Confinement of surface state electrons in self-organized Co islands on Au(111)

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Abstract. We report on detailed low temperature scanning tunneling spectroscopy measurements performed on nanoscale Co islands on Au(111) films. At low coverages, Co islands self-organize in arrays of mono- and bilayer nanoscale structures that often have an hexagonal shape. The process of self-organization is induced by the Au(111) ‘herringbone’ reconstruction. By means of mapping of the local density of states with lock-in detection, electron standing wave patterns are resolved on top of the atomically flat Co islands. The surface state electrons are observed to be strongly confined laterally inside the Co nanosized islands, with their wavefunctions reflecting the symmetry of the islands. To complement the experimental work, particle-in-a-box calculations were performed. The calculations are based on a newly developed variational method that can be applied to ‘2D boxes’ of arbitrary polygonal shape. The experimental patterns are found to fit nicely to the calculated wavefunctions for a box having a symmetry corresponding to the experimental island symmetry. The small size of the Co islands under study (down to 7.7 nm\textsuperscript{2}) is observed to induce a strong discretization of the energy levels, with very large energy separations between the eigenstates up to several 100 meV. The observed standing wave patterns are identified either as individual eigenstates or as a ‘mixture’ of two or
more energetically close-lying eigenstates of the cobalt island. Additionally, the Co surface state appears not to be limited to mono- and bilayer islands, but this state remains observable for multilayered islands up to five monolayers of Co.

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1. Introduction

The growth and characterization of self-organized nanostructures is one of the most active research areas of recent solid state physics. Detailed knowledge of the intriguing electronic behavior of such nanoparticles persistently gains interest, not only from a fundamental standpoint but also in the view of technological applications, since nowadays the building blocks of electronic devices are entering the nanometer size regime. At this scale, quantum mechanical confinement phenomena play a dominant role in the electronic properties and the discrete nature of the electron charge needs to be taken into account. For detailed investigation of the nanoworld, simultaneous registration of both the local geometrical and electronic properties is needed, a requirement that is fulfilled by combining scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). In order to gain new insights into the properties of novel types of nanostructures, well-defined nanostructures have to be grown or deposited on equally well-defined substrates.

It was already shown earlier by STM and STS that metallic nanoparticles exhibit fascinating size dependent physical properties, which are not present in the bulk. Nanoparticles that are isolated from the metallic substrate by an artificial tunnel barrier, e.g., exhibit pronounced single-electron tunneling phenomena with Coulomb charging and discretization of the electron energy levels, both properties being relevant for applications such as the single-electron transistor [1]–[3]. An alternative route for studying the intrinsic properties of nanoparticles is to grow or deposit them directly on a metallic substrate. Such configurations exhibit intriguing electronic phenomena such as surface state scattering and effects due to the lateral confinement of electrons within nanosized islands [4]–[6], vacancy islands [7, 8] and corrals [9]–[12].

The Au(111) surface reconstruction is an ideal candidate to use as a template for the controlled growth of nanostructures by atomic deposition. It grows in large atomically flat islands of over 1000 nm² and exhibits a remarkable type of surface reconstruction, known as the ‘herringbone’ reconstruction [13, 14]. It has been shown earlier by Voigtländer et al [15] that atomic deposition on Au(111) results in the formation of aligned structures of equally
spaced islands. This result initiated a variety of both experimental and theoretical studies on the organized growth of metals on Au(111) [16]–[19]. Various materials, including Fe [20], Co [15], Ni [21] and Cr [22], show island formation according to this mechanism. Here, we focus on the electronic properties of Co islands, which grow, unlike other materials, in individual islands of both monolayer and bilayer height (1 monolayer (ML) of Co(0001) = 0.205 nm) and hexagonal shape. The upper limit of the island diameter is determined by the surface reconstruction and is around 6 nm [15, 18]. The Au(111) reconstructed surface thus offers an adequate means of creating metallic nanoparticles with a well defined size, simply by depositing more or fewer atoms. This is in contrast to other atomically flat substrates that do not exhibit fixed nucleation points (e.g. Ag(111) and Cu(111)) and for which the island size distribution is therefore more difficult to tune.

