# Spin Polarized Surface States of Cobalt Nanoislands on Cu(111)

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**Abstract.** The electronic structure of thin Co nanoislands on Cu(111) has been investigated by scanning tunneling spectroscopy at low temperature. Two surface related electronic states are found. An energetically localized state in the spectrum at 0.31 eV below the Fermi level ($E_F$) and a mainly unoccupied dispersive state, giving rise to quantum interference patterns of standing electron waves on the Co surface. *Ab initio* calculations reveal that both electronic states are spin-polarized, originating from $d_{3z^2-r^2}$-minority and *sp*-majority bands, respectively.

Ultrathin magnetic films and nanostructures on nonmagnetic metal surfaces have been investigated intensively for decades. The understanding of how the magnetism is governed by the electronic structure may help to control the magnetic properties of nanostructures, which is important to advance magnetic storage technology and other magnetoelectronics applications [1, 2, 3]. States that form at interfaces or surfaces are particular important since they were found to determine the spin polarization of electrons in tunneling-magneto-resistance (TMR) devices [4]. Cobalt thin films on Cu(111) are model systems for magnetic studies, but only few investigations focusing on the electronic structure have been reported so far [5, 6, 7, 8].

The scanning tunneling microscope (STM) is well suited to investigate surface electronic states, due to their slow decay into the vacuum in comparison with bulk states. The first observations of standing electron waves at the surface of noble metals gave a direct image in real space of surface state electrons creating quantum interference patterns by scattering off steps and defects [9, 10]. This opened up many new experiments using the STM as a local probe [11, 12, 13]. In particular the dynamics has been studied in great detail, e.g. determining the lifetime of noble metal surface states [14, 15, 16] and recently also of image potential states [17].

We here present a combined experimental and theoretical study of cobalt islands of a few monolayers (ML) thickness and lateral dimensions of the order of 10 nm ("nanoislands") and thin layers on the Cu(111) surface. Using scanning tunneling spectroscopy (STS) we observe two surface related electronic features on the Co nanoislands on Cu(111): A free-electron-like, mostly unoccupied state showing Friedel oscillations in the local density of states (LDOS) over a wide energy range, and an energetically localized state below $E_F$ giving rise to a very intense and sharp peak in the LDOS. In
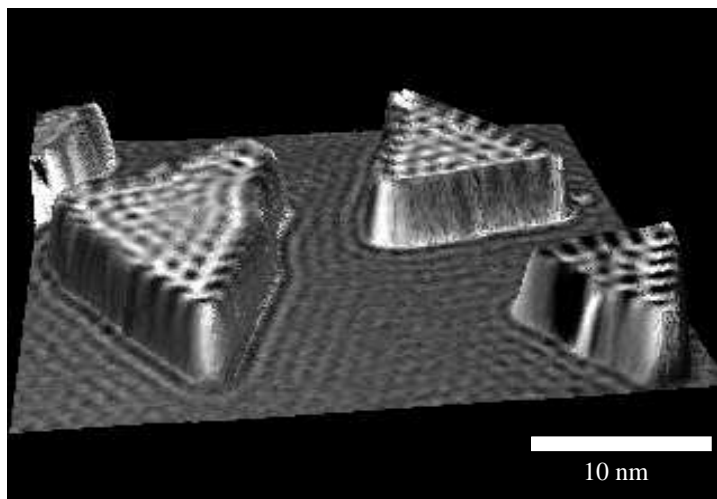
**FIGURE 1.** Representation in 3D of the topography of 2 ML high Co islands on Cu(111), where the *dI/dV* signal ( LDOS) has been superimposed as gray-scale. *V*=0.5 V, *I*=1.8 nA.

order to identify the origin of these states we performed *ab initio* calculations based on density functional theory (DFT) and the Korringa-Kohn-Rostoker (KKR) Green's function method for low-dimensional systems [18]. The calculations are found to be in good agreement with the experiment and show that the former observed state is an *sp*-majority state and the latter originates from mostly a $d_{3z^2-r^2}$-minority state with a contribution from an *sp*-minority state.

