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Potential energy landscape of metallic Moiré patterns

Jakob Bork^{1,2}, Peter Wahl¹, Lars Diekhöner^{2,4} and Klaus Kern^{1,3}

¹ Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1,
D-70569 Stuttgart, Germany

² Institut for Fysik og Nanoteknologi, and Interdisciplinary Nanoscience Center
(iNANO), Aalborg Universitet, Skjernvej 4A, DK-9220 Aalborg, Denmark

³ Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de
Lausanne (EPFL), CH-1015 Lausanne, Switzerland

E-mail: ld@nano.aau.dk

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Abstract. The modulation of the electronic structure of cobalt islands on Cu(111) by the Moiré pattern of an Ag overlayer is investigated. Acquisition of tunneling spectroscopy maps reveals a local modification of both the energy and the amplitude of the cobalt-related *d*-states on the length scale of the periodicity of the Moiré superstructure. The modulation of the energy can be rationalized by the spatially varying hybridization of the cobalt atoms with the silver *sp*-bands. We propose that Moiré modulated *d*-states at metal interfaces with a periodicity of a few nanometers may provide a novel route to manipulate the chemical reactivity of surfaces and might serve as a template which modulates magnetic properties such as the spin density.

The ability to precisely control the electronic structure of solids and their surfaces is crucial for the engineering of materials and devices with properties and functionalities tailored to specific needs. A number of strategies have been developed in the past to tune the electronic structure of metal surfaces globally and locally [1], including the growth of pseudomorphic thin films [2] and bimetallic surface alloys [3]. The reactivity of a transition metal surface is strongly dependent on the energetic position, relative to the Fermi level, of the localized *d*-states [4]. Whereas flat metallic films lead to an overall shift of the electronic states [2], alloying creates sites where the reactivity is locally enhanced, e.g. sees molecules preferentially adsorbing at specific sites of the alloy [3]. The latter thus represents a structured surface with an atomically varying local electronic structure across the surface. Many surfaces in nature

⁴ Author to whom any correspondence should be addressed.

show large-scale reconstructions, either in their clean state or during growth. In heteroepitaxial growth this restructuring is driven by strain often inducing complex patterns of ordered surface dislocations or Moiré structures [5, 6]. At these surfaces, bonding and diffusion energies change on a much larger length scale than for individual atomic sites. The periodically patterned surfaces can thus serve as nanotemplates to guide nanostructure formation via predefined nucleation sites or energetic sinks. The directed self-ordering growth strategy has very successfully been used for the fabrication of highly ordered nanostructure arrays [7]–[11]. Surprisingly, the spatial modulation of the electronic structure that inherently must accompany the structural inhomogeneity of the interface has only been studied for non-metallic systems so far [9], [11]–[15]. In this paper, we demonstrate how a silver adlayer, forming a Moiré pattern, modulates the electronic structure of an underlying cobalt layer on the nanometer scale. The local electronic structure is measured using scanning tunneling spectroscopy and the analysis of spectroscopic maps acquired over areas on the order of $10 \times 10 \text{ nm}^2$. A prominent feature from a d -derived surface state is tracked over the unit cell of the Moiré pattern to detect local changes in the electronic structure. To this end, we have investigated silver-capped cobalt islands on a Cu(111) surface.

The growth of silver on bilayer cobalt nanoislands on Cu(111) has recently been investigated [16]. It was found that at room temperature silver preferentially nucleates on top of cobalt islands and that these are either completely capped with 1 ML Ag or remain uncovered. Thus cobalt islands with a closed Ag cap layer can be investigated. It was furthermore found that the low-energy electron diffraction pattern of Ag/Co/Cu(111) shows the same symmetry as Ag/Cu(111), evidence of a similar reconstruction or Moiré pattern due to the lattice mismatch between the silver overlayer and the cobalt island to that between Ag and Cu(111) [17]. The growth and electronic structure of cobalt on Cu(111) are well known: cobalt grows pseudomorphic on Cu(111) and forms triangular islands of bilayer height [20, 21]. The cobalt islands exhibit a very pronounced electronic feature in the local density of states, which can be easily probed by tunneling spectroscopy. This feature has been characterized both experimentally [22, 23] and theoretically [22, 24] and has been shown to be a spin-polarized state related to the d -states of cobalt. The cobalt islands are found to expose a stable out-of-plane magnetization at 14 K [23].

