Interplay between electronic states and structure during Au faceting

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Abstract. Au(111) vicinal surfaces are characteristic examples of two-phase segregation or faceting. Between \(\sim 4^\circ\) and 9.5\(^\circ\) miscut, the surface exhibits hill-and-valley structures formed by bunches of relatively wide (\(d_w \sim 36-41\) Å) and narrow (\(d_n \sim 14\) Å) terraces. The evolution of surface electronic states in such a faceted system is followed using a curved crystal. Beyond 4\(^\circ\) the surface state splits into distinct \(d_w\) and \(d_n\) bands. Our analysis suggests the crucial role of surface states in defining the characteristic \(d_w\) and \(d_n\) sizes during Au faceting.

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1. Introduction

Surface electrons in metals have become widely popular thanks to scanning tunneling microscopy and spectroscopy (STM/STS), which allows the creation of electron-confining nanostructures of varied shape, such as atom corrals, and the ability to map the standing wave patterns inside [1]. Beyond the striking visualization of the wave nature of the electron, STM/STS experiments show that surface electrons undergo significant scattering at atoms, defects or steps on metal surfaces. This results in a strong spatial modulation of the density of states at $E_F$ (period $\sim \lambda_F/2$) that affects the effective surface potential. In fact, Cu adatoms on Cu(111) [2], and, more strikingly, H and Ce atoms on W(110) and Ag(111), respectively [3, 4] self-assemble forming ordered structures with characteristic $\lambda_F/2$ spacings. In metallic nano-object arrays, such as quantum dots and steps, the periodic perturbation of the electronic density of states originated by surface state scattering extends over the entire two-dimensional (2D) surface plane [5]. In such systems the question that arises is how the structure responds when the lattice constant $d$ matches $\lambda_F/2$, i.e. what happens if we force the nesting of the Fermi surface with $2k_F$ superlattice vectors.

Noble metal surfaces display a variety of periodic self-assembled structures that are stable at 300 K. These comprise 1D step arrays and surface reconstructions in vicinal surfaces [6, 7], as well as 2D dislocation patterns in monolayers and bilayers [8, 9]. All of them exhibit superlattice bands, as a clear signature of coherent surface electron scattering in the array. Vicinal (111) surfaces are particularly attractive to tune 1D Fermi surface nesting. This occurs when the radius of the ring-like Fermi surface $\kappa_F$ matches the superlattice wavevector $\pi/d$ [10], where $d$ is the terrace size. The latter can be selected via the surface misorientation (or miscut angle $\alpha$) with respect to the (111)-direction with $\sin \alpha = h/d$, where $h$ is the step height. Macroscopic angles $\alpha \sim 1^\circ-15^\circ$ turn into nanoscopic lattice constants $d \sim 100-10$ Å, covering the variation range of $\pi/\kappa_F$, i.e. from 15 Å in Cu(111), to 19 Å in Au(111) and 39 Å in Ag(111) surfaces [11], and intermediate values in overlayer systems [8, 12]. In copper, for example, 1D nesting occurs near the (443) surface orientation, where a Fermi gap opening has been observed [10]. In this case, the step lattice disorder has been claimed as the structural instability associated with nesting, although clear proof of such structural/electronic interplay has not been reported.

In this work, we use a curved crystal surface to study the connection between structure and electronic states in 1D step superlattices. The curved surface allows one to smoothly vary the miscut $\alpha$, and hence the step lattice constant $d$, as sketched in the lower panel of figure 1. The local structure is determined by STM (middle panels in figure 1), whereas locally resolved surface bands are measured by angle resolved photoemission spectroscopy (ARPES, top panel in figure 1) using a very small synchrotron light spot. The system of choice is an Au crystal that covers a $\Delta \alpha = \pm 15^\circ$ range of miscut angles around the [111]-direction ($\alpha = 0$). As depicted in figure 1, Au(111) vicinals are not stable within the $4^\circ-9.5^\circ$ miscut range, exhibiting faceting in two phases of large ($d_w$) and small ($d_n$) (111) terraces [13]. The ARPES data indicate the presence of distinct $d_w$ and $d_n$ bands in the faceted range, whose intensities evolve with the miscut angle. At the onset of faceting ($\sim 4^\circ$) a superlattice gap opens at the Fermi energy, suggesting that the faceting is triggered by electronic energy gain in the $d_w$ phase. It is also found that $d_n$ corresponds to the critical size for surface state occupation of a single terrace, which may have an influence in both surface energy and faceting kinetics.
Figure 1. ARPES (top) and STM (middle) analysis of faceted Au(111) surfaces from a curved crystal (bottom). This allows a smooth variation of the local miscut around the (111)-direction. The surface bands displayed above belong to the 4°–9.5° faceting range, either for A- (left) or B- (right) type steps. As shown in the sideview sketch, the unit terrace sizes $d_w$ and $d_n$ are similar for both A and B sides, but the faceting structure changes. $d_w$ and $d_n$ phases give rise to distinct surface states, as indicated in the top panel.
2. Experimental details