The experiments were carried out using a home-built ultra high vacuum (UHV, $P < 1 \times 10^{-10}$ mbar) low temperature ($T = 6$ K) STM equipped with a W tip [19]. The single crystal Cu(111) sample was cleaned in UHV by sputter-anneal cycles. Cobalt was evaporated with a rate of $\sim 0.1$ ML/min on the Cu surface at 290 K using an e-beam evaporator. Immediately after evaporation, the sample was cooled quickly in order to prevent intermixing of Co and Cu and segregation of Cu to the surface of the Co islands [20]. STS was performed to obtain differential conductance (*dI/dV*) maps and spectra, which are proportional to the LDOS [21], using a lock-in technique with a 4.6 kHz bias voltage modulation of 5-50 mV. All bias voltages given are sample voltages with respect to the tip.

The growth of Co on Cu(111) has been an extensively studied. At room temperature Co grows at low coverage as compact islands of triangular shape and bilayer height above the Cu surface [22]. Furthermore, one Co layer is believed to be buried in the Cu surface thus leading to 3 ML thick islands [23, 24]. At higher coverage additional single layers of Co grow on top of the islands leading to 3-dimensional (3D) growth. This emphasizes the necessity of using a local probe like the STM to study Co islands on Cu(111). At lower coverage Co continues the fcc stacking of the Cu substrate, whereas at higher coverages bulk-like hcp stacking dominates [25, 26]. In the following the thickness of the Co islands will be given in ML above the Cu surface. The theory also includes a buried layer. Since the Co islands are modelled as films, this is equivalent to an additional layer and the theoretical results for a coverage *n* ML, as given in the text
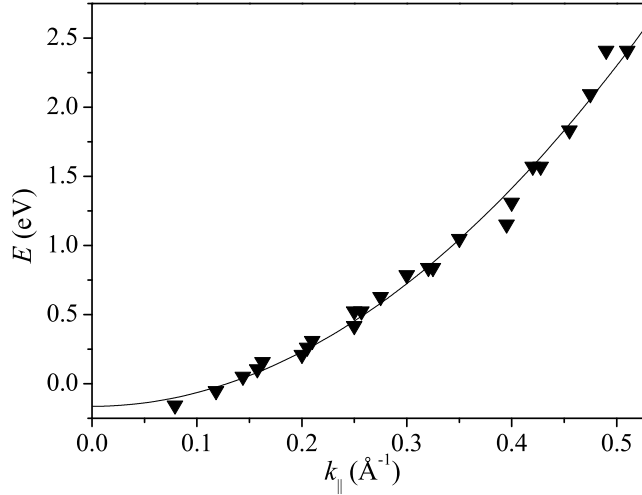
**FIGURE 2.** Dispersion relation of the electronic state determined from standing electron waves on Co islands. The solid line represents a parabolic fit.

below, is thus a calculation for $n+1$ ML.

