One-dimensional Ag-Cu superlattices on vicinal Cu(111)

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Regular arrays of one-dimensional Ag stripes can be grown by adsorption and annealing of Ag on vicinal Cu(111). The Ag adlayer induces a periodic hill-and-valley nanostructure with alternating Ag-covered (112)-oriented facets and clean Cu stepped areas. The superlattice has been studied as a function of Ag coverage using a wedge (0.34–0.52 monolayers). The width of the Ag stripes is constant across the wedge ($\approx$45 Å), such that the wavelength of the hill-and-valley structure varies from 140 Å to 90 Å and the width and step density of the Cu stepped areas is reduced accordingly. The structure of the Ag-covered stripes is consistent with a rotated, uniaxially compressed, close-packed layer that wets the Cu(112) plane.

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Vicinal surfaces with regular distributions of straight steps appear as natural templates for self-assembling lateral one-dimensional nanostructures due to their strong uniaxial anisotropy. If the substrate is stable during adsorption it is possible to produce regular arrays of quantum wires and stripes by step decoration and step-flow growth[1] or by shadow deposition at faceted substrates.[2] Another option for nanostructuring takes advantage of adsorbate-induced faceting. In the ideal case, the system self-organizes forming a striped, hill-and-valley nanostructure with two alternating phases of different crystallographic orientations, i.e., adsorbate-covered facets and clean substrate stripes.[3] In this Brief Report we present an example of one-dimensional, two-phase mesoscopic ordering induced by adsorption at a vicinal surface. We show that submonolayer amounts of Ag deposited on Cu(223) and annealed to 500 K result in a lateral structure, namely Ag-covered Cu(112) nanostripes spaced by clean Cu areas. This lateral system is interesting from various fundamental points of view. On the one hand, the strong differences in the optical behavior between Ag and Cu makes it attractive for optical studies. On the other hand, it is a model system to investigate the electronic structure on lateral superlattices because of the presence of the well-known p_z-like surface state at both Ag and Cu surfaces.

We used an Omicron scanning tunneling microscopy (STM) I setup, equipped with Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED). The Cu(223) surface is vicinal to (111) with a 11.4° miscut about the $[\bar{1}12]$ direction. The crystal was obtained from mechanical erosion of a Cu(111) disk and the resulting surface was mechanically and electrochemically polished to obtain a mirrorlike termination.[4] After a short sputter-annealing treatment in ultrahigh vacuum, we obtained a clean surface, as revealed by the AES spectra and the sharp beam splitting in LEED. The STM topography from this surface displayed a regular array of linear, monoatomic steps along the dense $[\bar{1}10]$ direction with {100} minifacets at the step edges. The average terrace width measured with STM is 10.3 Å, i.e., an 11.4° miscut, with a majority of terraces consisting of $4\frac{2}{3}$ atomic rows, as expected for Cu(223). All STM images were taken at 300 K. Ag deposition was done by means of an electron-beam heated source at a sample temperature of 300 K. Completion of the nanostructuring is obtained after annealing to at least 500 K. The annealing time does not have any significant influence on the resulting surface topography. In order to have a continuous variation of the coverage, Ag is deposited as a wedge by simply placing the Ag source in a slightly eccentric position with respect to the sample. The coverage is calculated from the STM topography in large (3000 Å$\times$3000 Å) frames, assuming that Ag-covered areas consist of packed, one-monolayer-thick patches. This assumption is consistent with the detailed analysis of the atomic structure of Ag-covered areas and also with AES measurements.

Figure 1 shows two STM topographies of the Cu(223) surface with (a) 0.52 and (b) 0.34 monolayers (ML) of Ag. They represent the two extremes of the same 5-mm-wide Ag wedge. The plane of the image is the average surface (223). We clearly observe the presence of two alternating phases forming a hill-and-valley structure, i.e., a striped array of clean stepped Cu- and Ag-covered facets. Ag-covered areas are immediately identified in STM pictures as bright stripes, because their density increases across the wedge. The AES cross-check allows us to ensure that Ag cannot significantly be present at the clean Cu areas in between the Ag stripes. This analysis is based on the assumption that the thickness of the Ag stripes is a single adlayer, and surface alloying can be ruled out.[5] A reference for the calibration of the Ag Auger signal was made by means of one-monolayer Ag films, that is, beyond the coverage limit where the (112) facets appear.[13] In Fig. 2 we show the schematic profile of the Ag/Cu nanostructure. The local orientation of the Ag-covered facets is (112), independent of the coverage. (112) is a crystal plane that deviates 19.5° with respect to the (111) plane. Such facet orientation is deduced from STM linescan analysis. At 0.52 ML the hill-to-hill distance is 90 Å and the width of the Ag and Cu stripes is 44 Å and 46 Å, respectively. Inside the clean Cu areas, we can distinguish (111) terraces and monoatomic steps with their characteristic frizzy edges. The local miscut within the Cu stripes becomes very low at such high coverages. Flat Cu(111) facets with 0° miscut would be