We have performed detailed low temperature STM and STS on Co nanoparticles with well defined sizes and shapes. We report on the systematic observation of standing wave patterns of the confined Co surface state for various Co islands on Au(111), with lateral sizes as small as 3 nm. These are, to our knowledge, the smallest particles investigated so far for which standing wave patterns are measured in detail. Furthermore, we have performed particle-in-a-box calculations, which are based on a newly developed variational method that can be applied to ‘two-dimensional (2D) boxes’ of arbitrary polygonal shape. The experimental patterns are found to fit extremely well to the calculated wavefunctions for a box having a symmetry corresponding to the experimental island symmetry. Moreover, the calculations enable us to identify the observed standing wave patterns as either individual eigenstates or as a ‘mixture’ of two or more energetically close-lying individual eigenstates. It appears that the very small size of the Co islands under study (down to 7.7 nm²) results in a strong discretization of the energy levels, with large energy separations between the eigenstates up to several 100 meV. Our results differ from the results of previous studies of Ag islands on Ag(111), for which it was shown by particle-in-a-box calculations that the observed local density of state (LDOS) patterns consist always of a ‘superposition’ of multiple eigenstates [4]. Because of the larger island size in these studies (of around 100 nm²), the energy separation between adjacent eigenstates is on the order of 10 meV.

All our Co islands show a similar feature in the STS spectra: a sharp occupied state peak that appears in the island centers around −160 meV. The existence of a similar peak has been reported recently by Rastei et al [6] relying on both STS experiments and ab initio calculations. Moreover, we observe empty state peaks at higher positive energies that are more pronounced near the island edges. In contrast to Rastei et al (Co islands on Au(111) [6]) and Diekhöner et al (Co islands on Cu(111) [5]), we do not attribute these maxima to hybridization effects, but to electron confinement effects within the nanoscale islands. Additionally, we show that the standing wave patterns resulting from the surface state remain present on multilayered (up to 5 ML) Co islands.

2. Experimental

Epitaxially grown 140 nm thick Au(111) films on freshly cleaved mica were prepared ex situ by molecular beam epitaxy at elevated temperatures. We refer to Vandamme et al [23] for the deposition parameters. The Au(111) surfaces are cleaned in situ by repeated cycles of Ar⁺ sputtering (at about 4 keV and 10⁻⁶ mbar) and annealing (at about 720 K). The resulting films
consist of atomically flat regions with dimensions up to 500 × 500 nm². For all samples, surface quality is checked by STM prior to the Co island growth. A typical example of the Au(111) surface after in situ cleaning is shown in figure 1(a).

The Co islands are produced in situ by room temperature atom deposition with an ultra-high vacuum (UHV) e-beam evaporator (Omicron Nanotechnology) at pressures below 10⁻⁹ mbar and with low deposition rates in the range 0.01–0.05 nm min⁻¹. A high purity Co rod (2.0 mm diameter, 99.995% purity) is used for the Co atom evaporation.

Figure 1(b) shows a typical image of the island self-organization after 0.02 ML Co deposition on Au(111). At this low coverage, both mono- and bilayer islands can be routinely found. All islands show hemispherical shapes since the island sizes are so small that their shape is considerably influenced by tip convolution effects. At higher Co coverage (i.e. 0.12 ML), mainly bilayer islands are found and more distinct island shapes can be observed. Figures 1(c) and (d) illustrate the hexagonal shape of the Co islands on the Au(111) surface. It is found that this hexagonal shape of most of the islands can be enhanced by moderate annealing of the
substrate to temperatures around 330 K. This value is well below the temperature of 400 K at which intermixing of the Co with the Au(111) surface starts [19].