Scanning tunneling microscopy (STM) measurements have been performed in a purpose-built low-temperature ultra-high vacuum (UHV) STM which operates at 6 K. Tunneling spectra have been acquired with an open feedback loop recording the dI/dV signal from a lock-in amplifier (frequency 3.8 kHz and 3 mV modulation). For spectroscopic maps, spectra have been taken on a regular grid at each point of the grid. The tip-sample distance has been stabilized at each point and the spectrum has been measured after opening the feedback loop. The Cu(111) single-crystal substrate has been prepared by cycles of argon sputtering and annealing to 800 K. Silver and cobalt have been evaporated from a commercial electron-beam heated evaporator. To prevent ions from the deposition source from hitting the sample and damaging it, either a counter-voltage or a high voltage on a deflection shield has been applied.

A typical topography after deposition of a sub-monolayer coverage of cobalt and subsequently silver at room temperature is shown in figure 1. The Ag-capped Co island exhibits a Moiré pattern due to the lattice mismatch between the silver overlayer and the cobalt island. The apparent corrugation of the Moiré pattern amounts to 0.4 \AA at a bias of 100 mV, but varies only a little in the range $\pm 1 \text{ V}$ around the Fermi level. Three distinct points of high symmetry can be found as marked in figure 2(b). By comparison with the Moiré pattern formed by

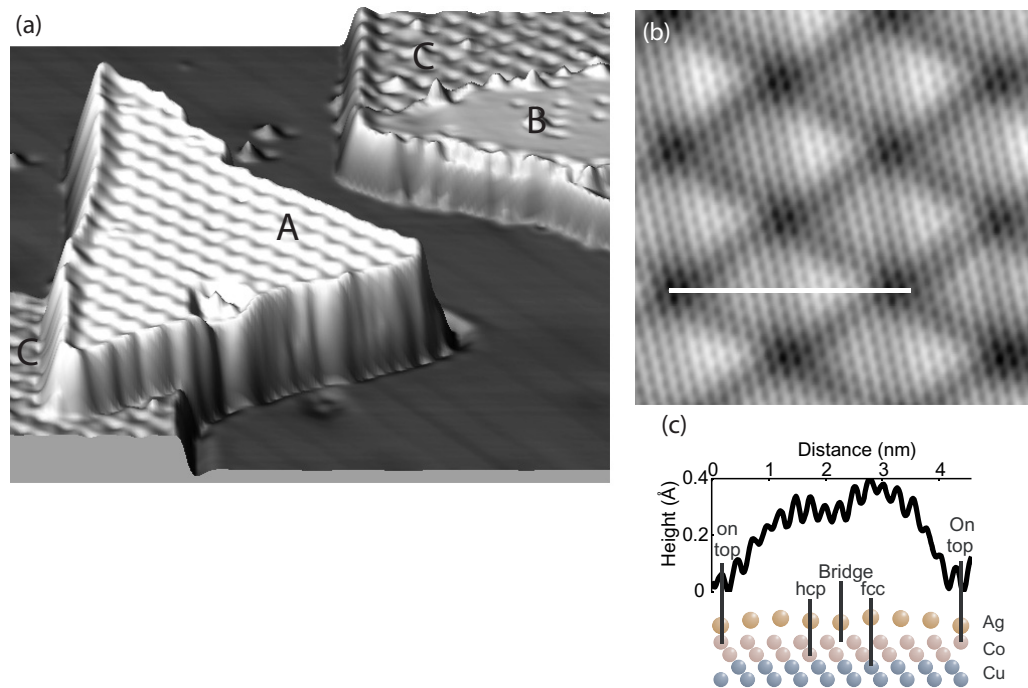


Figure 1. (a) Overview STM topography ($54 \times 54 \text{ nm}^2$) showing triangular cobalt islands either capped with Ag (A) or free of Ag (B). Ag directly on Cu(111) (C) can also be seen next to the islands. (b) Close-up image of an Ag-covered bilayer high Co island on Cu(111) acquired with a bias voltage of 50 mV [25]. (c) Line cut through the topography in (b) with an atomic model of the Moiré pattern along the same cut. The model is a sketch to illustrate the positions of the atoms and some of the atoms are therefore omitted for clarity.

