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# Scanning-tunneling-microscopy study of the growth of cobalt on Cu(111)

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Cobalt grows initially on Cu(111) in the form of bilayer islands with the shape of triangles of alternate orientation. This is probably related to the initial stacking sequence of the Co layers. The islands do not coalesce upon further deposition and the resulting film, although epitaxial and crystalline to the extent tested by diffraction techniques, is, actually, granular. Thus, microscopic evidence is provided for the existence of an intrinsic defect, namely, twinned fcc crystallites and their associated grain boundaries, which may be the much sought cause of discrepancy on antiferromagnetic coupling data in Co/Cu(111) superlattices grown in ultrahigh vacuum.

Thin films of metals epitaxially grown on metals have attracted sustained scientific and technological interest for more than half a century.[1] In particular, magnetic thin films and superlattices constitute a benchmark for producing new magnetic phases and finding exotic magnetic couplings. In this respect the discovery of oscillatory magnetic coupling of magnetic films across a nonmagnetic spacer layer has given rise to much excitement.[2] In a particularly studied model system, Co/Cu trilayers and superlattices grown on Cu(100), the coupling oscillates from ferromagnetic ($F$) to antiferromagnetic (AF) as a function of the thickness of the Cu spacer with a well-defined periodicity[3,4] dictated by the size of the vectors spanning the Fermi surface of Cu along $\langle 100 \rangle$ directions.[5] The magnitude of the magnetoresistance (MR) of Co/Cu multilayers has been found to oscillate as a function of the Cu thickness with very similar periodicity.[6]

While the situation is clear for Co/Cu superlattices oriented along (100), the results for Co/Cu superlattices grown along the (111) direction are rather confusing. Polycrystalline sputtered Co/Cu multilayers preferentially oriented along (111) display AF oscillatory coupling and oscillatory MR,[7] but crystalline superlattices grown by molecular-beam epitaxy (MBE) show no evidence for AF coupling[8] or weak, nonoscillatory AF coupling.[9] Moreover, MBE-grown Co/Cu(111) superlattices of comparable degree of structural perfection as judged by x-ray diffraction (XRD) and reflection high-energy electron diffraction give very different strengths of AF coupling.[10]

Understanding the microscopic aspects of film growth is crucial to correlate macroscopic measurements (magnetoresistance, surface magneto-optical Kerr effect, etc.) with the actual physical microstructure of samples and the idealized theoretical calculations. Such a detailed structural characterization has been already presented for Co/Cu superlattices on Cu(100).[3] In that case, Co grows in the fcc structure adopting the lateral lattice parameter of Cu and with a small vertical contraction. The growth mode is layer by layer and no misfit dislocations appear for Co thicknesses below 18 Å. Cu layers deposited on the Co film grow in their undistorted fcc bulk structure.[4] The sequence is maintained with a high degree of perfection for multilayers.[3]

Unfortunately, the same kind of information is not yet available for Co/Cu on Cu(111). Here we report on a preliminar scanning tunneling microscopy (STM) study of the growth of Co on Cu(111) that reveals structural aspects that may shed some light on the problems encountered to detect AF coupling in MBE grown Co/Cu trilayers and superlattices on Cu(111).[8–10]

The previous knowledge of the structure of Co films grown on Cu(111) is rather scarce. Based on Auger electron spectroscopy (AES) data, Co was reported in an early work to grow layer by layer on Cu(111) at room temperature.[11] This conclusion was accepted on a recent AES work.[12] The low-energy electron diffraction (LEED) pattern was $1\times1$ with a symmetry changing gradually from threefold to sixfold, which was originally interpreted as reflecting a change in the structure from fcc at coverages below 6 monolayers (ML) to hcp at higher coverages.[11] XRD data on (Co/Cu) (111)-oriented multilayers grown by MBE have detected the presence of hcp and fcc Co for Co thicknesses above 20 Å.[13]

The experiments have been performed in an ion-pumped ultrahigh vacuum (UHV) chamber equipped with a four-grid LEED optics, which allows us to perform AES, an ion gun for noble gas sputtering, and an STM of the type originally designed by Zeglinski *et al.*[14] The Cu crystal was oriented to within 0.2° of the (111) direction, mechanically polished, and cleaned by several hundreds of computer-controlled cycles of $\mathrm{Ar}^+$ sputtering at 500 °C (800 eV, 10 $\mu\mathrm{A/cm}^2$, 10 min) and annealing to 850 °C (10 min) until the AES spectrum shows no traces of contaminants and the LEED pattern displays the threefold-symmetric $1\times1$ pattern corresponding to the unreconstructed (111) surface of an fcc crystal. Co was deposited by electron bombardment onto the substrate at room temperature (RT). After each deposition, LEED pattern and AES spectra were recorded before and after transfer of the sample to the STM.