STM and STS measurements are performed with a commercially available STM (Omicron Nanotechnology). The STM operates under UHV conditions at a base pressure in the $10^{-11}$ mbar range and at low temperatures. Cooling is achieved by means of a cold finger. For maximum topography and energy resolution, all measurements are performed at liquid helium ($T_{\text{sample}} \simeq 4.5$ K) temperature. Both mechanically cut and preformed PtIr (10% Ir) tips were used. Tips were cleaned in situ by applying high voltage pulses up to 10 V while being in close proximity to a clean Au(111) surface, until stable topography and spectroscopy can be achieved. The known electron surface state of the Au(111) surface is used as a quality label for our measurements. STM topographic imaging is performed in constant current mode. Simultaneously, differential conductance images ($X-Y-dI/dV$), hereafter referred to as LDOS maps, and local spectroscopy data ($dI/dV$ versus $V$ with open feedback loop) are acquired at modulation frequencies in the 200–1500 Hz range. Modulation amplitudes are in the 10–20 mV range for the local spectroscopy and in the 10–100 mV range for the LDOS maps (typically around 10% of the applied sample voltage). $I$ and $V$ correspond to the tunneling current and voltage, respectively. Everywhere in the text the tunneling bias voltage $V$ refers to the sample voltage, while the STM tip is virtually grounded. Image processing was performed by Nanotec WSxM [24].

3. Theoretical background

To complement the experimental work, electronic structure calculations have been performed for the Co islands. At the simplest level of theory, the experimentally obtained LDOS maps can be simulated by a particle-in-a-box approach, where the surface state electrons are confined by an infinite potential (Dirichlet boundary conditions) near the edges of the island. These edges are taken to be the topographical contour lines of the bilayer island at half of the maximum island height [4]. Exact solutions for this model are only available for a very limited set of highly symmetrical shapes. Consequently, in most cases one has to rely on approximative methods [25].

The LDOS maps of the Co islands in the present paper were all simulated with the aid of a newly developed variational method that can be applied to ‘2D boxes’ of almost any shape [26]. One of the major advantages of the method is that it uses a very natural set of basis functions, which all individually comply with the boundary conditions. To create such a basis set, we start from the solutions of a particle in a circular disk which are subsequently rescaled in such a way that they obey the imposed boundary conditions. For a more thorough treatise on the actual rescaling process we refer to [26].

Expanding the wavefunctions in this rescaled basis set, a standard variational approach can be applied to determine the eigenvalues, $E_i$, and eigenfunctions, $\Psi_i$, of the island under investigation. With this at hand, the LDOS at a given energy (or voltage) can be simulated using the expression

$$\rho(\text{LDOS})(E, \vec{r}) = \sum_i |\Psi_i(\vec{r})|^2 \frac{\delta_i}{\pi (E - E_i)^2 + \delta_i^2},$$

where each calculated eigenstate $\Psi_i$ is given an appropriate Lorentzian broadening $\delta_i = 0.1 E_i$ in order to mimic the experimental broadening induced by the applied ac modulation.
4. The Au(111) reconstructed surface: a template for nanoparticle growth

The Au(111) surface is known for its growth in large atomically flat islands of over several 100 nm$^2$ and its remarkable herringbone reconstruction [13, 14]. Both its flatness and its reconstruction make the Au(111) surface an ideal candidate as a template for the controlled growth of nanostructures by atomic deposition. The mechanism behind the peculiar surface reconstruction is a reduction of the surface tension by local contraction of the top atomic layers along one of the three (110)-directions. A modulated surface structure is formed, locally varying between bulk FCC stacking and HCP stacking with a periodicity of 6.3 nm. At the domain boundaries between the two stacking regions, atoms are squeezed out and form two ridges which can appear along the three symmetry directions of the Au(111) surface. At the elbows of this reconstruction, a single atomic point dislocation is known to be present [21, 27].

