

Observation of Changes in the Electronic Structure on Normal and Reconstructed Au(100) using Angle-Resolved Photoemission

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Angle-resolved photoemission spectra of Au(100)-(1×1) and -(5×20) surfaces were obtained for the Γ LUX Γ and Γ XWK Γ mirror planes of the bulk Brillouin zone. Peaks were observed, which can be removed by changing the surface order, and were attributed to surface states near symmetry points of the corresponding surface Brillouin zones. Other emission peaks, attributed to bulk transitions show drastic changes in intensity for different surface order.

We have obtained angle-resolved energy-distribution curves (AREDC's) for photoelectrons emitted from normal and reconstructed Au(100), using the photon energies 21.22 and 16.85 eV. The main results of our measurements are as follows. (i) For certain emission angles, the AREDC's contain narrow peaks above the bulk d bands, which disappear when the surface configuration is converted from (1×1) to (5×20), or vice versa. These results show that localized surface states exist near the symmetry point \bar{M} of the square and hexagonal surface Brillouin zone, for the (1×1) and (5×20) configurations, respectively. The surface states are analogous to those recently observed¹ on Cu(100) and Cu(111). Our result for the (5×20) surface constitutes the first observation of surface-energy-band dispersion for a reconstructed metal surface, which is not present on the normal surface. (ii) Bulk d -band transitions around the surface normal exhibit a drastic increase in intensity for the reconstructed (5×20) surface. This behavior is explained by different selection rules for normal emission in the fourfold and sixfold symmetry of the two surfaces. (iii) Evidence is presented that the reconstruction induces bulk sp transitions which are dipole forbidden for the normal surface. This effect is attributed to the breakdown of reflection symmetry on the reordered top layer.

It is now well established that the metals Au, Ir, and Pt exhibit a reordered atomic structure on the (100) and (110) surfaces under clean surface conditions.² The (5×20) reconstruction of Pt(100) and Au(100) single crystals has been described as the formation of a close-packed hexagonal overlayer, in which six rows of atoms extend over five rows of substrate atoms.² A slight

buckling of the top layer may occur, because of the nonsymmetrical positions of the first-layer atoms with respect to the substrate. Two domains, oriented at right angles to each other, produce a fourfold low-energy electron diffraction (LEED) pattern with one-fifth-order spots.

Procedures have been devised to prepare well-ordered (1×1) surfaces for the (100) orientation of Au, Ir, and Pt. For Au(100) a reactive-ion bombardment produces a metastable surface with a sharp (1×1) LEED pattern³; heating to more than 100°C quickly converts the surface to the stable (5×20) configuration. For Ir(100) (Ref. 4) and Pt(100) (Ref. 5) adsorption of carbon monoxide or oxygen must be followed by a careful removal of the adsorbate layer.

Earlier photoemission studies of Ir(100) (Ref. 4) and Pt(100) (Ref. 5) showed that the emission spectra of the normal surfaces contain peaks near the Fermi energy E_F . These peaks, which can be markedly attenuated by converting to the (5×20) configuration, were attributed to features in the (1×1) surface density of states. It was conjectured that the surface density of states near E_F provides the driving force for the reconstruction.⁵ Electron-energy-loss spectra were obtained for Au(100) in both surface configurations.³ The spectra depended on the surface order, and were essentially unaffected by residual oxygen, deposited during the ion bombardment.

We obtained AREDC's of Au(100) using a photoelectron spectrometer⁶ whose energy and angular resolution is better than 60 meV, and $\pm 2^\circ$. The spark-cut samples were electropolished before insertion into a preparation chamber outfitted with LEED optics and an ion gun. Repeated cycles of Ar-ion bombardment and heating produced

a clean surface with a (5×20) LEED pattern. To convert the sample to the metastable (1×1) configuration we bombarded the surface with dry-air ions at 200-eV energy and $1\text{-}\mu\text{A}/\text{cm}^2$ current density for about half an hour.³ This treatment led to a sharp (1×1) LEED pattern. Auger spectra taken from the bombarded surface showed no impurity peaks. Annealing at temperatures higher than 100°C converted the surface back to its (5×20) form.