The Co coverage is given in monolayers, where 1 ML is defined by a one-to-one atomic ratio with the Cu(111) substrate. Due to the observed departure from the layer-by-layer growth (see below), the deposited coverage was directly obtained from the STM images. This method is meaningful since, in the coverage range shown here, there were always regions of the Cu substrate accessible to the STM tip. In fact, knowing the actual overlayer morphology, the recorded AES spectra were found to be consistent with the coverage visualized by the STM.

The clean Cu(111) substrate displayed atomically flat terraces separated by steps 2.0±0.1 Å high, corresponding to the interplanar distance between (111) planes in Cu. The average terrace size is 650 Å. Most of the steps are not pinned (and accordingly curved) by impurity-related pinning centers as seen in STM images of Cu(111) (Ref. 15) or Cu(100).[16]

Deposition of 0.6 ML of Co at a rate of 1 ML/min with the substrate held at RT, produces a sharp 1×1 LEED pattern and STM images like the one reproduced in Fig. 1. Co islands 2 ML high appear on the terraces and decorate the steps of the substrate. Step decoration is due to heterogeneous nucleation at defects, a phenomenon first used to visualize surface steps in NaCl by Basset.[17] More recently, STM images recorded during deposition of metals on metals have shown enhanced nucleation at *lower* step edges.[18] The islands which decorate the steps in the present case, however, nucleate both at the lower and at the *upper* step edge, as shown in Fig. 2(a). This suggests that, apart from the trapping of Co adatoms by the lower part of the steps, there is an activation barrier at the upper edge of the Cu steps preventing the mobile Co adatoms from jumping down the steps. This might be similar to the diffusion barrier across the edges of adatom islands first observed by means of field-ion microscopy[19] and proposed recently by Kunkel *et al.*[20] to explain a reentrant growth behavior during homoepitaxial growth. Preferential condensation at the upper step edges has also been noted for Fe/Cu(111).[15]

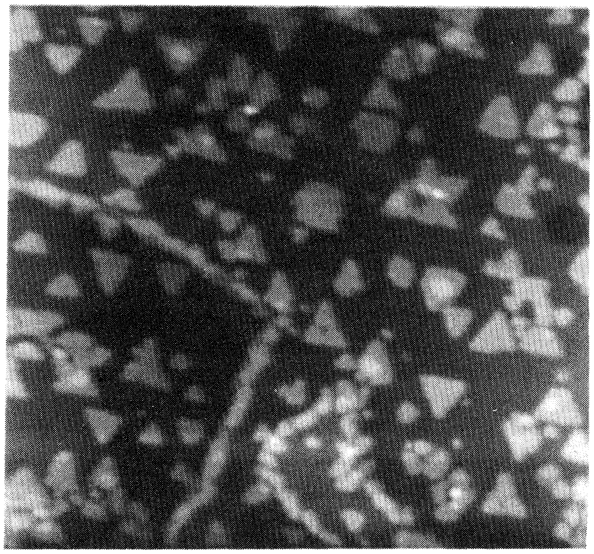

FIG. 1. Topographic image of 0.6-ML Co on Cu(111), recorded at a sample bias of $V = -2.7$ V and a tunneling current of $I = 0.9$ nA. The size of the image is 2000×2000 Å$^2$.

In addition to the islands decorating the steps, Co forms islands with *double*-atomic height (3.9±0.2 Å), nucleated at the terraces of the substrate by homogeneous nucleation. Single-layer islands are only exceptionally observed. In some cases third-layer nuclei are visible in the images. Thus, in contrast to Co/Cu(100),[16] the first monolayer on Co does not wet the (111) substrate. The island density at 0.6 ML calculated in numerous images ranges from 2.75 to 3.75×10$^{11}$ cm$^{-2}$ and their average size is 150 Å. Note that most of the islands are larger than the coherence length of conventional LEED diffractometers, and accordingly, the LEED pattern can be "perfectly sharp" to a visual inspection. Bilayer Co islands have also been observed during growth of Co/Au(111).[21] The double-layer growth was attributed in that case to

