

Surface electronic states in Co nanoclusters on Au(111): Scanning tunneling spectroscopy measurements and *ab initio* calculations

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Scanning tunneling spectroscopy measurements on Co nano-clusters grown on Au(111), revealed the presence of two peaks in the electronic states, below and above the Fermi energy. *Ab initio* calculations show that both peaks are due to spin-polarized surface states. The crystallographic stacking of the Co nano-clusters are shown to influence strongly the energy shift of filled surface states, providing a way to increase the low bias spin current of magnetic tunnel junctions. Due to the small lateral dimensions of the nano-clusters (~ 3 nm), edge effects dominate the amplitude of the empty states peak.

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The interplay between structural and magnetic properties has been one of the important issues in solid state physics for years. Although this topic has motivated many interesting studies in systems that are invariant by translation,¹ many interesting questions remain open when it comes to zero-dimensional nanostructures, a few atomic layers thick in epitaxy on substrates. With the development of ultrahigh vacuum, low temperature scanning tunneling microscopy (STM), it has become possible to identify the nanostructure sizes and shapes, and simultaneously to record their electronic structure by scanning tunneling spectroscopy (STS).²⁻⁵ However, theoretical investigations are usually required to make the unambiguous link between structure and the spectroscopic data obtained from STM. It should be noticed that in small structures such as clusters and islands on surfaces, various effects may arise from the small lateral dimensions, leading for example to surface state confinement and/or enhanced magnetic moments on edge atoms.⁶⁻⁸ Recently, spin-selective quantum interferences have been evidenced on Co nanostructures.^{8,9}

A well-known example of STM-STs study is given by the case of Co islands on Cu(111).²⁻⁵ These islands have a lateral size of about 20 nm and a height of two atomic layers (2 ML) with respect to the Cu(111) base plane. A pronounced *d*-like peak with a minority-spin character is found below the Fermi energy, at about -0.31 eV.^{2,3} In addition a mainly unoccupied dispersive state with *s-p* majority character is observed above the Fermi energy, giving rise to spatial local density of states (LDOS) oscillations on the Co surface. Recently, two orientations of Co islands grown on Cu(111) (the so-called faulted and unfaulted Co islands identified previously⁴) could clearly be identified in STS spectra by the shift they produce in the main peak from -0.35 eV to -0.28 eV.³ Some results obtained on Co films on W(110) (Refs. 10 and 11) are reminiscent of the situation described above. Although it is admitted that the main peak reacts to the stacking of Co, no detailed analysis involving a substrate with a substantially different lattice parameter is available presently. In particular, effects cannot be anticipated from previous results since the lattice mismatch between Co and the Cu substrate is only about 2%; the position of the main

peak is therefore identical (-0.3 eV) to what is found on thick, quasibulk Co films.¹⁰

In this work, the electronic structure of small Co clusters with a lateral extension of only 3 nm and a height of 2 ML on Au(111) are investigated by STS and *ab initio* calculations for the first time. The Au(111) substrate induces a large lattice mismatch of 13% on Co which, together with the two types of surface domains available on Au(111), leads to a large variety of stackings and lattice parameters influencing on the position of minority electron peaks. The pronounced peak observed in STS below the Fermi level (which, according to *ab initio* calculations, originates from strong hybridization of Co *d*-states with *s-p* states), is found to shift by as much as $+0.25$ eV with respect to Co/Cu(111), leading in this case to a larger contribution to the LDOS close to the Fermi level. In addition, due to the different stacking orders of the Co clusters on Au(111), the surface states further shift by 0.07 eV as evidenced both experimentally and theoretically. Finally, it is demonstrated by STS that bilayer Co clusters on Au(111) have a peak in the unoccupied states of the LDOS, belonging to minority state electrons as revealed by the *ab initio* calculations. This peak is not affected by the Co stacking.

The experiments were performed in an ultrahigh vacuum system, with a base pressure of 5×10^{-11} mbar. The setup consists of a preparation chamber coupled to a low temperature STM (down to 4.6 K) apparatus from Omicron. Prior to Co deposition, the surface of the Au(111) single crystal was prepared by Ar⁺ sputtering and flash annealing at a maximum temperature of 900 K. When the sample reached room temperature the Co deposition was performed with a rate of 0.2 ML/min from an *e*-beam evaporator and then it was immediately transferred in the STM, which was previously cooled to 4.6 K. Electrochemically etched W tips, cleaned *in situ* by ion bombardment, were used. The differential conductance dI/dV spectra were acquired using the lock-in technique with a bias voltage modulation of $V_{pp}=20$ mV at 2.4 kHz.

