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Surface states of ordered Au, Ag, and Cu overlayers on Si(111) studied by inverse photoemission

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The $\sqrt{3}\times\sqrt{3}$-Au, $\sqrt{3}\times\sqrt{3}$-Ag, "5×5"-Cu, and 6×6-Au overlayer interfaces on Si(111) are studied with k-resolved inverse photoemission. Strong surface-state emission is observed at ~2.0 eV above the Fermi level for all these surfaces, which is attributed to the local bonding between the metal atoms and the Si(111) substrate. The long-range order of the larger unit cells manifests itself as weak surface states at the Fermi level.

Lately, the geometric and electronic properties of ordered overlayers of metals on semiconductor surfaces have gained increasing interest in experimental as well as in theoretical studies. To this day though, very few direct observations of the unoccupied surface-state bands have been made from such interfaces. The technique of k-resolved inverse-photoemission spectroscopy (KRIPES) has so far been applied mainly to the study of unoccupied states on clean surfaces of metals and semiconductors.[1-4] In these studies, KRIPES has made possible accurate determinations of bulk and surface band structures. In the present work, KRIPES is applied to the ordered interfaces of Au, Ag, and Cu overlayers on Si(111).

In a recent study of image and field states of surfaces,[5] the close relationship between inverse photoemission and tunneling spectroscopy[5] has been stressed. A particularly interesting surface system studied with tunneling spectroscopy (TS) and scanning tunneling microscopy (STM)[6] is that of the Au/Si(111) interface.[7] In this study, regions of $\sqrt{3}\times\sqrt{3}R(\pm30°)$ and 6×6 reconstructed areas on the same sample surface have been observed to show different surface electronic structure. [The $\sqrt{3}\times\sqrt{3}R(\pm30°)$ unit cells are hereafter denoted $\sqrt{3}\times\sqrt{3}$.] The electronic structure of the Au/Si(111) interface as revealed by the spatially very local probe of TS and STM is compared in the present study with that probed locally in reciprocal space by KRIPES.

Room-temperature-deposited overlayers of noble metals on Si(111) are known to give several different surface reconstructions upon annealing.[8] Among the systems studied are the $\sqrt{3}\times\sqrt{3}$-Au,[9-11] 6×6-Au,[9] $\sqrt{3}\times\sqrt{3}$-Ag,[12-15] and quasi-5×5-Cu overlayers.[16,17] One of the most interesting properties of these surfaces is the local atomic geometry and the type of bonding involved. Do the noble metals form similar local bonds on the Si(111) surface in analogy with that observed for group-III metals on Si(111)?[18,19] Unfortunately, no detailed band-structure calculations for the noble-metal overlayers exist.[20] However, by comparing the measured electronic structures of the different metal overlayers, valuable information can be gained, and the differences and similarities can be related to the various unit cells present.

In the inverse-photoemission experiment, a well-collimated electron beam (beam divergence $\Delta\theta\leq3°$) is produced from a custom-made electron gun[21] with an indirectly heated BaO cathode. A Geiger-Müller-type photon detector filters photons of energy $h\nu=9.7$ eV, and a total energy resolution (photons and electrons) of $\Delta E\sim0.7$ eV is obtained.[22]

The clean and metal-deposited surfaces were characterized with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS) ($h\nu=21.2$, 40.8 eV). Clean and well-ordered Si(111)7×7 surfaces were produced by resistive heating of the sample (p doped ~0.03 Ωcm) up to $\sim1100\,°$C. The ordered metal overlayers were produced by evaporating ultrapure metals from well out-gassed Ta filaments, with the sample at room temperature, followed by careful annealing. During evaporation, no simultaneous registration of the deposited amounts was made, but coverages were subsequently determined from the AES signal ratios. The base pressure in the ultrahigh-vacuum (UHV) system was $\leq5\times10^{-11}$ Torr, and remained below 3×10^{-10} Torr during evaporation and annealing.