The curved Au crystal (Mateck GmbH, Germany) was mechanically polished defining a 30° cylindrical section (11 mm radius) around the (111)-direction. The surface was prepared in vacuum following standard sputter-annealing cycles. The procedure ends after the complete removal of point defects and contaminants, which give rise to step pinning and bunching. The middle panels in figure 1 display two STM images from the curved surface taken at the right side (positive α) and the left side (negative α) of the sample. At a given α, the structures are analogous to those observed in regular vicinal Au(111) crystals with flat surfaces [13]. The advantage of the new approach is that the curved surface delivers all miscut angles in a single sample. Left and right sides of the crystal correspond to surfaces with A- ((001)-oriented microfacet) and B-type steps ([111] microfacet), respectively. Spontaneous faceting occurs for both step types within the same ~4°–9.5° miscut range. At the lower faceting onset (~4°), one observes monatomic step arrays made of relatively wide \(d_w = 41 \pm 1 \text{ Å}\) and \(d_w = 36 \pm 1 \text{ Å}\) terraces, for \(A\) and \(B\) steps, respectively, whereas at the upper \(\alpha \sim 9.5°\) onset both sides exhibit a single phase with \(d_n = 14 \pm 1 \text{ Å}\) lattice constant. For \(A\)-type steps, the \(d_n\) phase is defined by a single terrace and the \(d_n\) phase by bunches [13], whereas in the \(B\)-type both \(d_n\) and \(d_w\) form bunches. The STM image of the \(A\)-type steps of figure 1 corresponds to \(\alpha = -7.5°\) with a \(d_n\) phase containing six terraces. In contrast, the \(B\) side at \(\alpha = 8.3°\) displays large, alternating bunches of \(d_w\) and \(d_n\) terraces. This difference between \(A\) and \(B\) faceting is connected to their distinct atomic packing at step edges, which results in significant step energy variations [14]. However, there is no apparent structural reason for the system to prefer specific \(d_n\) and \(d_w\) values. These are explained on the basis of electronic surface states, as discussed below.

STM experiments were carried out using a variable temperature Omicron STM in San Sebastián (Spain), while the photoemission data are taken at the PGM beamline of the Synchrotron Radiation Center (SRC) of the University of Wisconsin in Stoughton (USA). For ARPES measurements, we used a hemispherical Scienta SES200 spectrometer with energy and angular resolutions set to 25 meV and 0.1°, respectively, and p-polarized light with the polarization plane set parallel to the steps on the sample, i.e. along the [110]-direction in figure 1. Characteristic surface bands within the faceted regions are shown on top of figure 1. The miscut \(\alpha\) is selected by scanning the 100 μm synchrotron light beam across the curved surface. The spot size defines an effective miscut broadening \(\Delta \alpha < 0.5°\). In the spectra of figure 1, the wavevector scale is referred to the center of the second Brillouin zone of the local (nominal) surface plane, i.e. \(k_\theta = ((\hbar \omega - \Phi - E_B)2m/\hbar^2)^{1/2} \times \sin(\theta - \alpha) + 2\pi/d\), where \((\hbar \omega - \Phi - E_B)\) is the electron kinetic energy, \(m\) the electron mass, \(\theta\) the emission angle with respect to the (111)-direction, and \(d\) is the average terrace size \(d = h/\sin \alpha\), with \(h = 2.35 \text{ Å}\) being the monatomic Au step height. To better observe different superlattice umklapps we choose \(\hbar \omega = 43 \text{ eV}\) [6]. Measurements have been performed at 150 K.