The herringbone reconstructed surface of Au(111) (Ref. 12) is ideal for self-organizing two-dimensional arrays of Co clusters.¹³ Its particular topology allows growing clusters in

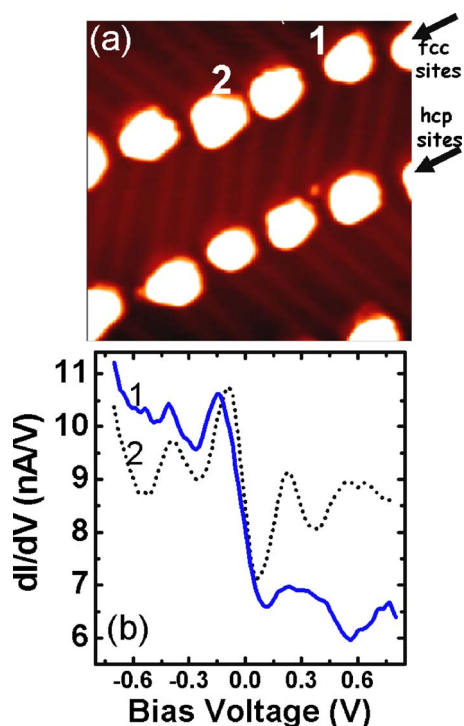


FIG. 1. (Color online) (a) Constant current ($320 \times 320 \text{ \AA}^2$) STM image of self-organized bilayer Co clusters on the herringbone reconstruction of Au(111). (b) STS spectra measured on clusters noted 1 and 2. Each spectrum is an average of four single point spectra. Set-point parameters before feedback opening were 530 pA and 0.095 V.

an ordered way on preferential nucleation sites pertaining to fcc and hcp zig-zag domains of the topmost atomic layer. On these domains, Co was found to grow in stable atomic bilayer clusters.^{13–15} Such a situation is presented in Fig. 1(a) for two rows of Co clusters, self-organized on fcc sites and hcp sites, respectively.¹⁶ We usually observed “nearly” triangular clusters, which may be found to point in two opposite directions. As an example, Fig. 1(a) shows an STM image, in which such clusters were labelled 1 and 2. STS measurements performed on these clusters are shown in Fig. 1(b). The spectrum acquired on cluster 1 shows a pronounced peak at -0.15 eV , whereas in cluster 2 this peak appears at -0.085 eV . The shift of this main peak is the signature of different stacking orders, similar to what was found on Co/Cu(111).³ Note however that these two peaks are found at energies much closer to the Fermi level than in the case of Co/Cu(111). This point is an issue on itself and will be discussed in detail later on in this paper. As a matter of fact, for a bilayer cluster, four possible stacking orders are possible on a fcc surface as shown in Fig. 2(a). Therefore, the STM image of Fig. 1(a) alone does not allow identifying *a priori* which of them correspond to clusters 1 and 2. However, the clusters are limited by either $\{111\}$ or $\{100\}$ steps. Due to the higher stability of the $\{111\}$ steps with respect to $\{100\}$ ones,¹³ the clusters are expected to adopt the particular shapes shown in Fig. 2(a). We adopt here a less restrictive condition than the one considered for the trilayer Co islands on Cu(111) (Ref. 4) where the minimization by $\{111\}$ steps

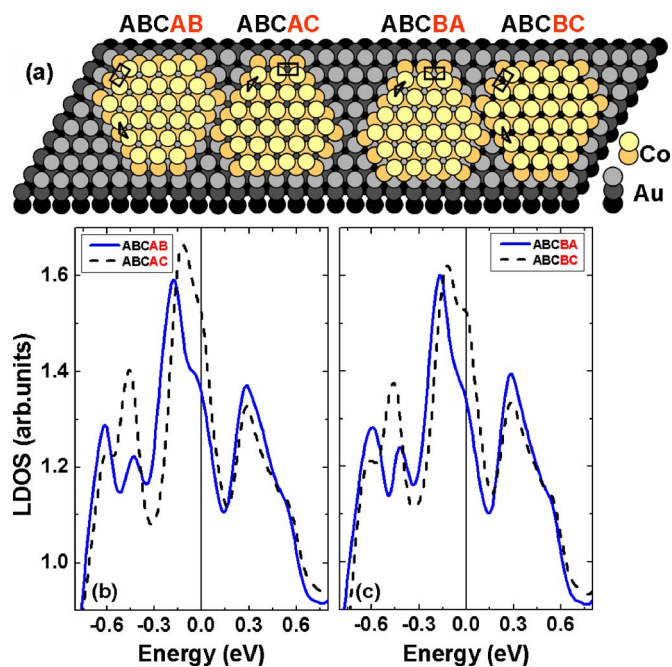


FIG. 2. (Color online) (a) Four possible stacking orders for 2 ML Co on fcc Au(111) with opposite islands orientation. The small black triangles show the $\{111\}$ facets, while the black rectangles show the $\{100\}$ ones. (b),(c) Calculated LDOS, 2.35 \AA above the Co bilayer on the fcc Au(111) surface. The LDOSs have been paired to satisfy both, orientations and the main LDOS peak shift.

