

Supplementary Information for: Interplay of Umklapp scattering and Sb–Au hybridization in surface-reconstructed Sb/Au(111)

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S1. ARPES band dispersion over a wide binding-energy range

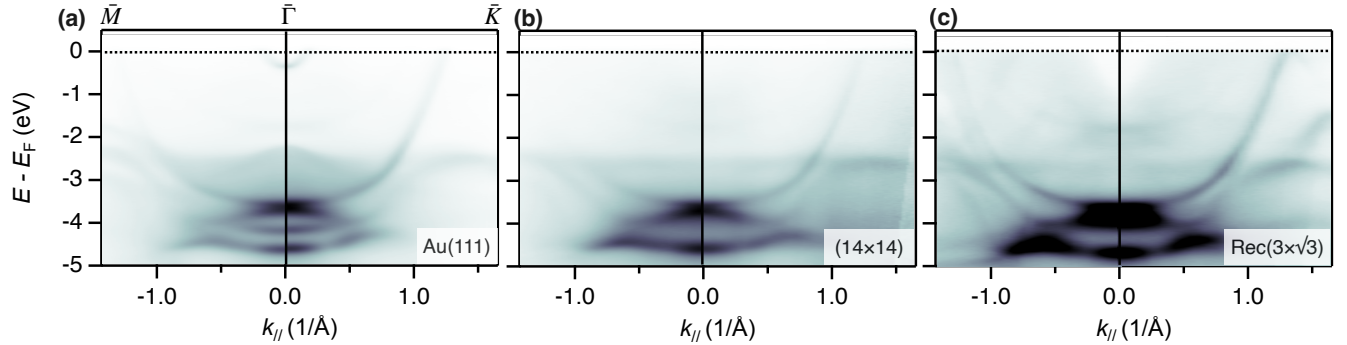


Figure S1. ARPES band dispersion along $\bar{M}-\bar{\Gamma}-\bar{K}$ over the full measured energy range. (a) Clean Au(111) surface. (b) The (14×14) Sb/Au(111) state. (c) The $\text{Rec}(3 \times \sqrt{3})$ Sb/Au(111) state.

S2. Phenomenological construction of the hexagonally warped Fermi contour and reciprocal-space folding

To visualize the expected band folding induced by the $\text{Rec}(3 \times \sqrt{3})$ reconstruction, we construct a phenomenological model of the Au(111) Fermi contour and perform reciprocal-space folding using the superlattice vectors. The purpose of this construction is to illustrate how triangular pockets can emerge from Umklapp scattering¹ of the Au-derived surface states.

The Au(111) Fermi contour is approximated by a phenomenological hexagonally anisotropic curve, using a warping term of the type commonly employed to describe hexagonal deviations from circular Fermi contours² and constrained by the Au(111) surface state, parameterized as

$$k(\theta) = k_0(1 + \beta \cos 6\theta), \quad \theta \in [-\pi, \pi],$$

where k_0 is the average Fermi wave vector and β quantifies the strength of the hexagonal anisotropy. The average wave vector is defined as