AREDC's of Au(100) obtained at 21.22-eV photon energy are displayed in Fig. 1, for normal emission ($\theta = 0^\circ$) and for a succession of polar angles $\theta \geq 45^\circ$ in the $\Gamma XWK\Gamma$ plane of the bulk Brillouin zone. Results for the (1×1) and (5×20) surfaces are given in the right and left part of Fig. 1, respectively. In the normal-emission spectra the main differences (indicated by vertical lines) appear as an intensity increase of the d -band emission especially on the high-energy side due to the formation of the reconstructed (5×20) surface. Although we use unpolarized light only initial states of Δ_5 and Δ_1 symmetry are allowed for the

normal surface.⁷ These selection rules are strongly affected when the surface reconstructs from the fourfold to the sixfold symmetry of the (5×20) configuration and give rise to different intensities of certain transitions. A similar effect can be seen in the emission spectra at higher polar angles. For $\theta \geq 50^\circ$, a broad peak observed near E_F for the reconstructed surface is absent for the normal surface. We conjecture that this extra emission is due to bulk sp -band transitions which are dipole forbidden in the (1×1) configuration. The (5×20) reconstruction breaks the reflection symmetry, and hence the selection rules,⁷ of the $\Gamma XWK\Gamma$ emission plane; see the insets of Fig. 1.⁸

The data of Fig. 1 also contain a peak (labeled *a*) which is present only for the normal surface; it appears about 1.6 eV below E_F at $\theta = 50^\circ$. Peak *a* lies close to a bulk d -band peak (labeled *b*) which is present for both surfaces. As seen in Fig. 2, for a photon energy of 16.85 eV a similar peak (denoted *a*) is observed from the (1×1) surface with somewhat higher intensity. Its sensitiv-

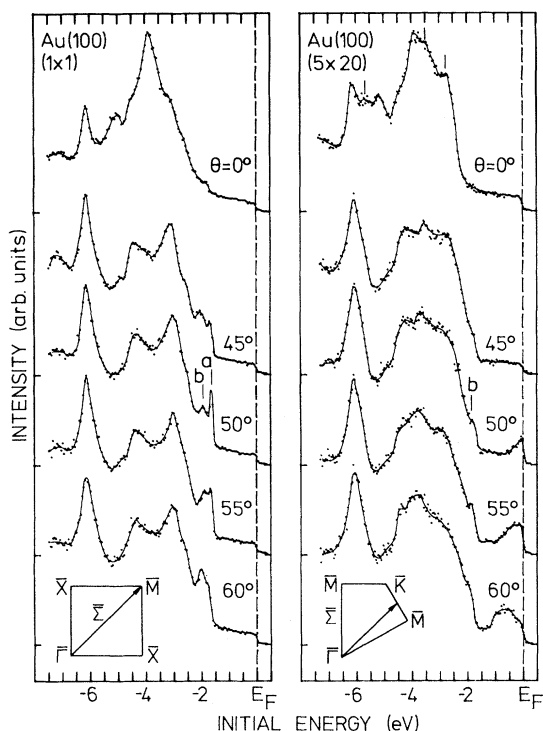


FIG. 1. AREDC's of Au(100) for the normal and reconstructed surface at a photon energy of 21.22 eV. The polar angle θ is measured from the surface normal. The electron emission plane ($\Gamma XWK\Gamma$) is indicated in the inset by an arrow.