3. Experimental results

The surface bands in figure 1 nicely reflect the structural differences between \(A\)-type and \(B\)-type faceting. In both, the free-electron-like, Shockley surface state splits into two different contributions, one for each phase. The \(d_n\) phase with narrow terraces leads to folded bands of lower binding energy \(E_B = 0.29 \text{ eV}\) at \(A\) and \(B\) sides. The multi-terrace \(d_w\) phase at the \(B\) side exhibits zone folding of a higher binding energy \(E_B = 0.45 \text{ eV}\) dispersing band. In contrast, the...
Figure 2. Surface state band measured with a photon energy of 21.2 eV for a plane Au(788) (top) and the corresponding +3.5° miscut in the curved crystal (bottom). The second derivative of the photoemission intensity is displayed. Bands are fitted using a 1D Kronig–Penney model (full lines, see [6]), showing that the second superlattice gap straddles E_F.

In figure 2, we compare photoemission intensity images (hω = 21.2 eV) for a regular flat Au(788) surface [6] and for the curved crystal at α = +3.5° (d_w = 38 Å), i.e. very close to the faceting onset in the B side (d_w = 36 Å). To better analyze the band topology, the second derivative of the photoemission intensity is displayed. The close similarity between top and bottom panels in figure 2 demonstrates the validity of the curved crystal approach for ARPES experiments. Surface bands deviate significantly from the free-electron-like behavior of the Au(111) surface in both cases. They show the signatures of superlattice scattering, namely band folding with 2π/d vectors and small ∼0.1–0.15 eV energy gaps, namely the first superlattice gap at ∼E_F − 0.3 eV and a second one around E_F. The existence of such superlattice gaps is further proven in figure 3(a), where we plot the photoemission intensity in a constant energy surface in the middle of the first gap (∼E_F − 0.28 eV). The data correspond to the faceting onset at the A side (α = −4.4°). The intensity drop at Γ is clear. The magnitude of the gap can be determined from a fit to the photoemission spectrum at this Γ point. This is shown in figure 3(b), together with a gapless spectrum, for the sake of comparison. The fit in figure 3(b) uses Lorentzian lines, giving a gap width of 124 meV. The second superlattice gap at the Fermi
energy is poorly resolved in individual spectra. In order to have an estimation of such a gap we can fit the overall band structure with a Kronig–Penney model, as done in figure 2 (red solid lines) [6]. For the spectra in figure 2, the Kronig–Penney fit gives a second superlattice gap of ∼100 meV right below the Fermi energy.

As demonstrated for Cu(443) [10], a Fermi gap leads to a significant reduction in the electronic energy per surface area. This can be estimated from the total energy difference $\Delta \gamma$ between gapped and nongapped 2D band structures with the same occupation [10]. For the 0.1 eV gap of figure 2 we obtain $\Delta \gamma \sim 0.25$ meV atom$^{-1}$, a number that falls within the range of the surface stress energy oscillations originated by the periodic fcc/hcp terrace reconstruction in vicinal Au(111) [14]. The latter was, up to now, thought of as the reason for the faceting transition in Au(111). Since reconstructed terraces have lower surface energy [13], one may naively expect that beyond 4° the system locks in the smallest terrace size ($d_w$) that allows the fcc/hcp reconstruction [15]. However, fcc/hcp discommensuration lines run perpendicular to the steps in the $B$-side [14], and hence there is no a straightforward restriction to limit the size of a reconstructed terrace with $B$ steps. In contrast, the data in figure 2 suggest that $d_w$ is a magic terrace size that provides a significant reduction in electronic energy, and hence can trigger surface faceting.