$$k_0 = \frac{1}{2\pi} \int_{-\pi}^{\pi} k_F(\theta) d\theta.$$

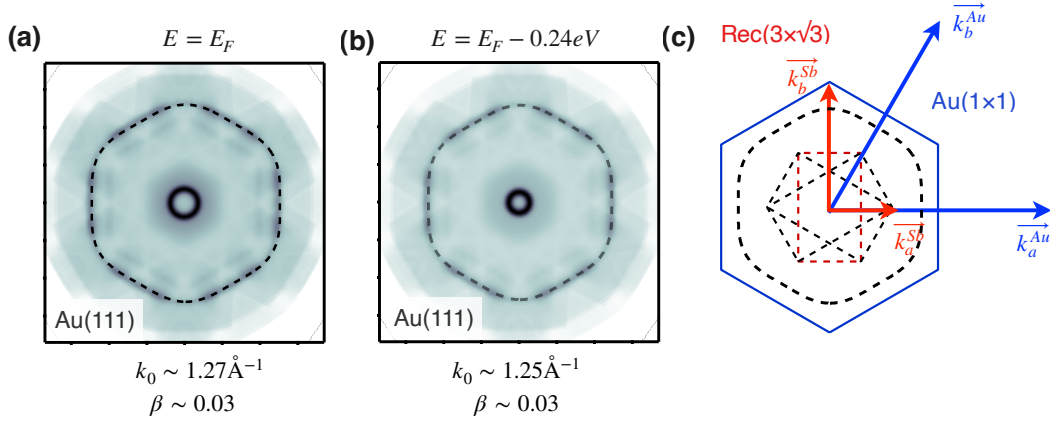


Figure S2. Phenomenological model of the Au(111) Fermi contour and reciprocal-space construction used for the $\text{Rec}(3 \times \sqrt{3})$ folding simulation. (a,b) Constant-energy maps of Au(111) at E_F and $E_F - 0.24$ eV. Dashed curves indicate the phenomenological description of the hexagonally warped Au-derived contour used as input for the folding construction. (c) Reciprocal-space geometry of the Sb $\text{Rec}(3 \times \sqrt{3})$ reconstruction with respect to the Au(1×1) lattice. The Sb reciprocal-lattice vectors define the scattering vectors employed to fold the Au contour and generate the triangular pockets discussed in Fig. 3.

From the ARPES data, the parameters are estimated to be $k_0 \approx 1.27 \text{ \AA}^{-1}$ at the Fermi level, and $k_0 \approx 1.25 \text{ \AA}^{-1}$ at $E_F - 0.24$ eV, with a warping parameter $\beta \approx 0.03$ (Figure S2(a,b)). To simulate the effect of the $\text{Rec}(3 \times \sqrt{3})$ reconstruction, the spectral function is constructed by replicating the Au(111) Fermi contour using the reciprocal lattice vectors associated with the Sb-induced surface reconstruction. Within a simplified Umklapp picture, the spectral weight³ can be written as

$$A(\mathbf{k}, \omega) = \sum_{\mathbf{G}} |V_{\mathbf{G}}|^2 A_0(\mathbf{k} - \mathbf{G}^{\text{Sb}} - \mathbf{G}^{\text{Au}}, \omega),$$

where $A_0(\mathbf{k}, \omega)$ denotes the spectral function of the pristine Au(111) surface and where $\mathbf{G}^{\text{Sb}}$ and $\mathbf{G}^{\text{Au}}$ denote the reciprocal lattice vectors of the Sb-induced reconstruction and the Au(111) substrate, respectively,

$$\mathbf{G}^{\text{Sb}} = m \mathbf{k}_a^{\text{Sb}} + n \mathbf{k}_b^{\text{Sb}}, \quad m, n \in \mathbb{Z}.$$

$$\mathbf{G}^{\text{Au}} = r \mathbf{k}_a^{\text{Au}} + s \mathbf{k}_b^{\text{Au}}, \quad r, s \in \mathbb{Z}.$$

The resulting reciprocal-space geometry is illustrated in Figure S2(c), where the Au(1×1) Brillouin zone and the $\text{Rec}(3 \times \sqrt{3})$ reciprocal lattice vectors are shown together with the modeled Fermi contour. For the (14×14) state discussed in the main text, the displacement between the original and folded Au-derived sp bands can be described by the reciprocal-space translation $\Delta \mathbf{k}_{14 \times 14} = -3 \mathbf{G}_{14 \times 14}^{\text{Sb}}$, which corresponds to a momentum shift of approximately $-0.715(1/\text{\AA})$. For the $\text{Rec}(3 \times \sqrt{3})$ state, the triangular pockets appear in repeated zones of the reconstructed reciprocal lattice. Within the folding construction, one possible representation of the corresponding displacement is obtained from $\Delta \mathbf{k}_{3 \times \sqrt{3}} = -2 \mathbf{G}_{3 \times \sqrt{3}}^{\text{Sb}} + \mathbf{G}_{1 \times 1}^{\text{Au}}$, yielding a momentum shift of approximately $-0.455(1/\text{\AA})$.