was supposed to be satisfied even for the first, buried layer of the trilayer Co island.¹⁷ In order to discuss the energy shift of the main peak, four possible cluster pairs with opposite orientations were considered [see Fig. 2(a)].

Electronic structures of the various configurations have been calculated *ab initio* by the Korringa-Kohn-Rostocker Green’s function method. This method is based on the density functional theory and multiple scattering approach. A surface is treated as a two-dimensional (2D) perturbation of an infinite bulk. Therefore it is possible to write down and self-consistently solve the 2D Dyson equation to get the surface structural Green’s function. Clusters on the surface break the translational symmetry so the Green’s function of a surface-cluster system should be calculated in the real space. The structural Green’s function of infinite surface in the real space representation is considered as the reference for these calculations. The details of our method and its applications can be found in previous works.^{2,8,18,19}

All stacking orders sketched in Fig. 2(a) have been considered in the calculation. The calculated local densities of states (LDOS) above the two cobalt layers on fcc-Au(111) are shown in Figs. 2(b) and 2(c). The calculations, show that the pronounced peaks, below and above the Fermi energy, have minority state character. The LDOS are arranged two-by-two in order to satisfy both, opposite orientation of Co islands and to produce a shift of the main LDOS peak. Therefore, the stacking orders of the two experimentally analyzed clusters correspond either to those shown in Fig. 2(b) or to those shown in Fig. 2(c). Note that, in Fig. 2(b) the atoms from the first Co layer in contact with the Au surface

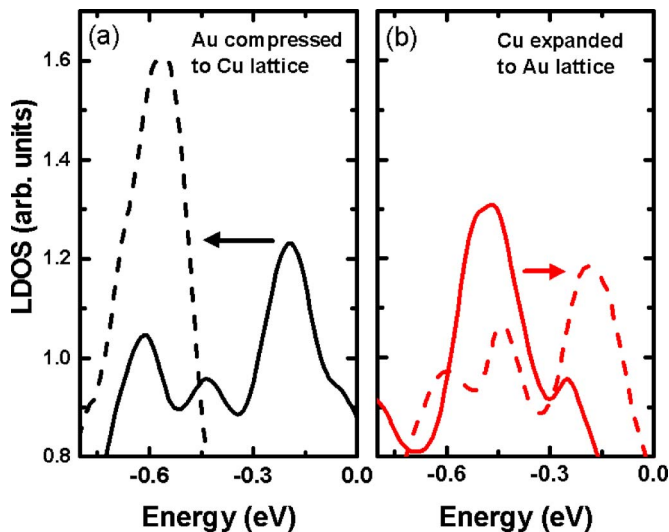


FIG. 3. (Color online) Minority component of the LDOS calculated 2.35 Å above the Co bilayers on normal (solid line) and strained (dashed line) fcc Au(111) (a) and fcc Cu(111) (b) substrates. A large shift of the main occupied peak towards the Fermi level occurs for substrates with large lattice constants (see text).

are placed in the fcc binding sites and the shift of the main peak towards Fermi energy appears to be produced by the topmost Co layer with atoms occupying the hcp binding sites. In contrast, when the atoms of the first Co layer in contact with the Au surface are located in hcp binding sites the shift of the main peak towards Fermi energy is the result of positioning the topmost Co atoms in the fcc sites, as observed in Fig. 2(c) [see also Fig. 2(a)]. A change in the two topmost layers stacking orders, breaks the symmetry of the lattice near the surface leading to a change in the multiple scattering processes. The main peak shift appears if three topmost layers are stacked in a hcp manner [*abcAC* and *abCBC* in Figs. 2(b) and 2(c)] and does not appear if these layers are stacked *fcc*-like [*abcAB* and *abCBA* in Figs. 2(b) and 2(c)].