The point dislocations at the reconstruction elbows act as nucleation sites for island growth by atomic deposition: the first atom arriving at the dislocation site undergoes a position exchange with a local Au surface atom, which then immobilizes further incoming atoms [15, 17]. The Au(111) reconstructed surface thus offers an adequate means of creating metallic nanoparticles with a well defined size, simply by depositing more or fewer atoms. This way, individual islands can be grown, with diameters up to a 6 nm limit that is set by the surface reconstruction.

Besides its characteristic topographical features, the Au(111) surface also shows intriguing electron properties, including an electron surface state. The presence of the surface state is a typical property of various (111) surfaces: surface electrons are being confined to the top atomic layers and therefore act as a quasi-2D free electron gas, giving rise to strongly energy-dependent standing wave patterns at the surface [28, 29]. Due to scattering at step edges and surface defects, the surface state is observed as a circular 2D Fermi contour in the Fourier transform image [30]. In local d$I$/d$V$ spectra, the signature of the surface state is a sudden increase in conductivity around $-480$ meV [31]. As indicated above, this specific feature of the Au(111) surface state is used as a quality label for the spectroscopy measurements on our Co islands.

5. Electron confinement effects in nanoscale Co islands

By means of lock-in detection, LDOS variations are visualized as a function of the applied sample voltage. Here, we focus on the results obtained for $\simeq 0.12$ ML Co coverage. We find that the self-organized Co islands on Au(111) exhibit an electron surface state as well. A nice example of the standing wave patterns caused by scattering of both the Co and Au(111) surface state electrons at the island edges is shown in figure 2(a) for two Co islands that are barely in contact with each other. The LDOS map illustrates that, as soon as two Co islands are in contact, the resulting standing wave patterns smoothly run over each other. In figure 2(b), which is a zoom-in picture of figure 1(c), we present the case of two Co islands that are in very close vicinity of each other (less than 1 nm distance). In this case, no significant interference of the LDOS standing wave patterns between the two islands can be observed even up to energies as large as +2600 meV. So, in spite of the small inter-particle distance, both islands still act as single non-interacting entities. Furthermore, the observed standing wave patterns like the ones presented in both figures 2(a) and (b) reveal that the island geometry imposes its symmetry on the island LDOS. Particle shape thus becomes a determining factor in the electronic distributions of metallic particles at the nanoscale.
Figure 2. (a) and (b) The LDOS of self-organized bilayer Co islands on Au(111) shows complex standing wave patterns on both the island and the gold. The island LDOS is dominated by its shape and symmetry \( T = 4.5 \text{ K}, \) coverage \( \simeq 0.12 \text{ ML}, \) \( I_{\text{set}} = 0.5 \text{ nA}, \) \( V_{\text{set}} = +1200 \text{ mV} \) and \( V_{\text{set}} = +2600 \text{ mV}. \) (c) Plot of the electron energy as a function of the parallel wavevector \( k_{||}, \) which is experimentally calculated as the average wavevector that is observed in the LDOS patterns of many Co islands for coverage \( \simeq 0.12 \text{ ML}. \) The dispersion data as measured for the Au(111) surface state are added as a reference in the inset. The parameters \( E_0 \) and \( m^*/m_e \) of the parabolic dispersion have been added for the two fittings.

The dispersion data for the well-known Au(111) surface state are added in the inset to figure 2(c). The presented data are obtained by taking the Fourier transform of the Au(111) standing wave patterns, which gives the known circular shaped Fermi surface of the Au(111) surface state [30]. For each applied bias voltage, a value for the corresponding parallel wavevector \( k_{||} \) can then readily be obtained by taking the radial average of this Fourier image [30]. Based on all the standing wave patterns in the LDOS maps taken at different (positive) bias voltages on many Co islands, we have constructed a similar ‘energy dispersion’-like relation for the Co surface state in figure 2(c). Since the Co islands are too small to contain sufficient standing wave maxima and minima to apply the Fourier transform procedure, we determined the wavevector of the standing wave patterns for the Co islands by manually measuring the lateral distance in the LDOS images between hundreds of neighboring maxima on various islands for different bias voltages. The indicated uncertainty in \( k_{||} \) corresponds to
the statistical error of this wavevector. On the other hand, the uncertainty in $E$ corresponds to the voltage modulation that is used for the LDOS imaging (typically around 10% of the applied bias voltage). The solid lines shown in figure 2(c) and in the inset to this figure are fits of the experimental data to the parabolic dispersion relation