S3. Multi-Voigt analysis of the EDCs

To characterize the evolution of the deeper valence states upon Sb adsorption on Au(111), representative energy distribution curves (EDCs) were analyzed using a multi-component fitting procedure based on Voigt line shapes^{3,4}. The EDCs were extracted around $\bar{\Gamma}$ from the ARPES data presented in the main text (Fig. 4), within the energy range from approximately -5 to -2.5 eV relative to E_F .

The spectral line shape was modeled as a sum of Voigt components together with a Shirley-type background^{5,6},

$$I(E) = \sum_{i=1}^N A_i V(E; E_i, \Gamma_i, G) + B_{\text{Sh}}(E) + B_0,$$

where A_i denotes the amplitude of the i th component, E_i its peak position, and $V(E; E_i, \Gamma_i, G)$ the Voigt profile centered at E_i . Here, Γ_i denotes the Lorentzian FWHM and G the Gaussian FWHM.

The measured Fermi edge of each surface state was fitted by a step function convoluted with a Gaussian. Because the measurements were performed at room temperature, the resulting width should be regarded as an effective Fermi-edge width rather than as the instrumental resolution alone. It reflects the combined influence of the instrumental response, including the analyzer and photon-source contributions, the finite-temperature occupation cutoff, and other experimental effects that broaden the measured edge. In the deep-valence analysis, this effective Gaussian width was used as a fixed empirical constraint to stabilize the phenomenological Voigt decomposition, while the Lorentzian contribution was allowed to vary freely.

The effective Gaussian FWHM values obtained from the Fermi-edge fits were 104.489 ± 5.397 meV for clean Au(111), 108.624 ± 1.640 meV for the (14×14) state, and 107.313 ± 2.834 meV for the $\text{Rec}(3 \times \sqrt{3})$ state. The corresponding central values were fixed in the respective deep-valence-band fits.

The Shirley background $B_{\text{Sh}}(E)$ accounts phenomenologically for the inelastic photoelectron background and was constructed from the cumulative spectral intensity toward higher binding energy,

$$B_{\text{Sh}}(E) \propto \int_E^{E_{\text{max}}} I(E') dE',$$

where E_{max} denotes the high-binding-energy end of the analyzed spectrum. The direction of integration was chosen consistently with the binding-energy axis of the experimental data. In addition, a constant offset term B_0 was included to account for residual background contributions.

The fitting routine was implemented in Igor Pro 8 using a custom fit function. The minimum number of spectral components required to reproduce the experimental line shape was employed for each surface state. Initial estimates for the peak positions, amplitudes, and Lorentzian widths were supplied prior to fitting, followed by nonlinear least-squares optimization using the built-in Levenberg–Marquardt algorithm. After convergence, the fitted coefficients were used to reconstruct the individual Voigt components and visualize the spectral decomposition.

The fitted peak positions provide an additional reference for the assignment of the deeper valence-band features. For clean Au(111), the components are found at binding energies of 4.607 ± 0.001 , 4.145 ± 0.002 , and 3.588 ± 0.001 eV, close to previously reported Au(111) features at approximately 4.60, 4.24, and 3.62 eV⁷. Contributions from He $I\beta$ cannot be excluded because a non-monochromatized He discharge source was used. The approximately 1.87 eV photon-energy separation between He $I\alpha$ and He $I\beta$ ⁸ shifts deeper Au-derived features into the same apparent binding-energy range when the spectrum is referenced to He $I\alpha$. We consequently assign P2 to predominantly Au-derived spectral weight with a possible He $I\beta$ admixture.

State	Peak	E_i (eV)	Lorentzian FWHM (eV)	Voigt FWHM (eV)
Au(111)	P1	-4.607 ± 0.001	0.291 ± 0.007	≈ 0.326
	P2	-4.145 ± 0.002	0.239 ± 0.009	≈ 0.279
	P3	-3.588 ± 0.001	0.434 ± 0.004	≈ 0.458
(14×14)	P1	-4.556 ± 0.003	0.454 ± 0.016	≈ 0.480
	P2	-3.664 ± 0.003	0.707 ± 0.012	≈ 0.724
$\text{Rec}(3 \times \sqrt{3})$	P1	-4.648 ± 0.002	0.306 ± 0.008	≈ 0.341
	P2	-3.900 ± 0.007	0.426 ± 0.019	≈ 0.452
	P3	-3.582 ± 0.002	0.314 ± 0.008	≈ 0.349

Table S1. Peak positions and linewidth parameters obtained from the multi-Voigt decomposition of representative EDCs around $\bar{\Gamma}$. The Gaussian FWHM for each surface state was fixed to the effective broadening obtained from the corresponding Fermi edge, while the Lorentzian FWHM was treated as a free fitting parameter. The quoted uncertainties are those returned by the least-squares fitting routine, whereas the total Voigt FWHM values are approximate.