Inverse-photoemission spectra recorded for the clean Si(111)7×7 surface and for the ordered gold overlayer surfaces Si(111)$\sqrt{3}\times\sqrt{3}$-Au and Si(111)6×6-Au are shown in Fig. 1. For a wide interval of angles of the incident electrons, three structures are present on the Si(111)7×7 surface, here denoted S_1, A_1, and B_1 at normal incidence. As previously reported,[23] a surface state (S_1) is present at ~0.5 eV above the Fermi level (E_F) on this surface. The structures A_1 and B_1 show no sensitivity to contamination and are associated with unoccupied states in the bulk conduction-band structure. Further, the energy positions of these structures are in good agreement with two conduction bands observed with inverse photoemission by Straub, Ley, and Himpsel[24] on the Si(111) 2×1 surface.

Spectra recorded for the Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface are shown in Fig. 1 for various angles of incidence along the $\bar{\Gamma}$-$\bar{K}$ direction in the 1×1 surface Brillouin zone (SBZ). For normal incidence ($\theta=0°$), a strong Au-induced surface feature (S_2) is situated at ~1.7 eV above the Fermi level. For larger angles of incidence on both sides of the surface normal, the S_2 peak decreases in intensity and is not clearly separated from the bulk features. Similar emission patterns with strong intensity close to normal incidence are observed for dispersing unoccupied adatom-induced surface states for the group-III metals on

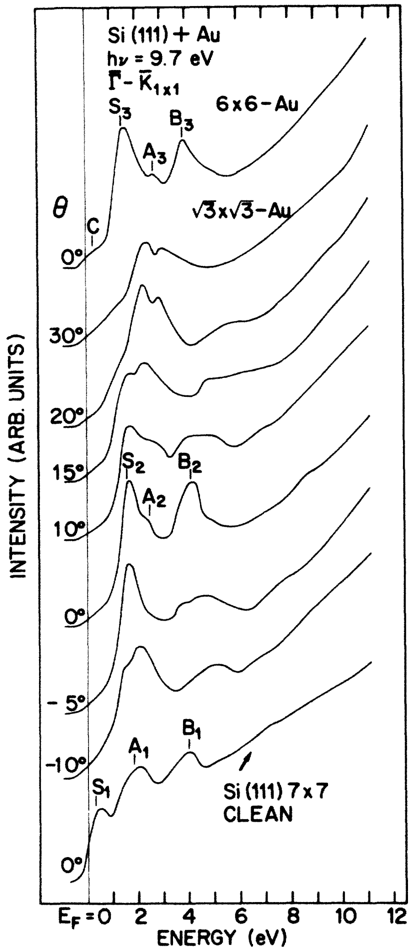

FIG. 1. Inverse-photoemission spectra from the Si(111)7×7, Si(111)$\sqrt{3}\times\sqrt{3}$-Au, and Si(111)6×6-Au surfaces. Strong surface states are observed for the overlayer surfaces, different from that of the clean surface. For the 6×6-Au reconstruction, the surface state (S_3,∼1.5 eV) is shifted relative to that of the $\sqrt{3}\times\sqrt{3}$ reconstruction (S_2,∼1.7 eV), and an additional shoulder (C) is present at the Fermi level.

Si(111).[19] A comparison with the inverse-photoemission spectra of the clean Si(111)7×7 surface, to sort out fully the surface and bulk contributions for larger angles, is not possible since the spectra from this surface do not reveal the bulk features clearly enough. Instead the bulk features are smeared out, probably owing to surface umklapp scattering. To verify that the S_2 peak corresponds to an interfacial state of the ordered Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface, spectra were also recorded from the surfaces of thick room-temperature Au deposits. These spectra showed only a uniform distribution down to the Fermi-level cutoff, and no features similar to the S_2 peak were present. At normal incidence, two structures (A_2, B_2) are present at about the same energies as the A_1 and B_1 structures for the clean Si(111)7×7 surface, and consequently these are associated with the Si bulk conduction-band structure. The peak B_2 is more pronounced for the Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface, probably owing to less scattering from the ($\sqrt{3}\times\sqrt{3}$)-reconstructed surface, as compared to the (7×7)-reconstructed surface.