silver on Cu(111), as well as by symmetry arguments, we can assign these to the silver atoms sitting in fcc, hcp and on-top sites of the underlying cobalt island. Calculations for the Moiré pattern of Ag on Cu(111) [26, 27] reveal in agreement with experiments [17] that the vertical positions of the silver atoms above the substrate are modulated with the periodicity of the Moiré pattern, i.e. the surface is reconstructed. It turns out that the silver atoms in on-top sites of the substrate are the ones that exhibit the strongest displacement towards the surface and are also imaged with the smallest apparent height by STM. The silver-covered cobalt islands expose a strong spectroscopic feature in tunneling spectroscopy similar to that of bare cobalt islands on Cu(111) [22]. This feature is shown in comparison with that of an uncovered cobalt island in figure 2(a). The peak position shifts towards the Fermi energy when going from a bare cobalt island to a silver-covered one and the peak energy depends on where in the Moiré pattern the spectrum is measured; fcc, hcp or on-top. This can be seen from the point spectra in figure 2(b). The designation of the positions is explained in the model in figure 1(c) and defines whether the Ag atoms of the overlayer reside in on-top, fcc or hcp positions of the two cobalt layers. Furthermore, a second peak (labelled peak B in figure 2(b)) appears with lower or comparable amplitude depending on the position in the Moiré pattern. It becomes evident that the two peaks exhibit their maximum amplitude at different locations. No similarly position-dependent feature is found on the Moiré pattern formed by silver on Cu(111), where only the onset of the

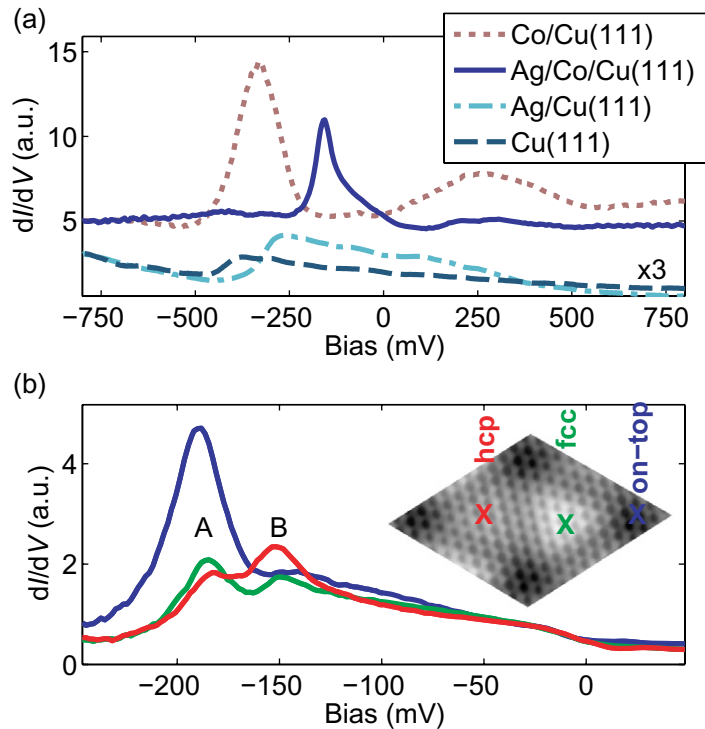


Figure 2. (a) Spectra acquired on the bare Cu(111) surface, on Ag-covered Cu(111) on cobalt islands on Cu(111) and on an Ag-covered cobalt island on Cu(111) in the on-top site. The spectra are normalized at -800 mV, the spectra for Cu(111) and Ag/Cu(111) are stretched vertically by a factor of 3 and the spectra for Co/Cu(111) and Ag/Co/Cu(111) are vertically displaced. (b) Spectra on the fcc, hcp and on-top positions in the Moiré pattern formed by the silver cap layer on a cobalt island on Cu(111).

delocalized two-dimensional (2D) surface state of Cu(111) is shifted towards the Fermi energy by the silver overlayer, as can be seen in figure 2(a) [17]–[19]. Thus we conclude that both features stem from the cobalt island underneath the silver layer.