$$E(k_{||}) = E_0 + \hbar^2 k_{||}^2 / 2m^*,$$

where $E_0$ is the energy onset of the surface state and $m^*$ is the effective electron mass. For the Au(111) data, fitting values are $-460 \pm 5$ meV for $E_0$ and $0.23 \pm 0.03$ for $m^*/m_e$. Both values are in agreement with previously reported values for both STM ($E_0 = -450$ meV and $m^*/m_e = 0.15$ [29]) and photoelectron spectroscopy ($E_0 = -487$ meV and $m^*/m_e = 0.255$ [32]). For the Co surface state, we find significantly different values, i.e. $60 \pm 80$ meV for $E_0$ and $0.32 \pm 0.03$ for $m^*/m_e$. These values are more or less comparable to the values recently obtained by Diekhöner et al [5] for Co islands on Cu(111), both experimentally ($-160 \pm 0.03$ meV and $0.38 \pm 0.01$, respectively) and theoretically ($-170$ meV and $0.42$, respectively). The experimental data for the Co surface state do not all fit to the dispersion relation curve very well. This can be understood by the fact that this dispersion relation is in principle only applicable to very large surfaces or at least much larger islands than we are dealing with here. In our case, instead of one single $k_{||}$ value, the observed LDOS pattern on the Co islands will consist of a range of $k_{||}$ values. Therefore, the obtained $E_0$ and $m^*$ value are only a rather rough estimate. Fitting of the particle-in-box calculations to the experimental LDOS data will result in more reliable values. We will come back to this later.

Our main interest is to study the effects of confinement of electron surface states that are expected inside the nanoscale Co islands, by performing LDOS measurements on islands with different sizes and shapes as illustrated in figures 2(a) and (b). The flexibility of our newly developed variational method allows us to perform particle-in-a-box calculations for all shapes of particles, where the potential barriers of the box mimic the shape and symmetry of the Co island.

In figure 3 (left column) a series of LDOS maps at various energies is presented for a bilayer Co island whose shape can be approximated as a triangle with truncated edges. Brighter features correspond to a higher LDOS, while darker features correspond to a lower LDOS. The island’s top surface is free of any defects and atomically flat with an inner diameter (top to base) of only 3 nm. The right island edge suffers from additional broadening and artificial doubling when compared to the other two edges. This is due to tip convolution effects resulting from an asymmetric tip (the doubling was observed at the same edge for all similarly oriented Co islands that were investigated with this STM tip). It must therefore not be regarded as a signature of an incomplete second Co layer of the island. Apart from the strong dependence of the electron density on particle shape, the LDOS series nicely illustrates the strong variation of the local electron density with the electron energy.