S4. Constant-energy maps over a wide binding-energy range

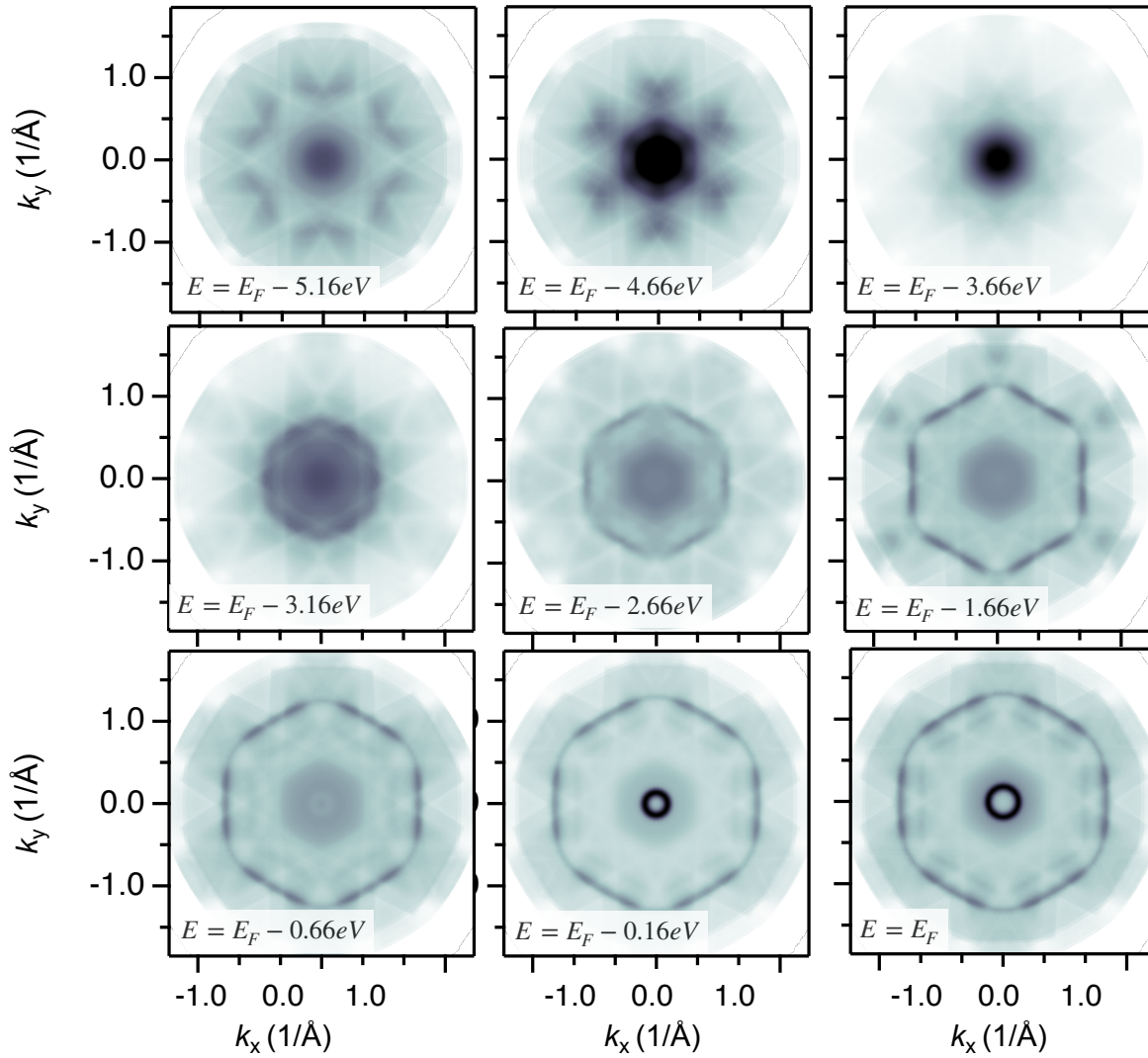


Figure S3. Constant-energy maps of Au(111) over a wide binding-energy range. ARPES constant-energy maps measured at energies from $E_F - 5.16\text{ eV}$ to E_F . The momentum-space intensity evolves from broad features at large binding energy to the hexagonally warped Fermi contour characteristic of the Au(111) surface state near the Fermi level. The faint streak-like features arise from the merging of multiple momentum maps during data reconstruction and do not reflect intrinsic electronic structure.