Figure 4 illustrates the detailed surface state evolution within the faceted region at the $B$ side of the sample, where one can follow the changing contribution from each phase. To better identify the nature of the different bands, the solid lines represent parabolic envelopes (circles in figure 3(a)) that fit $d_w$ and $d_n$ bands, respectively, at faceting onsets. The data at 4.4° and 9.9° are shown as direct intensity maps, and the rest as second derivative plots. The latter show that the gapped topology of the bands in figures 2 and 3, and in particular the $E_F$ gap, is also present in the $d_w$ phase. Between 4.4° and 9.9°, the $d_n$ emission builds up, whereas the $d_w$ bands are progressively quenched. $d_w$ bands exhibit $\Gamma$-folding with $g_w = 0.175$ Å$^{-1}$ vectors,

Figure 3. (a) Constant energy surface at $E_F - 0.28$ eV showing the depleted intensity at the first superlattice gap for $\alpha = -4.4°$. (b) Energy distribution curves at the ($k_x$, $k_y$) points marked in (a) with the same colors. At $\Gamma$ (spectrum at the bottom) the two peak features delimit (124 meV) the first superlattice gap.
Figure 4. Surface bands within the $B$-type faceted region of the curved crystal. Photoemission intensity maps correspond to the miscut angles indicated on the bottom right. $k_x$ is the wavevector perpendicular to the step array on the local surface plane. From $4.4^\circ$ to $9.9^\circ$ the system smoothly evolves from $d_w$ to $d_n$ bands, with mixed contributions at intermediate miscuts. The solid lines are parabolic fits to $d_w$ and $d_n$ bands at the onset of faceting. The dotted parabolas mark the position of second-order umklapps. The latter prove that, in the $d_w$ phase, bands are nested at $E_F$. 

i.e. $d_w = 36$ Å, whereas $d_n$ bands are folded with $g_n = 2\pi/d_n = 0.45$ Å$^{-1}$, in agreement with the value $d_n = 14$ Å found in STM. Within the error limits, both $g_n$ and $g_w$ are constant values across the faceting regime, reflecting the stability of the $d_w$ and $d_n$ lattice constants in each phase. In figure 4, the arrows join folded parabolas at the Fermi energy defining the nesting vector $2k_F$ for each phase. For the $d_w$ bands, the parabolic fit gives $2k_F = 0.177 \pm 0.005$ Å$^{-1}$, i.e. $2k_F \sim g_w$, as expected for Fermi surface nesting and gap opening with $4\pi/d$ umklapp vectors (dotted lines). Furthermore, for $d_n$ bands, the Fermi level crossing defines $2k_F = 0.180 \pm 0.005$ Å$^{-1}$. Thus, we may conclude that, within error bars, $2k_F \sim g_w = 2\pi/d_w$ is the same for both $d_w$ and $d_n$ phases.

To better analyze the electronic states in the $B$-like faceted surface, we have simulated a photoemission intensity map in figure 5(a). In detail, the model has the following key elements: (i) we solve Schrödinger’s equation in 1D, with the spatial coordinate representing the distance

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Figure 5. (a) Calculated photoemission intensity maps from a faceted system with large phases, using the finite system sketched on top. The size of the phases is enough to develop distinct surface bands, with discrete $d_n$ states inside the $d_w$ gap at $E_F$. (b) Photoemission map calculated for a $60 \times d_w$ network and one $d_n$ terrace of variable size inserted in the middle. The $d_n$ terrace gives rise to a single QW level that becomes occupied at $d_n \sim 13$ Å.

measured along the $\langle 1\overline{1}2 \rangle$-direction; (ii) the potential is fixed as zero inside $d_w$ terraces, whereas a small offset for $d_n$ terraces ($\sim 0.1$ eV) and the potential step barrier (width = 2 Å and height = 1 eV) are needed to fit both $d_w$ and $d_n$ band minima; (iii) the surface electron wavefunction is then assumed to be separable into the product of a function that depends on the coordinate along the $\langle 111 \rangle$-direction and a function depending on the coordinates parallel to the surface [16]; (iv) this separation leads to a factorization of the photoemission matrix element into a factor that is the Fourier transform of the parallel component of the wavefunction times the matrix element of the normal wavefunction going to an emitted plane wave; (v) each terrace contributes with a term to the first of these factors (i.e. the Fourier transform), and each term is multiplied by a phase that takes into account the difference in path-length of the emitted photoelectron for each emitting terrace; (vi) finally, the matrix element of the normal wavefunction is calculated from rigorous solutions for surface-state and free electron-wavefunctions corresponding to a 1D model potential along the $\langle 111 \rangle$-direction that is adjusted to yield the main characteristics of the measured surface and bulk electronic structure of the Au(111) surface [17]. In practice, a finite set of terraces is considered in each calculation, and in particular, we have considered a system consisting of a periodic succession of 30 small $d_n = 14$ Å terraces, embedded between two $30 \times d_w$ ($d_w = 36$ Å) facets, as sketched on top of figure 5. The similarity of the model
calculation with the data in figure 4 is remarkable. Both $d_w$ and $d_n$ phases are indeed large enough to develop separate bands (blue and red, respectively). Interestingly, the simulation shows that $d_n$ states change their nature within the second $d_w$ superlattice gap, i.e. at the Fermi energy. Inside the gap, we observe discrete levels due to confinement within the $d_n$ phase. Out of the gap, $d_n$ electrons are transmitted, displaying continuous band dispersion.