At negative sample voltages below $-200$ meV, the LDOS map shows only a repeated image of the sample topography: the LDOS map remains featureless for the whole atomically flat area on top of the Co island. Around $-200$ meV a white central spot can be observed, indicating a high LDOS at the island center when compared to the darker (lower LDOS) island edges, consistent with the particle’s ground state. While no additional distinct features are observed for negative energies (occupied states), a series of pronounced features is observed at positive energies (unoccupied states). At relatively low energies (around 400 meV), the island LDOS shows already a first single dark feature at the island center, whereas the truncated
Figure 3. Left column: topographic image and a series of LDOS maps of a truncated triangular Co nanoisland on Au(111) for a broad range of energies. The standing wave patterns are dominated by the island shape and symmetry and reveal increasing complexity for increasing energies ($T = 4.5$ K). Right column: topographical height profile along one of the island bisectors and particle-in-a-box calculations for a truncated triangular box of $7.7 \text{ nm}^2$ surface area. Calculations are obtained at energies identical to the experimental LDOS maps. The energy values are based on table 1 with $m^* = 0.40$ and $E_0 = -200 \text{ meV}$. See movie 1, available from stacks.iop.org/NJP/10/043016.
Figure 4. Idealized boundary geometry for the truncated triangular Co island of figure 3, which is used for the theoretical LDOS simulations of the truncated Co island of figure 3.

Figures show a higher LDOS, indicating that one starts to probe the first excited state. For higher energies, all electron densities exhibit pronounced features with near perfect triangular symmetry. As the energy is increased, the surface state wavelength decreases and more features appear, resulting in an increased triangular complexity.

There exists a very large energy spacing between intrinsically different LDOS patterns. The spacing is of the order of several hundreds of milli-electron-volt (meV), in contrast to recent similar studies performed on both islands and vacancy islands, where the energy spacing is only of the order of several tens of meV \([4, 7, 8]\). The energy spacing between adjacent states corresponds fairly well to the energy gaps between subsequent eigenstates inferred from the relation

\[
E_n = E_0 + \frac{\lambda_n}{m^* \Omega}, \quad n = 1, 2, 3, \ldots,
\]

where \(\Omega\) denotes the surface area of the Co island under investigation and the \(\lambda_n\) values correspond to the different eigenvalues obtained by the particle-in-a-box approach. In table 1 we list the ten lowest eigenvalues \(\lambda_n\) (in atomic units) for the idealized geometry of figure 4, which closely mimics the shape of the Co island. In order to facilitate direct comparison with the experiment, we also list the corresponding set of eigenvalues (in units of meV) obtained by using the relevant parameters for the Co island under investigation (\(\Omega \simeq 7.7 \text{ nm}^2\)). LDOS simulations were performed with the help of equation (1), where the broadening factor \(\delta_i\) is taken to be 10\% of the applied bias voltage. The correspondence between theory and experiment is nicely illustrated in figure 3, where both simulated and experimental LDOS maps are shown for different bias voltages. For the given experimental size, optimal agreement can be achieved by assuming \(m^* = 0.4\) and by taking \(E_0\) to be around \(-200\) meV. The value for \(E_0\) is below all of the \(dI/dV\) maxima in our STS spectra (see figures 6(a)–(e)). We attribute these maxima to a discretization of the energy levels within the nanoscale Co islands. The STS spectra will be discussed in more detail below. The obtained values for \(m^*\) and \(E_0\) are significantly different from those derived from a fitting of the dispersion relation (see figure 2(c)). This is to be
expected, as already discussed above. The discrepancy can be directly related to the finite size effects that dominate the electronic properties of the nanosized particles.

Since in most experimental cases the energy spacing between the individual eigenstates is rather small, a superposition of a series of these individual confined states is observed. In our experiments, however, due to the extremely small particle size, the very large energy spacing allows us to visualize individual confined states (see table 1). Theoretical particle-in-a-box calculations of these LDOS maps enabled us to identify the observed standing wave patterns as either individual eigenstates, e.g. the ground state, the 1st excited state and the 8th excited state (at bias voltages of −200 meV, +400 meV and +2400 meV, respectively) or more as a ‘mixture’ of two (at +1000 meV) or more (at +1400 meV and at +2000 meV) energetically close-lying individual eigenstates.