In order to gain insight into the local modifications of the electronic structure and the origin of the two peaks, we have acquired spectroscopic maps of the silver-covered cobalt islands. For the spectroscopic maps, spectra have been taken at each point of a grid of 64×64 lattice points. These maps, consisting of ≈ 4000 spectra, allow a detailed analysis of the behavior of the two features as a function of position in the Moiré pattern. We used a set point bias value of $+50$ mV to stabilize the tip in each position. In this region above the Fermi level there is only very little corrugation in the local density of states (LDOS) across the unit cell, which could otherwise influence the amplitude distribution of the spectra across the surface. For the analysis, we have fitted the two peaks by the sum of two Lorentzians and a slowly varying background consisting of another two Lorentzians, which are much wider and have a smaller peak height compared to those describing peaks A and B (see figure 3(a)). Each spectrum in a map has been fitted by this function, allowing us to analyze the behavior of the two peaks separately. We have also attempted to describe the background by a polynomial up to the sixth order, which however did not describe the data as well.

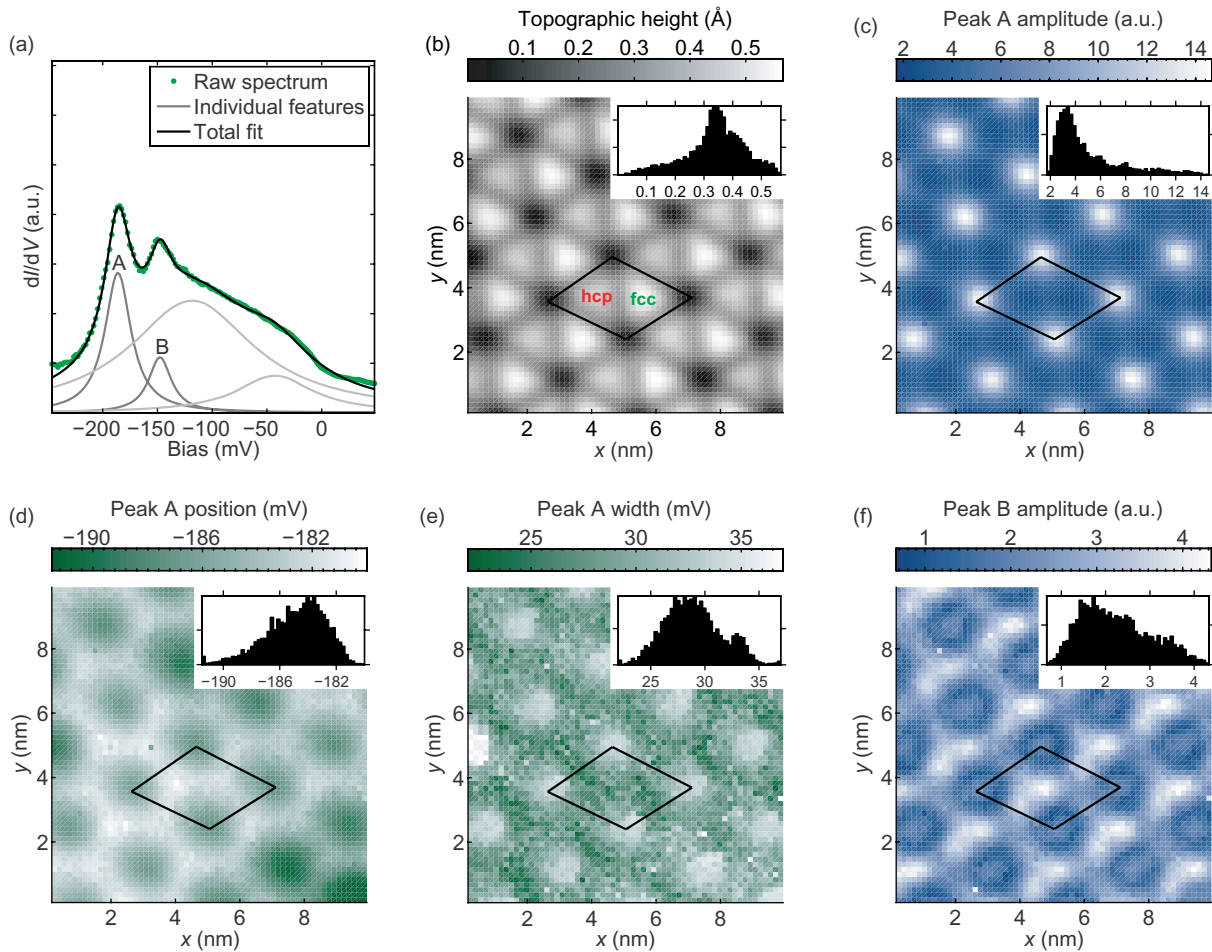


Figure 3. (a) An example fit to a spectrum acquired at an fcc site of the Moiré pattern. The fit function consists of two Lorentzians to describe the two pronounced peaks at -150 and -180 mV plus two broader Lorentzians to account for the background. (b) Topographic image of the area in which the spectroscopic map has been acquired from which the following maps have been extracted. (c) Map of the amplitude of the lower energy peak (A) as extracted from the spectra acquired at each position in the shown area. (d) Map of the energy position and (e) of the FWHM. (f) Amplitude of the higher energy peak (B). The inset in each panel shows a histogram of the respective quantity. All data maps consist of 64×64 points.

The images in figures 3(b)–(f) display the topography and the maps resulting from the analysis of the spectroscopy map. Figure 3(c) shows the amplitude distribution of the lower energy peak (peak A) as a function of position within the Moiré pattern. It is evident that the amplitude of the peak is strongly enhanced in on-top positions. Figures 3(d) and (e) show the energy position and width of the peak. Both turn out to be correlated with the morphology of the Moiré pattern. The peak position shifts by up to 10 mV between fcc and on-top positions, whereas the full-width at half-maximum (FWHM) varies between 24 and 35 mV. The amplitude map of the higher energy peak (peak B) shown in figure 3(f) also exhibits a modulation with the periodicity of the Moiré pattern. However, in contrast to the lower energy peak (peak A)