It is interesting to note that the $d_n = 14$ Å size is sharply defined in the faceted region of the curved surface for both $A$ and $B$ sides. This suggests a local energy minimum also for this terrace size, but this cannot be readily proven. On the one hand, the elastic energy curve for Au(111) vicinals does not show any free energy minimum at $d_n = 14$ Å [13]. There is only a shallow inflection point for $A$-type facets, resulting from the cross over of the dominating terrace energy at low miscuts and the steadily increasing step energy at high miscuts. From electronic energy arguments, one may rather expect faceting with $d_n \sim 17$ Å, such that the first superlattice gap would straddle $E_F$ for $d_n$ bands [10]. Instead we observe the first superlattice gap well above the Fermi energy for the $d_n$ phase. Yet figures 4 and 5 contain clues that allow us to consider the role of the electronic structure in a different way.

Note that the unique $k_F$ observed in figure 4 implies crossing of $d_w$ and $d_n$ bands near $E_F$. As shown in figure 5, such a band overlap permits nesting between Fermi surface sheets that belong to bonding $d_n$ states and antibonding $d_w$ states at $\bar{\Gamma}$. We can find the same topology in systems with coexisting periodic potentials, where such an indirect nesting leads to the Fermi gap opening and electron energy reduction [18]. However, the large size of laterally coupled phases in the present case suggests a weak electronic interaction between $d_n$ and $d_w$ facets, and hence an irrelevant energy gain. On the other hand, the presence of $d_n$ discrete states within the Fermi energy ($d_w$) gap can lead to a different phenomenon, namely the change in surface state occupation of $d_n$ terraces by quantum size shift, which may influence not only system energetics but also faceting kinetics. It is known that surface band depletion eliminates the Ehrlich–Schwoebel barrier for atom diffusion across surface steps [19], thereby speeding interlayer mass transport and favoring kinetics. Since band occupation lowers the electron energy, we may expect a critical $d_n$ size that balances fast kinetics (favoring depletion) and surface energetics (favoring occupation). Using the same parameters of figure 5(a), we calculate in figure 5(b) surface states for one $d_n$ terrace inserted between two $30 \times d_w$ arrays. The $d_n$ size is varied in $\pm 1$ atomic rows around $d_n = 14$ Å, i.e. we consider $d_n$ terraces containing $4(1/3)$, $5(1/3)$ and $6(1/3)$ atomic rows ($11$ Å, $13.5$ Å and $16$ Å). The single $d_n$ terrace leads to a single quantum well level inside the $d_w$ Fermi gap, which becomes occupied for $d_n \sim 13$ Å, i.e. within the error bars of the measured $d_n = 14$ Å size. Thus, at the onset of the faceting transition, when the $d_n$ phase segregates, $d_n \sim 14$ Å appears as a critical terrace size that may prompt fast kinetics, while reducing surface energy.

4. Summary

In summary, we have explored the rich behavior exhibited by vicinal Au surfaces probed continuously in a cylindrical crystal with a wide range of miscut angles. Faceting extends over a large miscut range, although, remarkably, the facets are defined by terraces of fixed widths $d_w$ and $d_n$. In light of the measured band structures and the photoemission simulations, the $d_w$ width appears clearly as a magic size that lowers the electronic energy. In contrast, $d_n$ is explained as a critical size at which the system may improve the faceting kinetics. Further experiments to clarify this later point are encouraged.

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