The presence of surface states appears not to be limited to mono- and bilayer Co islands. We performed additional LDOS measurements on higher Co coverage samples (up to 2 ML of Co deposition), where it is possible to find multilayered islands up to several monolayers in height. This can be seen in the topographic image in figure 5(a), for which the corresponding height profile in figure 5(b), taken along the white bar in figure 5(a), shows heights up to 1 nm, corresponding to 5 ML of Co. The Co maintains the tendency to grow further in higher individual islands upon increasing the deposition, rather than forming a complete Co monolayer on the Au(111) surface. Since at this coverage many islands with smaller top layer area are present on the islands with larger bottom area, a significant fraction of the corresponding LDOS images is dominated by topographic height variations, as can be seen in figures 5(c) and (d). In spite of the multitude of topographic features appearing in the LDOS image, it is still possible to discern standing waves of the surface state on the atomically flat areas of the top Co layer. Similar to the bilayer islands, standing wave patterns gain in complexity for increasing bias voltage (i.e. (c) \( V_{\text{set}} = +600 \text{ mV} \) and (d) \( V_{\text{set}} = +1200 \text{ mV} \)). We therefore conclude that the Co surface state of Co islands on Au(111) is not limited to monolayer and bilayer islands, but is a property of multilayered islands as well [5].

The Au(111) and Co surface state can not only be observed as standing waves in LDOS maps, but in local \( dI/dV \) versus \( V \) spectra as well. A sudden increase in tunneling conductance around −480 meV is the well-known signature of the Au(111) surface state. As shown by Chen et al [31], it turns out that STS can even distinguish between the wider FCC and the smaller HCP regions of the reconstructed surface: more low-energy electrons are present in the HCP

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**Table 1.** Calculated eigenenergies \( \lambda_n \) (in atomic units) for a particle confined to the truncated triangular island shown in figure 4 and simulated eigenenergies \( E_n - E_0 \) (in meV) for the Co island of figure 3, based on the idealized geometry of figure 4 \((m^* = 0.40 m_e, \Omega = 7.7 \text{ nm}^2 = 2750 a_B^2 \text{ with } a_B \text{ being the Bohr radius})\).

| \( n \) | \( \lambda_n \) | \( E_n - E_0 \) (meV) | \( n \) | \( \lambda_n \) | \( E_n - E_0 \) (meV) |
|---|---|---|---|---|---|
| 1 | 10.0670 | 251.54 | 6 | 72.0293 | 1799.80 |
| 2 | 24.1471 | 603.36 | 7 | 74.3210 | 1857.07 |
| 3 | 44.3800 | 1108.93 | 8 | 100.3479 | 2507.47 |
| 4 | 44.9832 | 1124.00 | 9 | 108.9580 | 2722.55 |
| 5 | 69.4334 | 1734.94 | 10 | 109.2685 | 2730.31 |

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Figure 5. (a) Multilayered individual Co islands are formed at higher Co coverage. Small atomically flat areas remain present. (b) The height profile taken along the white bar in (a). Heights range up to 1 nm, corresponding to 5 ML of Co. (c) and (d) LDOS images taken at $V_{\text{set}} = +600\,\text{mV}$ and $V_{\text{set}} = +1200\,\text{mV}$, respectively, confirming the presence of the surface state on multilayered islands (coverage $\simeq 2.0\,\text{ML}$, $I_{\text{set}} = 0.5\,\text{nA}$ and $T = 4.5\,\text{K}$).