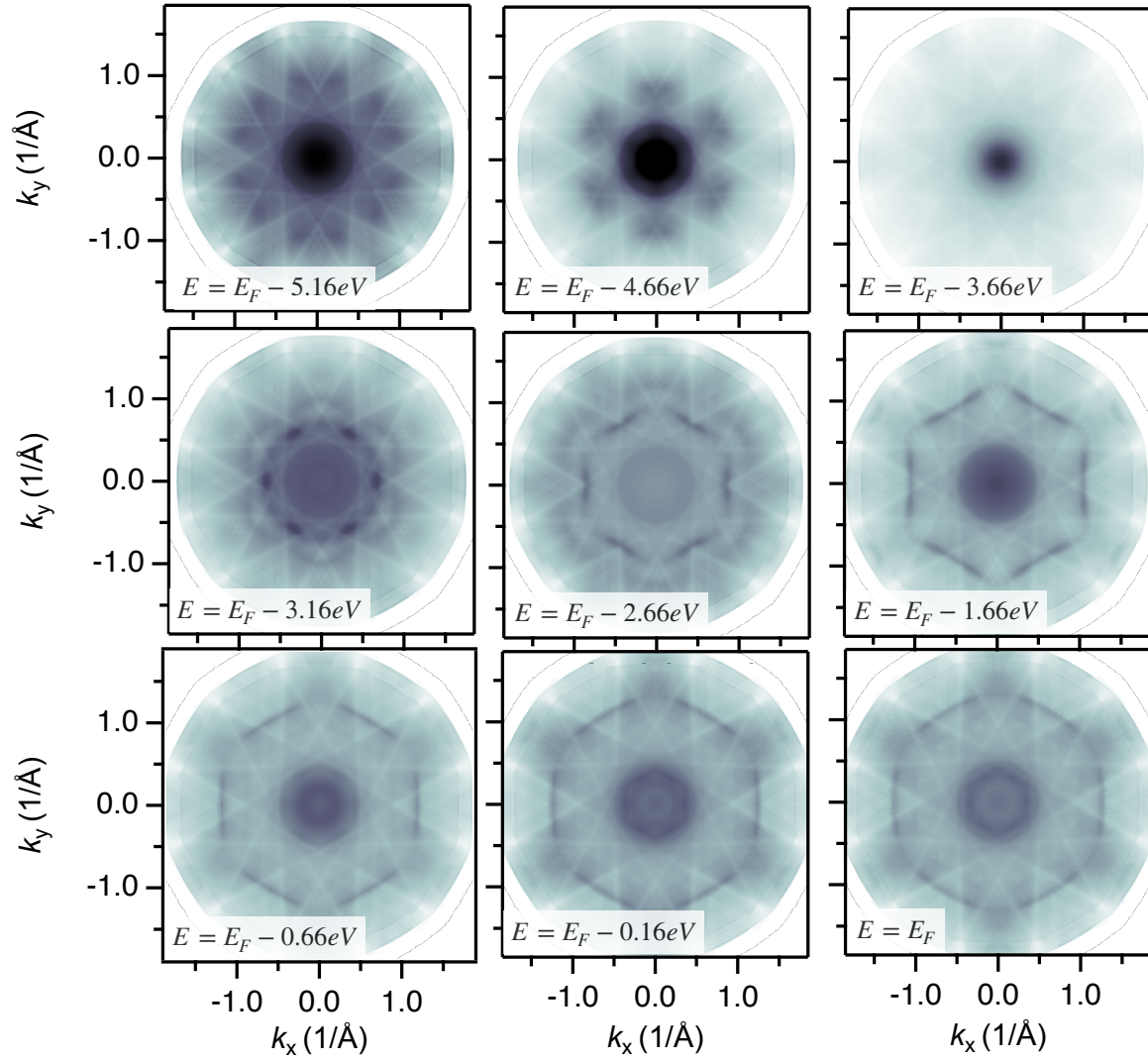


Figure S4. Constant-energy maps of Sb/Au(111) in the (14×14) reconstruction state over a wide binding-energy range. ARPES constant-energy maps measured at energies from $E_F - 5.16$ eV to E_F .