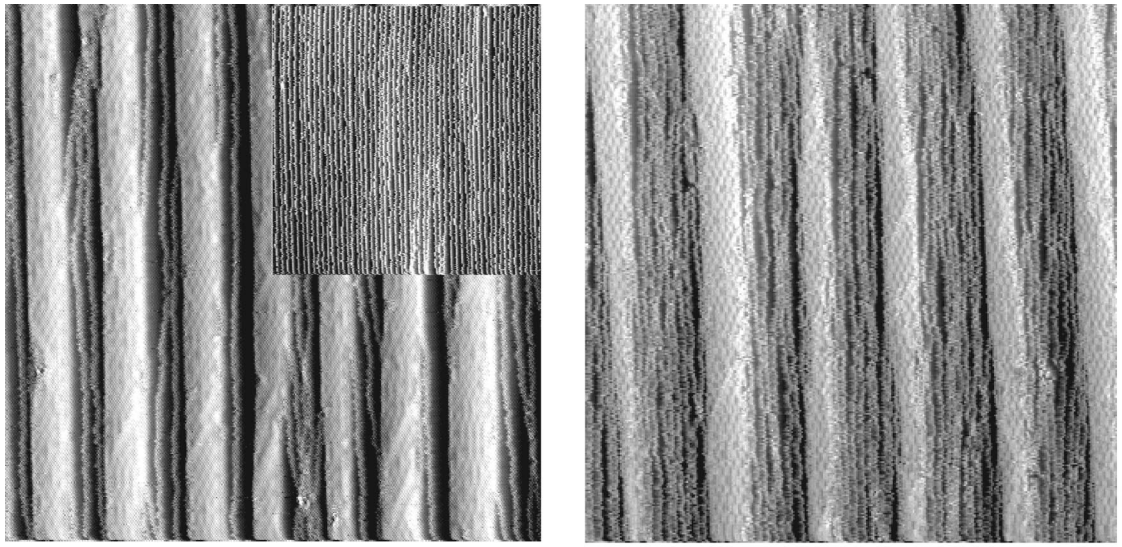

FIG. 1. STM topographies (815×815 Å^2) of a Ag wedge (0.52–0.34 ML) deposited on Cu(223) and annealed to 500 K. The images are taken at the edges of the wedge and display a local coverage of 0.52 ML (a) and 0.34 ML (b). A fairly regular hill-and-valley structure of Ag-covered (bright) and clean stepped Cu (frizzy step edges) is observed in both cases. The Ag stripe width is approximately the same across the whole of the wedge. The clean Cu(223) surface prior to deposition is shown in the inset (500×500 Å^2). For contrast enhancement the surface is illuminated from the left by a virtual light source.

reached at a coverage of 0.59 ML (see caption of Fig. 2). For 0.34 ML the wave length is longer (140 Å), but the Ag stripes have approximately the same width (49 Å) and Cu stepped areas are wider (91 Å). For this reason, the local miscut at Cu stripes is 8.1°, i.e., in between the miscut of the initially clean surface and the flat (111) orientation. It is interesting to note that the Ag stripe width is kept fairly constant across the whole wedge, and that it does not depend on the annealing temperature. Thus, this nanostructure allows for the continuous control of the miscut and width of the remaining clean Cu stripes via Ag coverage at this range of coverage. This is of interest because the continuous change of the local miscut at clean Cu stripes is reflected in the electronic structure.[6] Typically, the binding energy and orientation of the reference plane of the Shockley surface state change with miscut.[7]

