'$ line in the Si(111)$\sqrt{3}\times\sqrt{3}$-Cs SBZ.

The appearance of an ordered $\sqrt{3}\times\sqrt{3}$ structure on Si(111) surfaces upon metal deposition has been found for a large number of metals. For most systems, including Al, Ga, and In,[12] the coverage was found to be $\frac{1}{3}$ ML and structure models have been derived from comparison be-

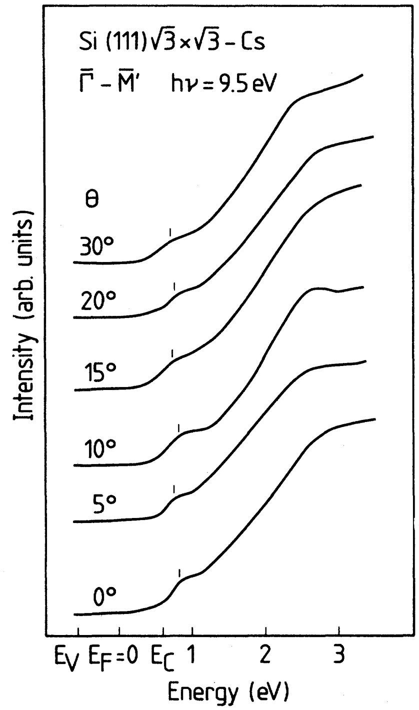

FIG. 3. As in Fig. 2, but probing states along the $\bar{\Gamma}$-$\bar{M}'$ line in the Si(111)$\sqrt{3}\times\sqrt{3}$-Cs SBZ.

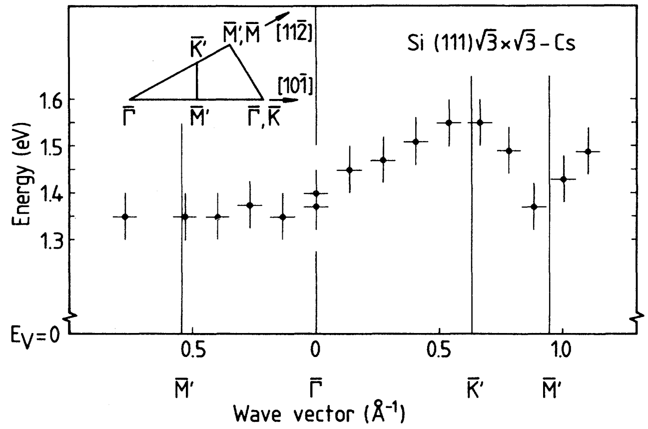

FIG. 4. The final-state energy dispersion $E_f(k_{\parallel})$ for the tick-marked peaks in Figs. 2 and 3. This represents the lowest unoccupied-surface-state on the Si(111)$\sqrt{3}\times\sqrt{3}$-Cs surface. The crosses indicate the estimated uncertainty. The inset shows the irreducible part of the SBZ in relation to the projected bulk Brillouin zone and the corresponding crystal directions.

tween calculations and experiments as well as from scanning tunneling microscopy work.[13] However, in two recent papers, the $\sqrt{3}\times\sqrt{3}$ reconstruction has been shown to appear at 1 ML coverage for Sb (Ref. 14) and Pd (Ref. 15) on Si(111) surfaces. A reflection high-energy electron-diffraction study has further shown that the alkali-metal Li on Si(111) can be annealed to a $\sqrt{3}\times\sqrt{3}$ reconstruction.[16]

The characteristic differences between the Si(111)$\sqrt{3}\times\sqrt{3}$-Cs and, e.g., Si(111)$\sqrt{3}\times\sqrt{3}$Sb (Ref. 14) are that the Cs structure appears at room-temperature saturation coverage and that the unoccupied-surface-state dispersion is upward along $\bar{\Gamma}$-$\bar{K}'$, for Si(111)$\sqrt{3}\times\sqrt{3}$-Cs, while it is downward for Sb. This is also true in comparison with Al, Ga, and In.[12] The differences in the surface-state dispersions indicate a considerably different bonding situation, the origin of which lies in the initial substrate surface structure, 2×1 or 7×7, as well as in the differing adsorbate-substrate and adsorbate-adsorbate interactions. In the existing theoretical models for alkali metals on the Si(111) surface,[4,6] the interactions have, in principle, already been calculated. It should be interesting to compute the electronic structure for different models of this surface.

In summary, we have found that room-temperature deposition of a monolayer of Cs on the cleaved Si(111)2×1 surface removes the π-bonded chains and produces a $\sqrt{3}\times\sqrt{3}R30°$ reconstruction accompanied by a change in work function of -3.70 eV and a band bending of 0.15 eV. The appearance of this ordered structure is at variance with all previous predictions and experiments. The energy dispersion of the lowest unoccupied-surface-state band has been measured and shows a nonmetallic, semiconducting state of this surface. The need for renewed attention to the problem of alkali-metal overlayers on Si(111) is obvious.

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