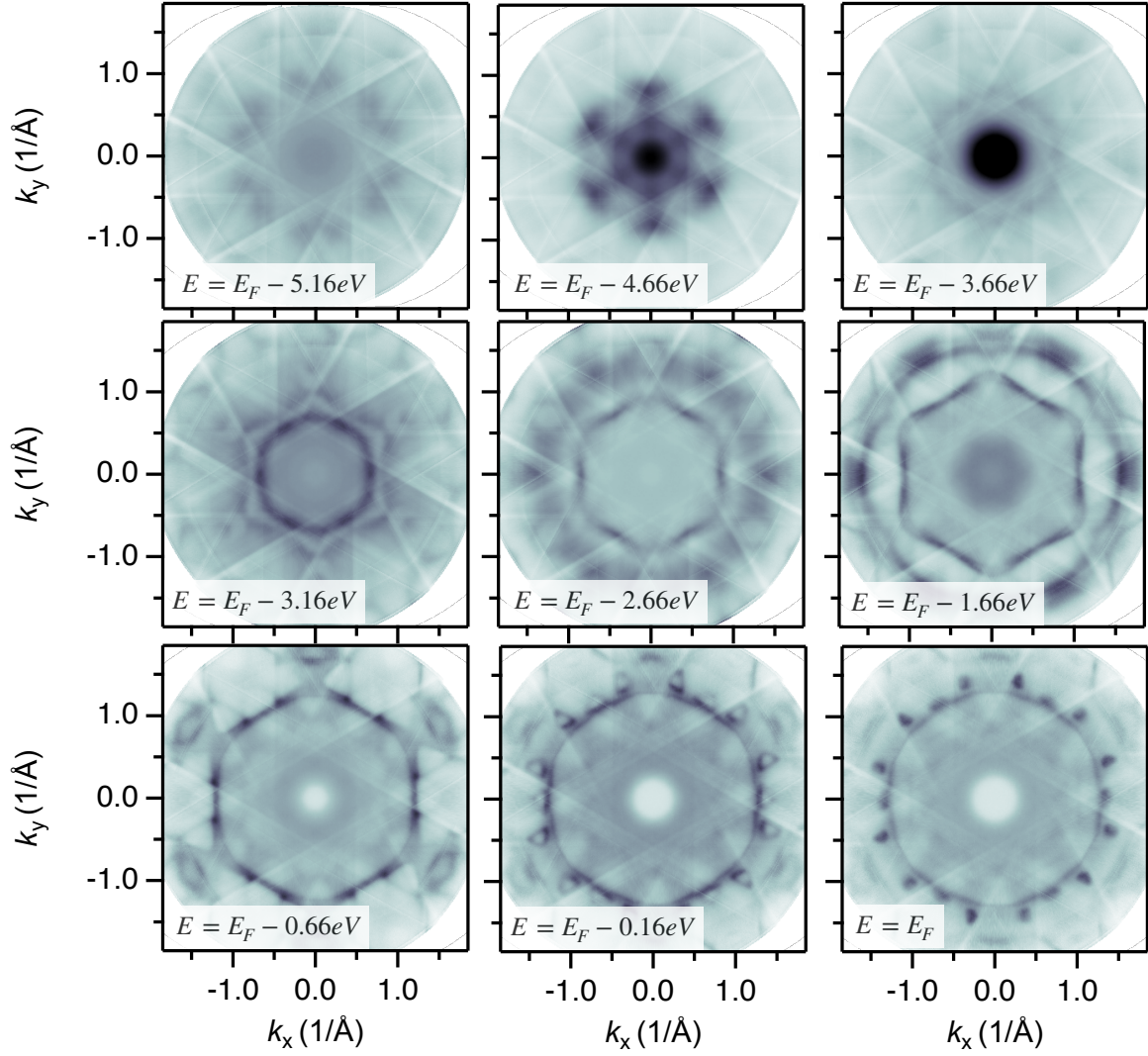


Figure S5. Constant-energy maps of Sb/Au(111) in the $\text{Rec}(3 \times \sqrt{3})$ state over a wide binding-energy range. ARPES constant-energy maps measured at energies from $E_F - 5.16$ eV to E_F .