In addition to the interesting issue of stacking order, it should be stressed that the pronounced peak in the STS of Co clusters on Au(111) is identified from LDOS calculations, to be of the same origin than the one found in Co/Cu(111).^{2,3} Therefore, its strong shift of about +0.25 eV towards the Fermi level with respect to Co/Cu(111) deserves particular attention. In order to get a better insight into the origin of the difference between these two systems, in particular the role of strain, we have performed *ab initio* calculations for Co bilayers on a Au(111) substrate compressed to the Cu lattice on the one hand and on Cu(111) substrate expanded to the Au lattice on the other hand. As shown in Fig. 3, in both cases a significant shift of surface states is revealed in the calculated LDOS. A compressed Au(111) substrate results in a peak shifted by 0.35 eV to the lower energies [Fig. 3(a)] while an expanded Cu substrate shifts the Co peak by approximately 0.25 eV to the higher energies [Fig. 3(b)].

The peak in the dI/dV spectra below the Fermi level, observed experimentally, originates from an area away from the center of the Brillouin zone (BZ). To prove that the

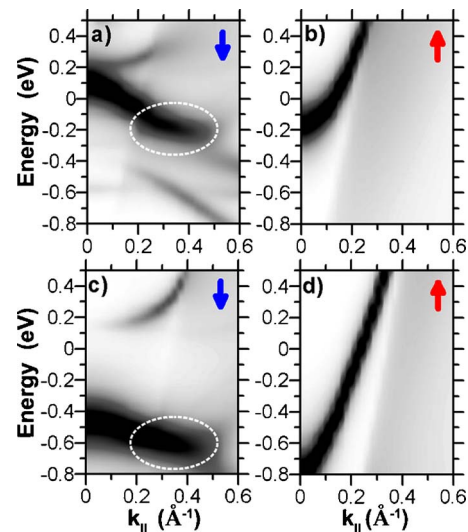


FIG. 4. (Color online) Spectral density maps of spin-polarized surface states calculated 2.35 Å above Co bilayers on normal (a),(b) and compressed (c),(d) fcc Au(111) along the Γ - M direction. The minority peak below the Fermi energy is determined by strongly hybridized *s-p-d* states. The region away from the Γ -point where these states are located is marked in (a) and (c) by the dashed white ovals. It is found that the compression results in the shift of the peak to the lower energies while the contributing region, remains nearly the same. Majority states have parabolic dispersion relations (b),(d).

shifted and unshifted peak arise from a change in energetic position of the same state we plot spectral density maps of spin-polarized surface states above Co bilayers on normal and compressed fcc Au(111) along the Γ - M direction (Fig. 4). For both substrates the peak below the Fermi energy is determined by strongly hybridized minority *s-p-d* states [Figs. 4(a) and 4(c)], similar to the Co/Cu(111) system.²⁰ The main contribution to the LDOS calculated 2.35 Å above the surface is given by a region away from the Γ -point, at about 0.3 \AA^{-1} . Therefore, a compression of the substrate leads to the shift of this state to lower energies but the contributing region seems to remain nearly the same. As a result, the lateral compression or expansion of the Co layers is found to be the driving force for the shifting of the minority peak below the Fermi level. A similar effect has been reported for strained Cu(111) films on Ru(0001).²¹ Vertical relaxations practically do not affect the character of surface states. Accounting for this effect in the calculation only leads a small shift of 0.015 eV in the position of the main peak in the case of two Co layers on fcc Au(111). It should be noted that the compression significantly shifts the band bottom of the majority dispersive state downwards [Figs. 4(b) and 4(d)] due to strongly enhanced hybridization between *s-p* states of gold and *s* states of cobalt.

A closer inspection of the STS of Fig. 1(b), reveals the presence of a peak in the unoccupied states. This peak originates from the unoccupied minority states visible in Fig. 4(a) above +0.2 eV. Our experimental studies have shown that the intensity of this unoccupied minority peak varies across the Co cluster. This behavior is observed for all clusters independently of stacking orders, despite the smaller intensity of this peak on one type of clusters (type 1 clusters of Fig. 1).