It is known that for deposits of more than 1.0 ML of Au on Si(111), a 6×6 reconstruction appears on continued annealing.[9] In the present case, a sharp surface feature is present for the 6×6-Au surface at a lower energy, $E_F+1.5$ eV (see Fig. 1, topmost spectrum). The bulk peak (B_3) now has a somewhat different shape with a weak shoulder on the high-energy side. A very weak shoulder at the Fermi level increased in intensity (structure C, topmost spectra) as the $\sqrt{3}\times\sqrt{3}$ reconstruction transformed to 6×6. Thus, it seems as if the strong peak corresponds to the Si-Au bonding for a complete monolayer, and that the weak structure at the Fermi level corresponds to Au-Au metallic bonding, forming from atoms on top of the first monolayer. Such an interpretation would be in analogy with the STM topography measurement,[7] where the 6×6 reconstruction is observed to consist of a regular pattern of incomplete $\sqrt{3}\times\sqrt{3}$ cells. In the TS measurement (dI/dV vs V) of the Au/Si(111) interface,[7] a relatively broad surface peak at ∼1.5 V was observed to shift to lower voltages and simulataneously sharpen up considerably when going from the ($\sqrt{3}\times\sqrt{3}$)- to the (6×6)-reconstructed surface.

To verify the surface-state character of the Au-induced peak (S_2) for the $\sqrt{3}\times\sqrt{3}$ reconstruction, the surface was exposed to various amounts of hydrogen and oxygen gas, activated by a hot filament. The inverse-photoemission spectra of the Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface were largely unaffected by these treatments, and not before exposure of several thousands of langmuirs (1 L$=1\times10^{-6}$ Torr sec) were any effects observable. Then, however, the whole spectrum including the bulk features was influenced, and a separation of surface features from bulk features could still not be performed unambiguously. The inertness of this surface[10] is natural in the case that the gold-induced feature originates from the bonding orbitals between the silicon "substrate" and the Au adatoms. In contrast, the unoccupied surface state on the clean Si(111)7×7 surface, originating from dangling-bond orbitals or weaker adatom bonds, is much more sensitive to contamination.[19]

To study further the nature of noble-metal–semiconductor interfaces, and to verify the surface-state character of the gold-induced features, ordered overlayers of silver and copper on Si(111) were also studied. On annealing a room-temperature deposit of silver on the Si(111)7×7 surface, a ($\sqrt{3}\times\sqrt{3}$)-reconstructed surface can be produced, and for this surface a bonding geometry similar to that of the Si(111)$\sqrt{3}\times\sqrt{3}$-Au surface can be expected. On annealing Si(111)7×7 surfaces with various amounts of copper (parts of monolayers to several monolayers) deposited at room temperature, an incommensurate structure is found, previously reported as a 5×5 superstructure.[25] Careful investigations of this surface show that the observed reconstruction relates neither to a 5×5 nor a 6×6 pattern, but that an average value of 5.3 is found for the surface periodicity with LEED.[16] This structure will hereafter be referred to as a "5×5" structure.

Figure 2 shows inverse-photoemission spectra for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface, along the $\bar{\Gamma}$-$\bar{K}$ direction in the 1×1 SBZ, and Fig. 3 shows spectra for the Si(111)"5×5"-Cu surface along the $\bar{\Gamma}$-$\bar{M}$ direction. For the $\sqrt{3}\times\sqrt{3}$-Ag surface, a surface state (S_4) is present at

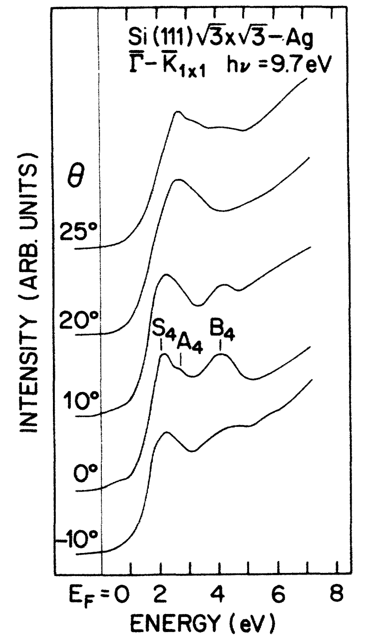

FIG. 2. Inverse-photoemission spectra from the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface. A surface state (S_4) similar to that of the $\sqrt{3}\times\sqrt{3}$-Au surface is present at ~2.0 eV above the Fermi level for normal incidence.