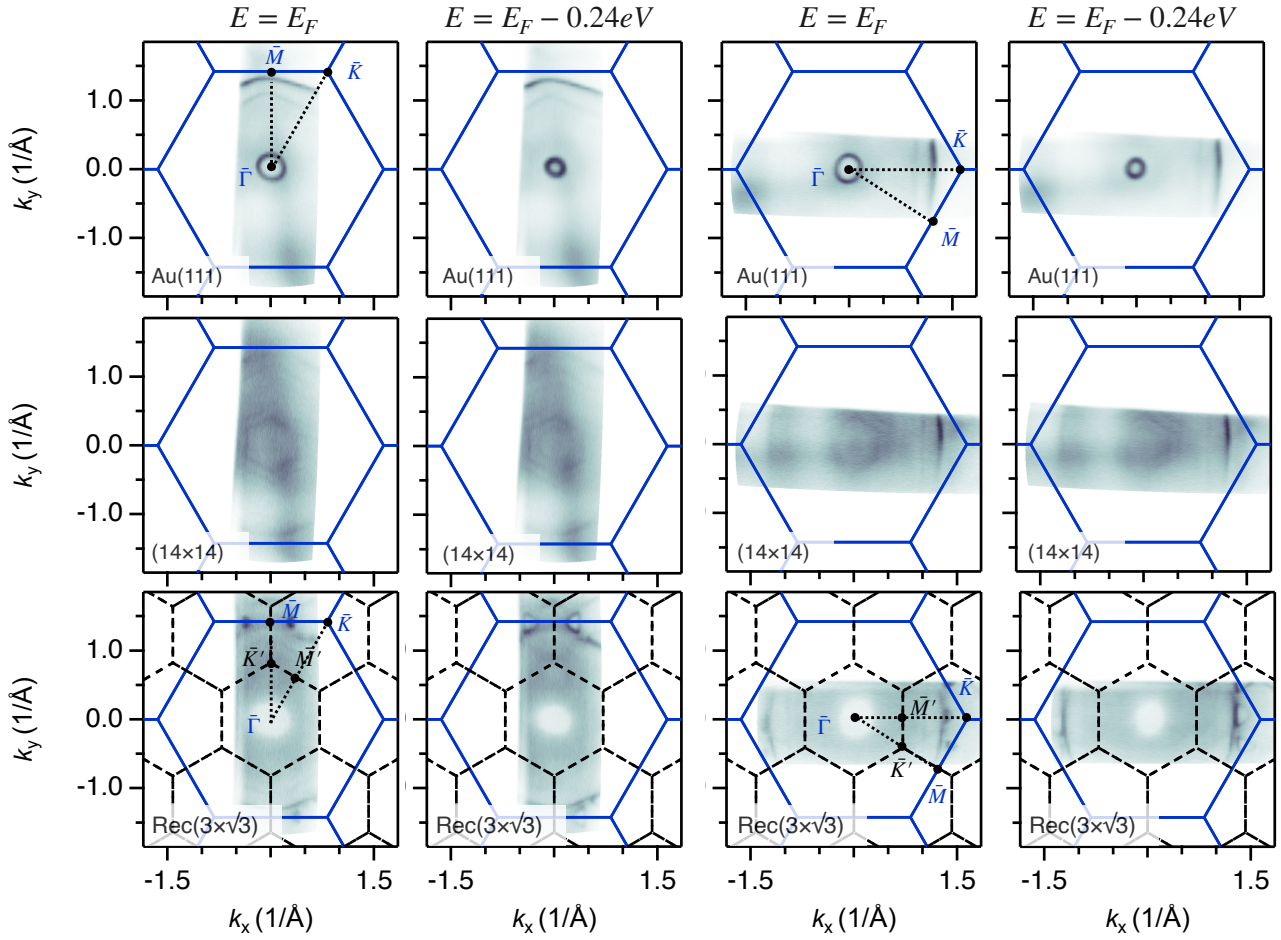


Figure S6. Representative unstitched ARPES constant-energy maps. Constant-energy maps of pristine Au(111), the (14×14) state, and the $\text{Rec}(3 \times \sqrt{3})$ state measured at E_F and $E_F - 0.24$ eV. The first two and last two columns correspond to individual momentum-space measurements acquired along two different orientations, shown without stitching. The blue hexagons indicate the Au(111) surface Brillouin zone, while the black dashed lines indicate the reciprocal-space periodicity of the $\text{Rec}(3 \times \sqrt{3})$ reconstruction. The reconstruction-related features discussed in the main text can also be identified in these unstitched raw constant-energy maps.

S5. Stepwise evolution of the LEED pattern in the low-deposited-amount regime

This stepwise series establishes the relative ordering of the early low-dose LEED patterns, namely an initially diffuse $(\sqrt{3} \times \sqrt{3})R30^\circ$ -like pattern followed by the long-period