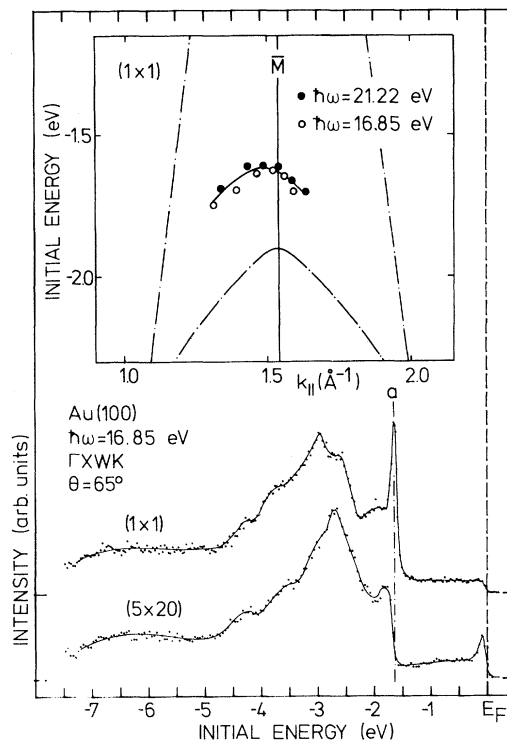


FIG. 2. AREDC's of Au(100) in the $\Gamma XWK\Gamma$ emission plane. The inset shows the dispersion of the surface-state peak along the Σ direction of the corresponding square surface Brillouin zone. The dash-dotted line indicates the bulk energy gap taken from Ref. 9.

ity to surface atomic order shows that the -1.6 -eV peak is due to a localized surface state, analogous so that previously observed on Cu(100), a surface which does not reconstruct. The dispersion of the Au(100)- (1×1) peak is given in the inset of Fig. 2, for measured values of the surface wave vector along the $\bar{\Sigma}$ line of the square Brillouin zone. The observed band, like that of Cu(100),¹ is independent of the photon energy, and lies in an absolute energy gap of the projected bulk band structure.^{9,10} The bulk d -band edge has been shifted to align it with the measured d -band edge at -1.9 eV.¹¹

AREDC's of Au(100) surfaces have also been measured in the Γ LUX plane of the bulk Brillouin zone; this plane makes an angle of 45° with the Γ XWKT plane and corresponds to the $\bar{\Sigma}$ line of the (5×20) surface Brillouin zone (see the inset of Fig. 1). Two representative AREDC's are given in Fig. 3. For this azimuth the (5×20) surface exhibits an emission peak (labeled c) about 1.7 eV below E_F , which is absent in the (1×1) data. The dispersion of this peak given in the inset of Fig. 3 is symmetrical around the \bar{M} point of the hexagonal zone associated with the top layer of the (5×20) surface. We attribute the observed peak to a surface state localized near the hexagonal top layer. It is therefore analogous to the surface state observed on the Cu(111) surface,¹ whose top layer is also hexagonal. Indeed, the dispersion shown in Fig. 3 is quite similar to that of the surface band found for Cu(111).¹ A similar surface-state band has been measured for the Au(111) surface and is indicated in Fig. 3 by the dashed line.¹² The dispersion of both surface-state bands agree quite well, only the energy position is different by about 0.1 eV. Whether the small horizontal displacement of the two curves is a real effect and may be explained by a small contraction in the overlayer cannot be decided on the basis of the present experimental data. Because of the existence of orthogonal domains, the surface band of Au(100)- (5×20) is observed at 30° azimuthal intervals (the normal surface displays fourfold azimuthal symmetry).

Our results contain no evidence for a spin-orbit-gap surface resonance¹³ associated with the Γ X line of the bulk Brillouin zone. A resonance of this type should be observable in normal emission and was discussed in Ref. 5 as possible origin of a peak observed in angle-integrated photoemission from Pt(100)- (1×1) .⁵ The surface states we observed for Au(100)- (1×1) and $-(5 \times 20)$ surfaces are confined to a relatively small