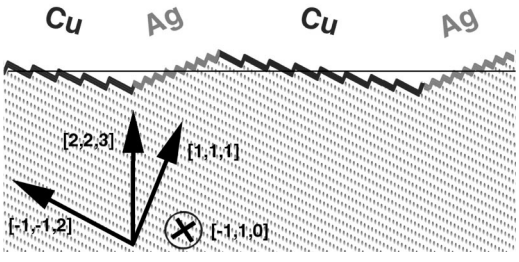

FIG. 2. Lateral profile of the Cu/Ag superlattice. The global (initially also local) miscut of the surface is $\varphi_{\mathrm{Cu,\,initial}}=11.4°$, which corresponds to the (223) plane. The angle of the Ag facet with respect to (111) is always $\varphi_{\mathrm{Ag}}=19.5°$, i.e., (112). Here the case of Fig. 1(b) with 0.34 ML of Ag is shown. Then the angle of the clean Cu stripes is $\varphi_{\mathrm{Cu,clean}}=8.1°$, which is the (334) facet. In the general case, the angles depend on coverage via $\Theta_{\mathrm{Ag}}\approx(\sin\varphi_{\mathrm{Cu,initial}}-\sin\varphi_{\mathrm{Cu,clean}})/(\sin\varphi_{\mathrm{Ag}}-\sin\varphi_{\mathrm{Cu,clean}})$.

Figure 3(a) shows the limited lateral coherence of the Ag/Cu mesoscopic structure. The decay length of the autocorrelation function is three to five periods in the direction perpendicular to the stripes (stronger autocorrelation with higher coverages), whereas the Ag stripes inside regular patches are longer than 3000 Å. Statistical evaluations of images of $(>2000$ Å$)^2$ size yield distributions of Gaussian type with standard deviations of 0.25 times the average width for the hill-to-hill-distance, the Ag-stripe-width and the Cu-stripe-width. This is the best superlattice we can obtain under these preparation conditions. As we show elsewhere,[6] the coverage range of the wedge was the optimum to obtain Ag/Cu superlattices. At coverages below 0.3 ML the length of the Ag-covered stripes is very much reduced. Above 0.55 ML the system makes a transition to a structure with three coexisting phases, i.e., Ag-covered facets with two different orientations.[7]

The small-scale image shown in Fig. 3(b) allows the examination of the inner structure of the Ag-covered facets. This structure displays a characteristic Moiré pattern. It appears that the high atomic mobility of Ag, that usually hampers STM measurements, is reduced at the densely packed patches of the nanostructure since stable scanning conditions at room temperature are achieved. The bumps do not represent single atoms, but the maxima of the Moiré structure. Parallel to the steps (vertical in the image), this pattern consists of sinusoidal modulations, exhibiting a longitudinal periodicity of 25 Å, corresponding to ten Cu nearest neighbor distances.[8,9] Adjacent modulations are in antiphase relation and separated by 6.3 Å, corresponding to the step separation in Cu(112), i.e., they indicate the presence of substrate steps

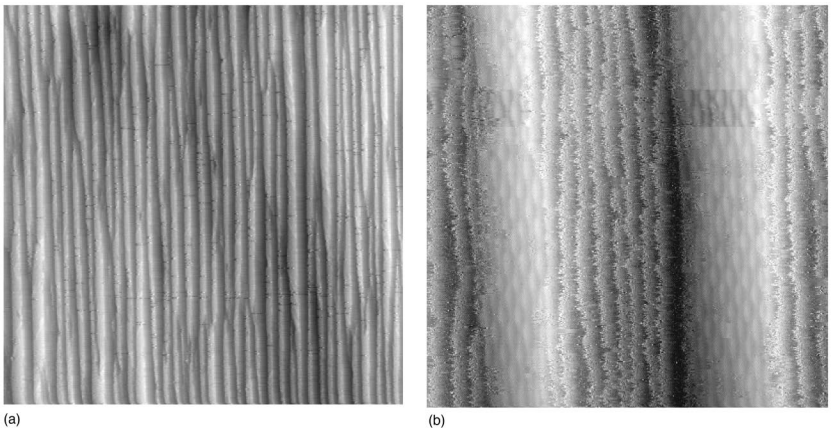

FIG. 3. STM topographies of the same Cu(223) surface, as in Fig. 1, taken at a region with 0.50 ML Ag (a) and 0.34 ML (b). The large-scale (3250×3250 Å) image shows the limited coherence of the lateral superlattice, whereas the small-scale (300×300 Å) picture in (b) shows the Moiré reconstruction of the (112)-oriented Ag-covered stripes. The mean corrugation amplitudes of the hill-and-valley and the Moiré structures are 7 and 0.6 Å.

underneath. Thus the Moiré reconstruction has a $c(2\times10)$ periodicity with respect to the substrate, i.e., at least at this large scale the unit mesh appears centered, rectangular and covers 10 Cu atoms and two Cu steps. Below, we show that at a smaller scale the structure slightly deviates from a rectangular unit mesh.