regions, whereas the FCC regions are populated by more high-energy electrons, as illustrated in figure 6 (top). In figures 6(a)–(e), we present typical STS spectra obtained on various Co islands. The spectrum in figure 6(b) is obtained on the Co island shown in figure 3. All Co islands reveal a sharp occupied state peak around $-160\,\text{meV}$ and one or more additional empty state peaks at high positive energies at the island edges with peak spacings on the order of 100 meV. Our STS data confirm the recent results by Rastei et al [6], where the Co on Au(111) system was studied for the first time in detail by STS measurements and by ab initio calculations. Rastei et al attributed the occupied surface state peak around $-160\,\text{meV}$ to a strong hybridization of the Co d states with s–p states. Diekhöner et al [5] showed that the surface state of Co islands on a Cu(111) substrate is considerably further away from the Fermi energy, at about $-310\,\text{meV}$. The measurements illustrate the strong influence of the underlying substrate on the electronic properties of metallic nanoparticles. At island edges Rastei et al further observed one single additional unoccupied state peak around $+200\,\text{meV}$, which they attribute to a hybridization of s–p Au(111) surface states with Co d states rather than to quantum confinement effects. These results differ from the results of, e.g. nanoscale Ag islands on Ag(111) by Berndt.
Figure 6. (a)–(e) $dI/dV$ spectra obtained on various bilayer Co islands. All islands reveal the presence a pronounced peak around $-160 \text{ meV}$ and one or more additional maxima appear at higher energies, with the exact energy position being different from island to island. In the inset on top of the figure $dI/dV$ curves taken on the HCP and FCC reconstructed Au(111) surface are shown ($T = 4.5 \text{ K}$).
and co-workers, where no hybridization effects take place. In that study STS peaks could be unambiguously linked to electron confinement and were nicely simulated by particle-in-a-box calculations [4].

We have measured the $dI/dV$ versus $V$ in a broader energy window ranging from $-1000$ meV up to $+1500$ meV and observe one or more unoccupied state maxima at elevated positive energies, as illustrated in figures 6(a)–(e). Considering the dimensions of our nanoparticles (see equation (3)), the energy spacing between the unoccupied states is of the same order of magnitude as the mean energy level spacing expected for energy level discretization due to electron confinement inside the particle. Furthermore, the positions of the maxima are observed to vary strongly from island to island, which excludes an interpretation in terms of hybridization only. Therefore, in contrast to Rastei et al., we attribute the observed empty state peaks to (a mixture of hybridization effects and) electron confinement effects within the nanoscale islands rather than to hybridization alone. Further investigation is needed to understand how hybridization effects can influence the quantized energy levels.

While in the case of pure 3D confinement discrete energy level peaks are expected, we observe considerably broadened peaks (full width at half maximum is $100$–$300$ meV, i.e. considerably exceeding the experimental broadening related to the lock-in detection technique) due to the strong metal–metal interaction between island and substrate. More details about these finite lifetime related broadening effects can be found in [33].

Additionally, we note that for metallic islands on Au(111) the observed surface states are not limited to Co only. We observe similar strongly energy dependent standing wave patterns in LDOS maps for Cr islands on Au(111) grown by e-beam evaporation [34]. Individual Cr islands of only one monolayer height and with trigonal/hexagonal shapes nucleate at the elbow dislocations of the Au(111) reconstruction [22]. STS spectra reveal a sharp occupied state peak around $-150$ meV at the island centers with additional empty state peaks appearing at the island edges, similar to the case of Co islands on Au(111).

6. Conclusions

By means of LDOS mapping using lock-in detection we have observed both strong shape and energy dependence of the electron density variations within nanoscale bilayer Co islands on Au(111). The islands have a nearly perfect hexagonal geometry, especially after minor annealing. We have performed particle-in-a-box calculations, for which we rely on a newly developed variational method that can be applied to ‘2D boxes’ of arbitrary polygonal shape. The good correspondence between experiments and calculations enables us to identify the observed standing wave patterns as either individual eigenstates or as a ‘mixture’ of two or more energetically close-lying individual eigenstates. The observation of individual eigenstates is experimentally possible because of the very large energy spacing, on the order of several $100$ meV, due to the strong electron confinement resulting from the extremely small size of the islands. The confinement effects are also observed as pronounced unoccupied state peaks with similar energy separation that appear in the $dI/dV$ spectra on the islands. Our spectroscopic data further confirm the result of Rastei et al. that for the Co on Au(111) system the occupied surface state shows a significant shift towards the Fermi level when compared to the case of Co on Cu(111).
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