its maxima appear in positions that correspond to silver atoms in hcp positions of the cobalt island⁵. The parameters of the two Lorentzians which describe the background of the tunneling spectra are only weakly correlated with the topography. The strong peak found in the tunneling spectrum on bare cobalt islands is a d_{z^2} -state of the cobalt [22], hence the strong peaks on the silver-covered cobalt islands can be assumed to be derived from this d_{z^2} -state. This is supported by the fact that a spectrum on a monolayer of silver on Cu(111), which forms a very similar Moiré pattern if deposited at low temperature, does not show a similar feature in the tunneling spectrum (cf the spectra in figure 2(a)). Instead of only one strong peak as on the cobalt islands we find two peaks on the Ag-covered cobalt islands. The amplitude of the one at lower energy is directly anti-correlated with the apparent height and shows a huge increase in the dI/dV signal; by more than a factor of two in on-top sites compared to the adjacent fcc and hcp regions. The strong increase in amplitude in on-top sites (see figure 3(c)) means that the wave function extends much further into the vacuum at these sites. It is therefore likely to have substantial overlap with wave functions of atomic or molecular adsorbates and could play an important role in bond formation at the surface. The peak is fairly narrow with a FWHM of only 24–35 mV, which is much narrower than the d -resonance of the bare cobalt island, which is 100 mV wide [22]. The peak found at higher energy has its maximum amplitude in positions where the silver atoms occupy hcp sites of the cobalt island. From symmetry arguments, this amplitude distribution cannot be rationalized by the presence of only two layers, the silver layer and the upper cobalt layer, where fcc and hcp cannot be defined for the silver atoms. Thus the difference between the spectra at the two positions as seen in figure 3(f) must be related to the influence of the lower cobalt layer, i.e. we ascribe this state to the inner interfacial layer at the Co/Cu interface. Note that a modulation of the morphology does not necessarily lead to a spatial modulation in the electronic structure. We have also measured spectroscopic maps on Ag/Cu(111), where a similar Moiré pattern as on Ag/Co/Cu(111) is seen. The electronic structure across the unit cell shows only very weak variations (roughly an order of magnitude smaller corrugation in the LDOS), which we mainly attribute to a setpoint effect.