The Moiré reconstruction of the Ag-covered stripes in Fig. 3 resembles in some aspects that of Ag/Cu(111),[10,11] and suggests that the Ag layer is close-packed. Assuming close-packed rows aligned parallel to the steps, the best lattice matching with respect to the substrate unit cell in the perpendicular direction is obtained for Cu(112). Cu(112) consists of (111) terraces with $2\frac{2}{3}$ Cu close-packed rows (row separation 2.214 Å[12]). This leads to a 6.261 Å unit cell in the direction perpendicular to the steps and we can accommodate five Ag rows (each 2.5 Å wide) into two Cu(112) unit cells [two (111) terraces] with only 0.10% mismatch.[12] Since lattice matching is known to be the driving force for hill-and-valley nanostructuring in a similar system,[3] such a small mismatch can explain the preference to form Cu(112) facets.[13] However, a slight rotation of this close-packed Ag(111) layer is necessary to explain the quasi $c(2\times10)$ structure, as we show below.

In Fig. 4 we analyze in detail the structure of the Ag-covered facet. The image shown in Fig. 4(a) corresponds to a small frame of Fig. 3(b) taken at the center of one Ag stripe. The $c(2\times10)$ structure consists of equivalent bumps aligned parallel to the steps in a single terrace, with adjacent terraces in antiphase. Figure 4(b) displays a Ag(111) layer model that agrees with the STM observations. The 25 Å (tenfold) periodicity along the steps is produced by a 5.21° rotation of the Ag(111) layer about the surface normal together with a small compression of the Ag(111) plane in two axes, i.e., 0.93 parallel to the steps and 0.994 in the perpendicular direction. Both are necessary to produce equivalent bumps along a single terrace.[14] The rotation of the layer is supported by the linescan analysis indicated in Fig. 4(a) and displayed in Fig. 4(c). The linescan goes through top positions in the micro-