In Fig. 1 we present a typical (constant current) STM image of Co islands grown on Cu(111) at low coverage. It shows the well-known compact islands of triangular shape and bilayer height [22]. The two island orientations have been explained by initial nucleation on the two different threefold hollow sites of the Cu(111) surface, thus leading to a stacking fault at the interface for the one island orientation, whereas the other continues the exact fcc stacking of the substrate [8]. The topography is shown in a 3D representation here where the grayscale coding is given by the simultaneously obtained $dI/dV$ signal. On the Cu(111) surface we observe the well-known standing electron wave patterns in the LDOS which are due to the quantum interference of surface state electrons scattering off steps and defects [9, 10]. We also observe a similar pattern of Friedel oscillations on the Co islands, evident of a free-electron-like surface state. From the interference pattern, the wave length and thereby the wave vector ($k_{\parallel}$) of the electronic state can be determined. As the bias was varied we observed a continuous variation of the wave length of the interference pattern, i.e. a dispersion of the electronic state. By Fourier transforming [27] the $dI/dV$ maps, we determined the dispersion relation of the surface state. Only the center part of an island was used, free of step edges. The Fourier spectrum was isotropic (ring-shaped) in the surface plane indicative of a free-electron-like state with isotropic effective mass [27, 28], except for directions of increased intensity given by the shape of the island. The standing waves on a triangular shaped island thus gave a Fourier pattern of 6 distinct brighter spots lying on a ring. A radial average of the Fourier spectrum was used to determine $k_{\parallel}$. The uncertainty in the determination of $k_{\parallel}$, given by the full width at half maximum (FWHM) of the radial average, was about 10 %. Care was taken to use islands large enough to contain at least 5 maxima in the standing wave pattern of the LDOS. The $E(k_{\parallel})$ dispersion is presented in Fig. 2. The data are perfectly fitted to a parabolic dispersion relation $E(k_{\parallel}) = E_0 + \hbar^2 k_{\parallel}^2/2m^*$, described by an onset just below the Fermi level at $E_0 = -0.16$ eV and an
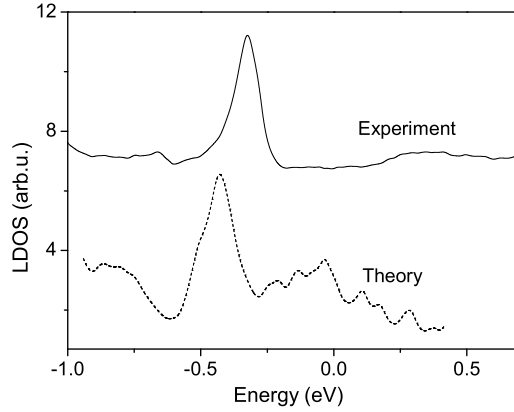
**FIGURE 3.** The upper graph (solid line) shows an STS spectum on a 2 ML high Co nanoislands. The lower graph shows the calculated LDOS 2.1Å above a 2 ML Co fi lm on Cu(111). ($E_F$ = 0 eV)

effective mass $m^* = 0.38\, m_e$, where $m_e$ is the free electron mass. All energies are relative to $E_F$. Islands of different shape, orientation and size were investigated without finding any significant differences.

On higher coverage islands the standing electron waves were also observed. The dispersion relation of this electronic state has been determined for 3 and 4 ML as described above. Also here we find a parabolic dispersion with an unchanged effective mass and a small shift of the onset to higher energies with increasing coverage such that the state becomes completely unoccupied at 4 ML [29].

The Co islands were further investigated by STS (Fig. 3). The *dI/dV(V)* spectrum on the Co island consists of the (mostly unoccupied) electronic state described above, and a very pronounced and sharp peak in the LDOS at -0.31 ± 0.02 eV with FWHM = 0.1±0.02 eV. We have taken spectra on a large number of islands of varying size, shape and orientation using different tips. The only differences observed were that the spectra of one island orientation have the peak centered approximately 30 meV lower than spectra taken on islands of the other orientation. Otherwise the spectra agreed over the energy range ± 1.5 eV. Although the observed difference is rather small, we believe that this is an effect of the stacking fault present in one island orientation leading to a different spatial and electronic configuration at the Co/Cu interface. To exclude any tip-induced effects, a reference spectrum on a clean part of the Cu(111) surface has been recorded with the same tip, reproducing the well-known onset of the surface state and being otherwise featureless [10]. Note, that a similar clear onset of the free-electron-like surface state on the Co islands is difficult to detect since it is buried in the tail of the strong feature at -0.31 eV.