As can be seen from figure 3(d), the lower energy peak is shifting down in energy at positions where atoms in the silver adlayer are imaged at a lower height, while it is moving towards higher energies when the topography shows a larger apparent height. This finding becomes more evident from a two-dimensional histogram (see figure 4(a)), in which the energy of the peak is plotted against the apparent height from the topography. The darkness of each pixel in the histogram represents the number of occurrences within the spectroscopic map of the specific combination of peak energy and height. Although there is some scatter, a clear trend can be observed. We find a similar correlation between the width of the peak and the apparent height as that displayed in figure 4(b). For lower apparent height, meaning the silver atoms are closer to the substrate, we observe a larger width of the peak. We note that also for the reversed case, cobalt grown on an Ag(111) surface, a Moiré pattern with a similar periodicity but reversed contrast in the topography is observed [28]. In this case, we see a similar behavior of the cobalt-related peak [29]. The behavior observed in the correlation plots can be rationalized by the so-called d -band model originally developed by Ruban *et al* [2] to explain the reactivity of bimetallic surfaces. In their model, the d -band center of an adlayer shifts away from the Fermi energy with increased hybridization, with the bulk sp -bands to maintain a constant occupation

⁵ The pattern could come from the topography as the hcp and fcc sites are imaged with different heights. We made sure that the same contrast is observed in quantities that do not depend on the setup condition [33].

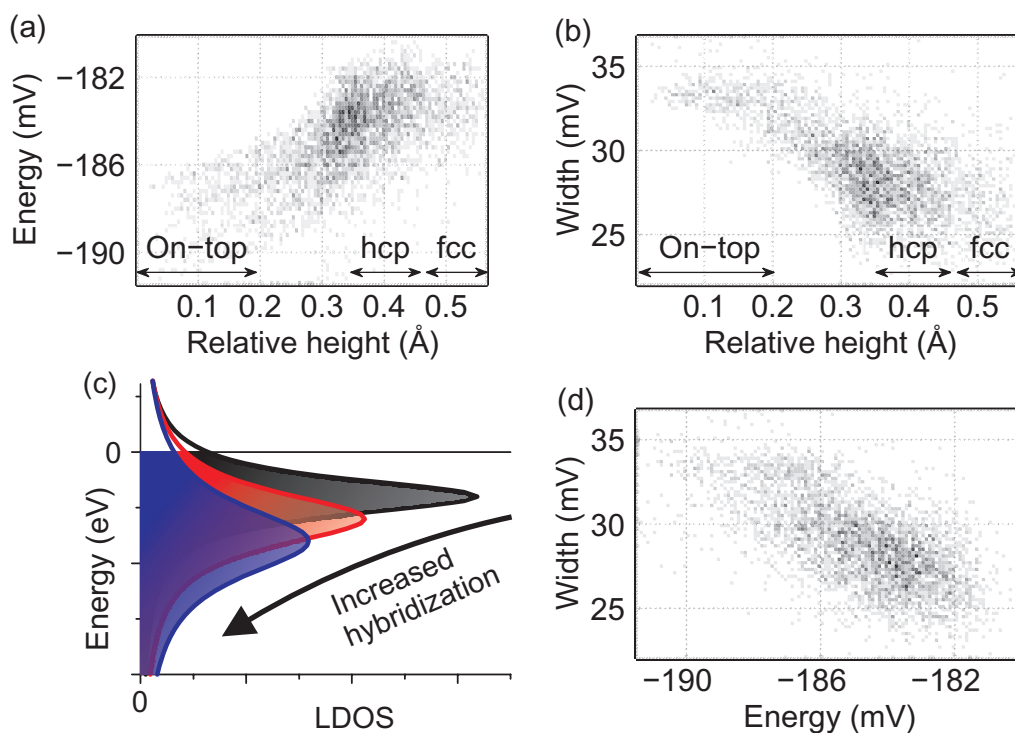


Figure 4. (a) 2D histogram of the energy position of peak A against the height extracted from figures 3(d) and (a), (b) 2D histogram of the FWHM of peak A against the height extracted from figures 3(e) and (a). (c) Sketch of the model by Ruban and coworkers [2] for a d -band hybridizing with the sp -states of a host metal. (d) 2D histogram of the FWHM against the energy position. The histogram shows a trend consistent with the model by Ruban and coworkers.