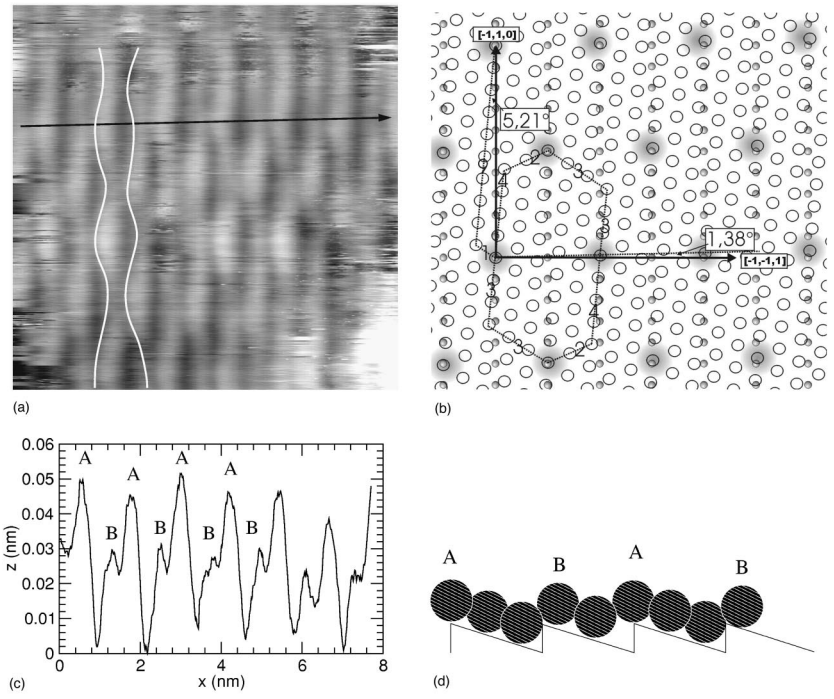

FIG. 4. (a) STM small-scale image (80×80 Å) of a Ag facet. The solid line represents the linescan that joins the top positions of the Moiré reconstruction, which is displayed in (c). The profile of the linescan is consistent with the side view model shown in (d) that is in turn inferred from a close-packed and rotated layer, as shown in (b). The slight angular deviation of the bumps from the direction perpendicular [hard to see in (a)] is compatible with the model of the 5.21°-rotated hexagonal Ag layer with uniaxial compression, as displayed in (b). The open circles represent Ag atoms, the balls represent Cu(112) step edge atoms and the soft spots represent bumps in the Moiré reconstruction. The bumps need not necessarily be Ag ''on top'' of Cu, as in this figure, but the atomic arrangement around the bumps must be equivalent for all of them. The 5.21° result from a triangle with side lengths 1 and 9 Ag atomic units including a 120° angle, almost hitting again a Cu substrate step edge atom (see text). The 1.38° are obtained from (b) via $5.21° - \arctan(\frac{1}{2}/5\cos 30°)$.

facet. We observe two different maxima, marked A and B, which are alternately separated by 7.8 Å and 4.7 Å. This corresponds to the 2-3-2-3-2 row series expected from the simple vertical relaxation of the Ag(111) layer on Cu(111) terraces, as shown in Fig. 4(d). Note that if the Ag(111) layer is not rotated, this packing sequence leads to two nonequivalent terrace types, i.e., terraces that contain either two or three Ag atomic atoms. By the azimuthal rotation this inequality is removed in a natural way: the terraces become physically identical and the sinusoidal modulations, i.e., the bumps, in adjacent terraces are aligned in antiphase, as indicated in Fig. 4(b). Odd periodicities in the parallel direction are ruled out automatically because the observation of equivalent bumps implies an equivalent atomic environment for them.

The direction perpendicular to the steps and the one along which the bumps line up do not exactly coincide, but include an angle of 1.38°, as shown in Fig. 4(b). In fact, our LEED and STM measurements reveal that the bumps in the Moiré pattern do not line up exactly perpendicular to the steps, such that the superlattice becomes slightly oblique. Thus, after a few transversal periods, the bumps must become slightly inequivalent again. This deviation is, however, marginal since the width of the Ag stripes is around 3.6 Moiré periods (45 Å), i.e., the accumulated phase shift at the border stays below a quarter of the Cu-nearest-neighbor-distance. One could even discuss whether this run-out-of-phase limits the width of the Ag stripes. With a constant Ag stripe width, the period of the faceting is determined by the coverage ($period \approx Ag\ stripe\ width/coverage$). A different approach to explain the wavelength of periodically ordered structures is given in Ref. 15. It is argued that the ratio between a single domain and the period of the structure with normal long-range interactions is always around 1:3. This is also true for our system. On the other hand, clockwise and counterclockwise rotations on the Cu(112) substrate facet imply the existence of two rotational domains. However, we do not observe any domain walls within the Ag stripes. We conclude that, at least within the stripes, the direction of the rotation does not change. The weak lines visible on the Ag facets of Figs. 1(a) and 1(b) are not domain boundaries but monoatomic steps in the (112) facets (height=0.74 Å). One structure probably dominates the other because no twin images are observed also by LEED.

In summary, we have found an interesting example of lateral nanostructuring at Cu vicinal surfaces induced by Ag adsorption and annealing. The superstructure consists of a regular distribution of Ag-covered (112)-oriented facets and clean stepped Cu stripes with a Ag stripe width that does not depend on Ag coverage or annealing temperature. The Ag-covered stripe appears to be made up from a 5.21° rotated and uniaxially compressed Ag close-packed layer, which is found to fit nicely in the Cu(112) stepped structure. Thus, lattice matching appears to be the driving force of the observed mesoscopic nanostructuring.

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[13] Other Cu(111) vicinal planes lead to good matching with Ag rows, but they involve more complicated unit cells. On the original Cu(223), 17 Ag rows are required to fit into 4 substrate unit cells, to give only a 1.2% misfit. On Cu(335) facets, i.e., vicinal Cu(111) with $3\frac{2}{3}$ atomic rows per terrace, three unit cells match to 10 Ag rows with a 0.24% mismatch. Thus Cu(335) faceting is also a good candidate from the point of view of lattice matching. The Cu(335) option, which requires less substrate mass transport, is chosen by the system when the coverage clearly exceeds 0.5 ML. Then a transition from (112) to (335) facets occurs (Ref. 7). At about one ML large (223) facets, exhibiting also a Moiré pattern, are observed by STM.

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