pattern indexed here as (14×14) . At larger nominal deposited amounts, additional long-period or transitional periodicities may occur before $\text{Rec}(3 \times \sqrt{3})$, and the same nominal deposited amount may yield different diffraction patterns depending on the detailed deposition and annealing history. In addition, the shutter-burst effect introduces extra uncertainty in the smallest deposition increments. The indicated amounts should therefore be interpreted as relative preparation parameters rather than absolute stoichiometric surface coverages.

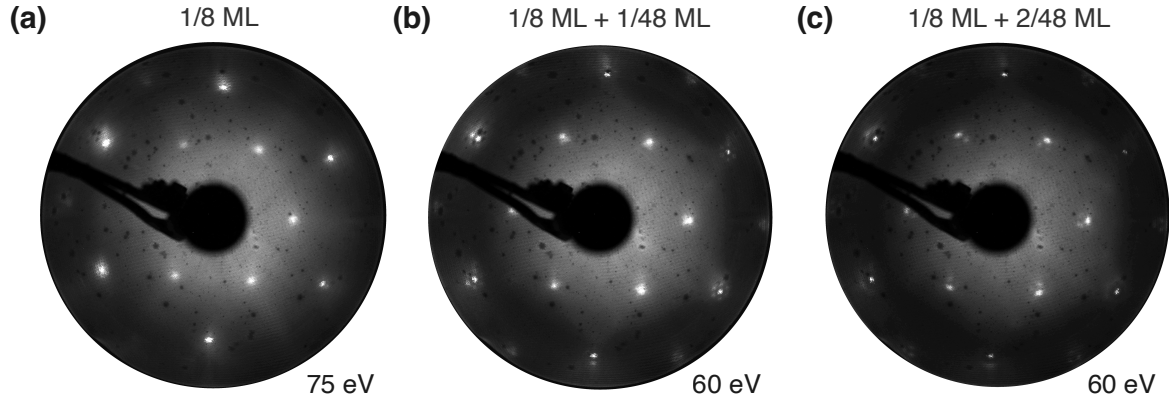


Figure S7. Stepwise evolution of the Sb/Au(111) LEED pattern during low-dose Sb deposition. LEED patterns recorded in one deposition series from a nominal amount of $1/8$ ML, with subsequent increments of $1/48$ ML. The initially diffuse $(\sqrt{3} \times \sqrt{3})R30^\circ$ -like pattern evolves into the long-period (14×14) pattern.

References

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