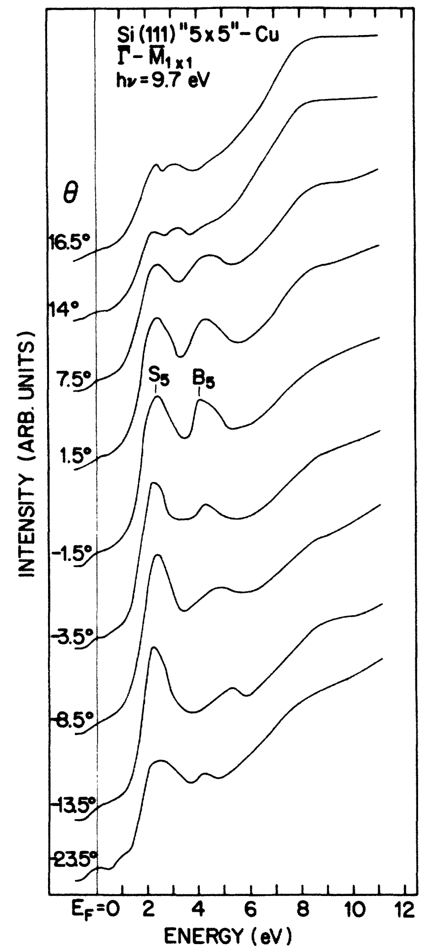

FIG. 3. Inverse-photoemission spectra from the Si(111)"5×5"-Cu surface. A strong surface state (S_5) is present for a wide interval of angles at ~2.2 eV above the Fermi level.

~2.1 eV above the Fermi level which is 0.4 eV higher in energy than the S_2 state for the $\sqrt{3}\times\sqrt{3}$-Au surface (see Fig. 1). For various angles of incidence, a relatively broad structure is present in the spectra as the surface state coincides with the bulk states. From comparison with the spectra of the $\sqrt{3}\times\sqrt{3}$-Au surface, it can be concluded that either the S_4 state undergoes strong intensity variations or it disperses towards higher energies. The "5×5"-Cu reconstructed surface shows an even stronger surface peak (S_5) at ~2.4 eV above the Fermi level, 0.7 eV above the Au-induced S_2 peak (see Fig. 3). The spectra from the Si(111)"5×5"-Cu surface have a general shape different from those of the $\sqrt{3}\times\sqrt{3}$-Au,Ag surfaces (Figs. 1 and 2). The surface peak S_5 is wider and remains with a high intensity at nearly the same energy for a wide region of angles.

For the clean Si(111)7×7 surface and for the other overlayer surfaces, the bulk structure A at about the same energy as the peak S_5 is of the same size or smaller than the bulk structure B, i.e., also for the ($\sqrt{3}\times\sqrt{3}$)-reconstructed surfaces, where a reduced umklapp scattering is expected. It is less probable therefore, that the strong peak S_5 in Fig. 3 would correspond to the bulk state A. For additional evaporation of Cu onto the "5×5"-Cu surface, the peak S_5 has disappeared while the bulk peak B_5 is still visible. This further indicates the surface-state character of the S_5 peak, and that it corresponds to the Cu-Si interface formation. However, the S_5 peak may also contain some contribution from the lower-lying bulk state (at some incidence angles the structure appears to be composed of two features). The less pronounced angular dependence of the bulk state B_5 as well as the existence of a structure of relatively high intensity at the Fermi level, suggest similarities between the Si(111)"5×5"-Cu and Si(111)7×7 surfaces.

Since the spectra in Figs. 1–3 are recorded with the electron gun and the photon detector in a fixed position relative to each other, and the angle of incidence as well as the acceptor angle of the photon detector are simultaneously varied, matrix-element effects may be expected and the intensity of the surface states may vary on the two sides of the surface normal. The bulk states are symmetric on both sides of the normal when the $\bar{\Gamma}$-$\bar{K}$ direction is probed, but also in this case strong intensity variations can be expected on different sides of the surface normal.

As sharp metal-induced structures are observed for all the noble-metal overlayer surfaces, but at different energies relative to the bulk states, there is little doubt that these features are really surface states. A somewhat surprising result is that the surface features are so similar in shape and in energy position for the small size $\sqrt{3}\times\sqrt{3}$ unit cells and the larger 6×6 and "5×5" unit cells. This indicates that the observed surface states originate from a similar bonding mechanism, and are predominantly local in nature. This is in analogy with that observed for the group-III metals on Si(111), where good agreement with existing band calculations is observed,[19] and the strong surface features can be assigned to the local chemical bonding of the interface. In contrast, the weak contributions at the Fermi level for the 6×6-Au and "5×5"-Cu surfaces can be attributed to the long-range order of the reconstructions.