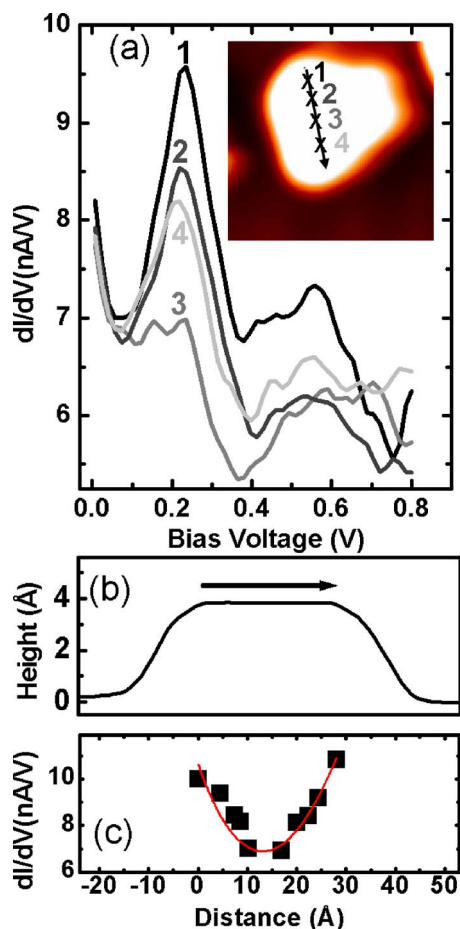


FIG. 5. (Color online) (a) STS measured on specific positions of the Co cluster shown in the inset. Inset: STM image ($55 \times 55 \text{ \AA}^2$) of a Co cluster and locations where STS spectra have been taken. Feedback set-points before loop opening: 500 pA and 0.076 V. (b) Topographic profile along the arrow drawn in the inset of Fig. 4(a), showing the flatness of the upper part of the cluster. (c) Peak amplitude (filled dots) as a function of distance along the arrow. The solid line is a guide for the eyes.

An example of such an STM-STS study is shown in Fig. 5(a) where STS measurements at different positions along the arrow are depicted. The spectra have been taken in the limit of the flat top of the cluster as shown in the cross section of Fig. 5(b), thus excluding an interpretation in terms of dislocations or topographic defects. While the peaks position is found to be unchanged (+0.23 eV), their amplitude strongly varies across the cluster. Peak amplitudes for many other spectra taken along the arrow are plotted in Fig. 5(c); they show a maximum at the clusters edge and a minimum in the clusters middle.

To find out the origin of the spatial changes in the peak amplitude, *ab initio* calculations were performed for the cluster of Fig. 6(a) with a size and a shape close to those observed experimentally. As can be seen in Fig. 6(b), the spatial distribution of the peak amplitude is in fair agreement with the experimental data shown in Fig. 5(c). Furthermore, as shown in Fig. 6(b), its variation is mainly determined by the minority states contribution. Calculations performed on Co

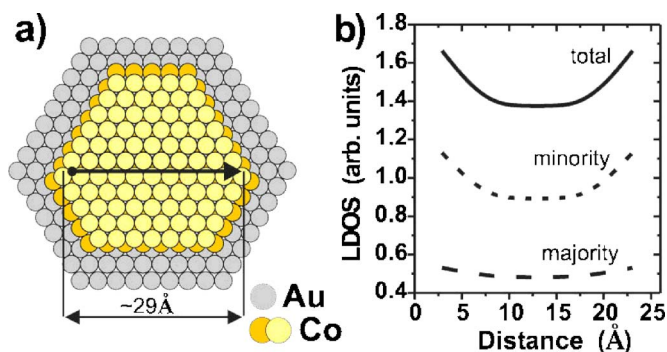


FIG. 6. (Color online) (a) Geometrical parameters of the cluster used in the calculation. (b) Spatial distribution of minority and majority contribution to the total LDOS above the surface at the empty states peak (0.26 eV).

clusters of different sizes show no shift of this peak, which is against an interpretation in terms of quantum confinement of surface electrons. Furthermore, an inspection of the infinite Co bilayer LDOS [see Figs. 2(b) and 2(c)] shows that this peak occurs even in the absence of confinement. Our analysis has revealed that this minority peak is mainly determined by the hybridization of *s-p* surface states with the *d* states of the Co cluster. Therefore, the spatial changes in the peak amplitude seem to be due to an enhanced *d*-LDOS on cluster edge atoms. This effect is well understood from simple tight binding considerations where the lower coordination of edge atoms leads to a band narrowing and in turn to an increase in the LDOS.

In summary, it has been demonstrated that a careful choice of the substrate for Co nanostructures may lead to a variety of conditions influencing the energy of surface states electron. In particular, the electronic structure of Co clusters on Au(111) have been investigated by means of STM-STS and *ab initio* calculations. A pronounced occupied states peak with minority character, has been found much closer to the Fermi energy than in the case of Co/Cu(111). The *ab initio* calculations revealed that this occupied surface state originating from strong hybridization of Co *d*-states with *s-p* states is of minority character. It produces a large contribution to the LDOS at the Fermi level, thus opening the possibility to increase low bias spin transmission in magnetic tunnel devices based on Co nanostructures. The interplay between the energy shift of the surface states and Co nanostructures stacking orders has been evidenced. STS data also show an empty state peak exhibiting a strong amplitude variation across the cluster surface. As revealed by *ab initio* calculations this empty state peak results from the hybridization of *s-p* surface states with *d* states of the Co cluster rather than from quantum confinement.

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