of the d -band (cf sketch in figure 4(c)). Specifically, the model proposes a linear relationship between the energy position of the d -band center and the width of the d -band. Transferred to our system, we apply the model to the d_{z^2} -state which is found in tunneling spectra. If we hypothesize that the hybridization between the cobalt d -states and the silver sp -states increases with the silver atoms moving closer to the cobalt layer, as evident from the measured lower apparent height of the silver adlayer (see figure 1(c)), the peak should get wider due to the increased hybridization and move further away from the Fermi energy. This is consistent with the correlation plots displayed in figures 4(a) and (b). To allow a direct comparison, in figure 4(d) the correlation between energy position and width of state is shown. A trend that is consistent with the model discussed above is found, where the state shifts away from the Fermi energy as it becomes wider. Note that the amplitude of the measured spectra does not follow the model sketch of figure 4(c), where a decrease in amplitude with increasing hybridization is expected. In figure 3(c) it can be seen that the amplitude increases at the on-top sites where the hybridization is strongest. Although the LDOS at the Ag–Co interface may behave as in figure 4(c), the difference to the measured spectra at the surface–vacuum interface could be explained by a decrease in distance between tip and Co-layer, but also by varying tunneling matrix elements across the unit cell originating from the varying atomic geometries of the first layers (see figure 1(c)). These would affect the amplitude but not the energy position or width of the resonance.

The formation of Moiré patterns is observed for a number of metallic heteroepitaxial systems with a lattice mismatch between the substrate and the deposited material (see e.g. [5, 17, 28]). It can be expected that quite generally a modulation of the electronic structure occurs in these systems similar to the one reported here. For example, we have also investigated Co islands on Ag(111) [29], where we have observed similar effects to those found on Ag/Co/Cu(111). We thus believe that our results can be generalized by varying the metal adlayer on top of the Co, but also expect to see similar effects in other metallic Moiré systems. This is also corroborated by the recently observed correlations between morphology and electronic structure in non-metallic Moiré systems like FeO(111), NaCl/Ag(100), boron nitride/Rh(111) and graphene/Ru(0001) [9], [11]–[15].

The observed modulation of the cobalt-related d -state invoked by the silver adlayer can be expected to result in a modulation of the local reactivity at the surface due to the change in the energy position, but also due to the spill-out of the state towards the vacuum making it more accessible for adsorbates. It should be mentioned that the observed changes in energy position on the order of tens of mV are most likely too small to significantly change the reactivity [4], and the variation in amplitude is therefore expected to be more important for this particular system. Besides the interesting local modifications of reactivity of these nanostructures, we can expect to observe modulations of the spin density across the surface. If some of the elements in the multilayered structures are magnetic and involve spin-polarized electronic states, a variation in local density of states will lead to a modulation of magnetic properties. The effects of the modulation can range from a locally modulated spin polarization at the Fermi energy to complicated spin structures. Such influences on magnetic properties have been discussed in terms of a modulation of the density of states by quasiparticle scattering from subsurface defects [30], or by the interaction of an overlayer with a substrate [31]. Since the prominent resonance found on bare cobalt islands is known both from theory [22] and spin sensitive STM measurements [23] to be spin polarized and of minority spin character, the magnetic properties of the cobalt/silver heterostructure will be modulated on a nanometer scale. This might be useful for the fabrication of novel magnetic phases or the self-assembly of ordered arrays of magnetic nanostructures or molecules [8, 32].

In conclusion, we have shown how the deposition of a metallic adlayer can modulate the electronic landscape of a heterostructured interface consisting of Ag/Co/Cu(111). By spectroscopic mapping of the local density of states we measure the electronic structure of the silver-capped cobalt nanoislands on Cu(111). We observe a modulation of the energy position, width and amplitude of the cobalt d -state which is correlated directly with the morphology of the silver Moiré pattern. Analysis of the amplitude distribution of the electronic states allows us to relate them to the inner and outer cobalt interface layers. By choosing a different metallic Moiré system, we expect that it is possible to shape the periodicity of the potential energy landscape.

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