From a number of different experimental techniques, several models have been proposed for the reconstructed noble-metal–Si(111) interfaces for various coverages.[8,11,12,15,17] It is evident though that band-structure calculations of energy-minimized geometries are needed for these surfaces for a detailed understanding of their geometric and electronic properties.

To summarize, different types of noble-metal/Si(111) surfaces have been observed to have similar but significantly different electronic structures. The small size unit-cell surfaces Si(111)$\sqrt{3}\times\sqrt{3}$-Au and Si(111)$\sqrt{3}\times\sqrt{3}$-Ag have strong unoccupied surface states at the center of the surface Brillouin zone, whereas the Si(111)"5×5"-Cu surface has a large unit-cell character with a nearly dispersionless surface-state band. The Si(111)6×6-Au surface has a strong unoccupied surface state, shifted relative to that of the $\sqrt{3}\times\sqrt{3}$-Au surface, in agreement with tunneling spectroscopy measurements. It is suggested that the pronounced surface states observed on these surfaces correspond to the local bonding between the Si(111) substrate and the noble-metal atoms.

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[1] N. V. Smith, Vacuum **33**, 803 (1983).

[2] V. Dose, J. Phys. Chem. **88**, 1681 (1984).

[3] F. J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. **2**, 815 (1984).

[4] B. Reihl, Surf. Sci. **162**, 1 (1985).

[5] G. Binnig, K. H. Frank, H. Fuchs, N. Garcia, B. Reihl, H. Rohrer, F. Salvan, and A. R. Williams, Phys. Rev. Lett. **55**, 991 (1985).

[6] G. Binnig and H. Rohrer, Physica B **127**, 37 (1984).

[7] F. Salvan, H. Fuchs, A. Baratoff, and G. Binnig, Surf. Sci. **162**, 634 (1985).

[8] For a review, see G. Le Lay, Surf. Sci. **132**, 169 (1983).

[9] G. Le Lay and J. P. Faurie, Surf. Sci. **69**, 295 (1977).

[10] F. Houzay, G. M. Guichar, A. Cros, F. Salvan, R. Pinchaux, and J. Derrien, J. Phys. C **15**, 7065 (1982).

[11] K. Oura, M. Katayama, F. Shoji, and T. Hanawa, Phys. Rev. Lett. **55**, 1486 (1985).

[12] G. V. Hansson, R. Z. Bachrach, R. S. Bauer,and P. Chiaradia, Phys. Rev. Lett. **46**, 1033 (1981).

[13] F. Houzay, G. M. Guichar, A. Cros, F. Salvan, R. Pinchaux, and J. Derrien, Surf. Sci. **124**, L1 (1983).

[14] T. Yokotsuka, S. Kono, S. Suzuki, and T. Sagawa, Surf. Sci. **127**, 35 (1983).

[15] J. Stöhr, R. Jaeger, G. Rossi, T. Kendelewicz, and I. Lindau, Surf. Sci. **134**, 813 (1983).

[16] E. Daugy, P. Mathiez, F. Salvan, and J. M. Layet, Surf. Sci. **154**, 267 (1985).

[17] S. A. Chambers, S. B. Anderson, and J. H. Weaver, Phys. Rev. B **32**, 581 (1985).

[18] J. M. Nicholls, P. Mårtensson, G. V. Hansson, and J. E. Northrup, Phys. Rev. B **32**, 1333 (1985).

[19] J. M. Nicholls and B. Reihl (unpublished).

[20] Preliminary calculations have been made for the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface: H. Nagayoshi, Solid State Sci. **59**, 167 (1985).

[21] P. W. Erdman and E. C. Zipf, Rev. Sci. Instrum. **53**, 225 (1982).

[22] V. Dose, Appl. Phys. **14**, 117 (1977); B. Reihl and R. R. Schlittler, Phys. Rev. B **29**, 2267 (1984).

[23] T. Fauster and F. J. Himpsel, J. Vac. Sci. Technol. A **1**, 1111 (1983).

[24] D. Straub, L. Ley, and F. J. Himpsel, Phys. Rev. Lett. **54**, 142 (1985).

[25] J. T. Grant and T. W. Haas, Surf. Sci. **23**, 347 (1970).