A state similar to the one reported here has previously been observed on Co(0001) by photoemission [30] and STS [31], whereas a theoretical study by Braun and Donath did not predict any surface state on Co(0001) in this energy range [32]. An earlier STM study of Co/Cu(111) by Vázquez de Parga *et al.* [8] observed a strong dependence on

the stacking of the Co island, where the LDOS appeared larger at positive energies for islands with a stacking fault. But they neither saw the standing electron waves nor did they see a peak in the LDOS below $E_F$, but rather a smooth featureless spectrum. These experiments were performed at room temperature (RT) and we believe that the data are affected by intermixing of Co/Cu or contamination of the surface. We have measured spectra on islands grown at 345 K, where intermixing occurs, and on RT-grown islands followed by carbon monoxide (CO) adsorption. In both cases we observed a strong suppression of the surface state features. We note that a recent low temperature STM experiment by Pietzsch *et al.* have reproduced the findings reported here [33].

In order to interpret the experimental observations we performed *ab initio* calculations of the electronic states for 2, 3 and 4 ML of Co on Cu(111). Our calculations are based on the local spin density approximation of DFT and the KKR Green's function method [18]. First, we treat the Cu surface as a two-dimensional (2D) perturbation of Cu bulk. Taking into account the 2D periodicity of the ideal surface, one can find the structural Green's function, using a Dyson equation. This is then used to calculate the Green's function of the perturbed system with the Co layer on the surface. The full charge density is taken into account and self-consistent spin-polarized calculations are performed for the dispersion relation and the density of electronic states. Our study of the interlayer relaxations shows that the main results presented in this paper are not affected by relaxations. Since the experiments showed that there was no significant dependence on island size, the calculations are done for Co fcc films on Cu(111). We find that the surface states are spin-polarized. The quantum interference in the LDOS observed with the STM is due to scattering of *sp* majority electrons. Our calculations show that the majority *sp*-states have a parabolic dispersion relation, which for 2 ML Co can be described by the theoretical parameters $E_0 = -0.17$ eV and $m^* = 0.42\,m_e$. The calculations are in agreement with the experimental results for all Co coverages and the trend of increasing $E_0$ with coverage is reproduced in the calculations [29]. We expect the spin-polarized surface state to influence the surface magnetic properties of the Co islands. Furthermore, since the changing onset with coverage results in a varying density of the state below $E_F$, it allows us to control the contribution to the surface magnetism by varying the coverage.

Our calculations of the LDOS for the vacuum position 2.1Å above 2-4 ML Co on Cu(111) show that the strong feature below the Fermi level is due to minority $d_{3z^2-r^2}$ states. As an example we present in Fig. 3 the LDOS above 2 ML Co on Cu(111), which is in good agreement with the experiment. The charge density distribution of the minority surface state at the $\bar{\Gamma}$ point has $d_{3z^2-r^2}$ character. Surface states of similar character have previously been observed with STS on e.g. Fe(001), Cr(001) [34] and Co(0001) [31]. Here, however, the calculations show that a small minority *sp* contribution is present as well. Due to the spin-polarized nature of this state and the very strong intensity we believe that the surface state observed in the present study may be of importance in tunneling magnetoresistance (TMR) devices [1, 2]. The possible influence of hybridization of this state with the oxide spacer layer in a real TMR device has to be investigated in more detail, though [4].

In conclusion, we have investigated the electronic structure of Co nanoislands on Cu(111), where we identify two electronic features with STS. A mainly unoccupied state showed Friedel oscillations in the LDOS, which were used to determine its dispersion

relation. Our *ab initio* calculations, which take into account the atomic arrangement at the interface and the interaction between Co layers and the Cu surface fully self-consistently, show that this state is an *sp*-majority state. The state shifts with coverage and is thus expected to have a coverage dependent influence on the surface magnetic properties. Furthermore, we observe an intense peak in the LDOS below $E_F$. This state is mostly due to a $d_{3z^2-r^2}$-minority band giving rise to a strong LDOS at the energy of its minimum.

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