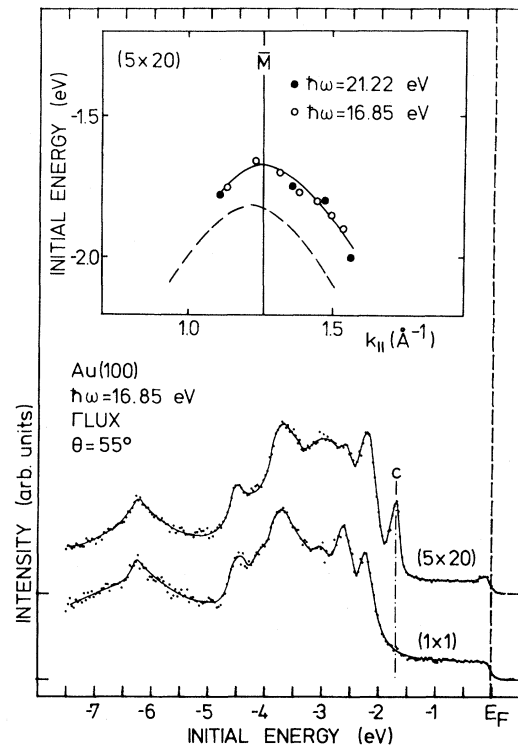


FIG. 3. AREDC's of Au(100) in the Γ LUX emission plane. The inset shows the dispersion of the surface-state peak along the $\bar{\Sigma}$ direction of the corresponding hexagonal surface Brillouin zone. The surface-state band of Au(111) (Ref. 12) is indicated by the dashed line.

region of the corresponding surface Brillouin zones, near the \bar{M} point for both configurations. We therefore believe that they do not play a large role in the energetics of reconstruction.

In summary, we have observed surface-state bands on either the normal or the reconstructed Au(100) surface. These states disappear by changing the surface order. In our opinion, arguments for the driving force of reconstruction, similar to that given for Pt(100) (Ref. 5), cannot be applied to our results for Au(100). Other emission peaks which are attributed to bulk transitions change their intensity. This effect is related to different symmetries of the surfaces, and hence to the validity of different selection rules.

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The selection rules given in this reference are no longer valid when the spin-orbit interaction becomes impor-

tant, which is probably the case for Au. This fact has to be considered for a quantitative assignment of the observed peaks, which, however, will not be attempted here.

⁸We cannot exclude, in principle, the possibility that the emission of extra peaks from the bulk is due to surface umklapp processes introduced by the hexagonal surface layer. From our studies of other clean metal single crystals we know, however, that such contributions may usually be neglected. In fact, we never saw a peak from a clean surface that we could unambiguously assign to such a process.

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Replicate Core Levels as a Probe of Valence-Fluctuation Materials

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For rare-earth elements having two different *4f* configurations in the same material, *3d* and *4d* core-level photoemission spectra will exhibit two sets of structures, or replicas, each corresponding to one of the *4f* configurations. Our estimates of the positions of these structures agree with the available data and suggest the utility of replicate core levels as a useful probe of valence-fluctuation materials.

Measurement of a rare-earth *3d*- or *4d*-core-electron binding energy by x-ray photoemission spectroscopy (XPS) can supply information about the *4f* configuration. For example, in a compound such as Sm_3S_4 the samarium ions occupy two crystallographically inequivalent sites with different *4f* configurations (f^5 and f^6), and an XPS measurement in the *3d* (or *4d*) region would reveal that the structure corresponding to f^6 is replicated at higher binding energy for f^5 —the increase arising from the larger effective nuclear charge in the f^5 case.

To date, such measurements have only been done for a few so-called valence-fluctuation ma-

terials¹⁻⁵: SmB_6 , $\alpha\text{-Ce}$, and CeN . Figure 1 shows *4d* and *3d* spectra for CeN . Each spectrum consists of two structures, with splittings of 11 eV and ~ 10 eV for the *3d* and *4d* replicas, respectively. Since the *3d* spin-orbit splitting is larger than the replicate separation, the *3d* structures overlap.

The understanding of valence-fluctuation materials is incomplete. The observation by XPS in a given material of two sets of *4f* spectra which can be identified with two integrally occupied *4f* configuration implies that each configuration is stable for a time greater than that characteristic of the XPS measurement process ($\sim 10^{-16}$