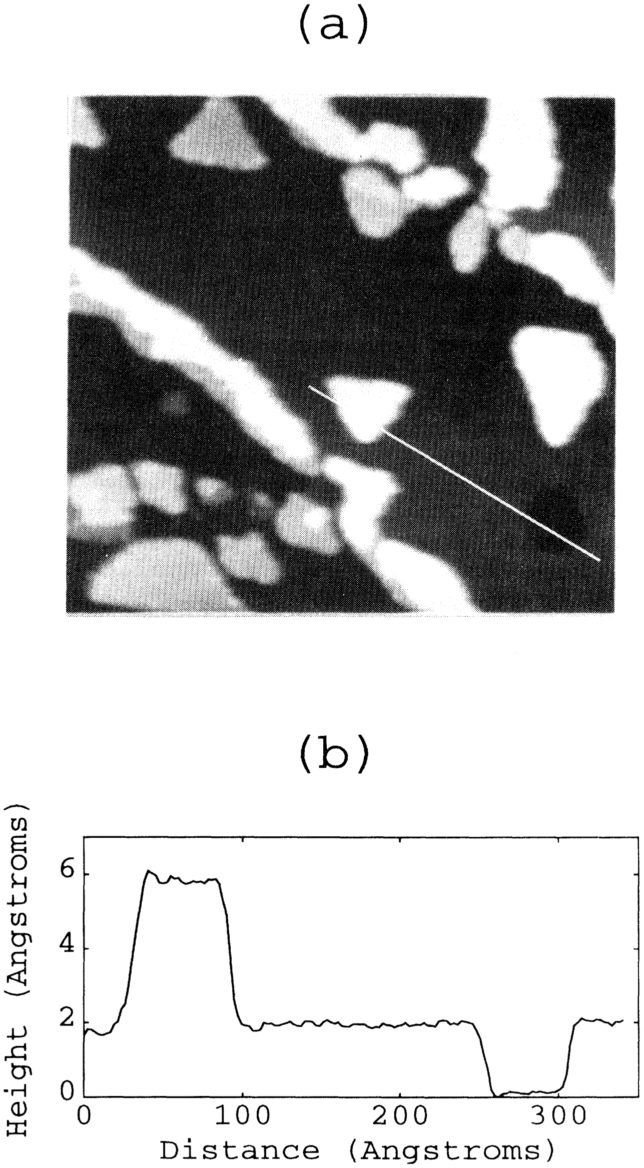

FIG. 2. (a) Topograph of 0.6 ML of Co/Cu(111) recorded at $V = -2.7$ V and $I = 0.8$ nA. The size of the image is 515×515 Å$^2$. (b) Profile along the line indicated in (a).

the large (13%) mismatch between Co and Au.[21] Note that the lattice mismatch for Co/Cu is small (2%) and double-layer islands are also detected here.

The existence of large islands nucleated at terraces indicates that Co atoms are highly mobile on clean Cu(111) at RT, a common observation on many metal/metal systems.[18] On the other hand, by comparing the present data with those reported for Co/Cu(100), where the island size for similar deposition rate (1 ML/min), substrate temperature, and deposited coverage (0.6 ML) was much smaller (30 Å),[16] one can conclude that RT diffusion of Co is faster on Cu(111) than on Cu(100).

Most of the islands in Figs. 1 and 2 exhibit *triangular* shapes with their edges aligned with the close-packed $\langle 1\bar{1}0\rangle$ directions of the Cu substrate. This is in contrast with the *hexagonal* shape of some holes observed on Cu terraces (see Figs. 1 and 2). They are 2.0 Å deep [as shown in the line profile of Fig. 2(b), which also highlights a bilayer Co island] and correspond to monoatomic vacancy islands, probably remaining from the sputtering and annealing process. It should be noted that homoepitaxial growth on fcc(111) substrates, e.g., Au/Au(111),[22] Pt/Pt(111),[23] also produces adatom and vacancy islands with threefold-symmetric hexagonal shapes.

The triangular shape of the Co islands reflects a significant difference in step energy between close-packed steps oriented along $\langle 1\bar{1}0\rangle$ with sides belonging to $\{111\}$ or $\{100\}$ microfacets. The highly perfect shape obtained already at RT indicates that migration of Co along the island edges is large allowing the islands to adopt an energetically favored shape, in contrast to other RT deposits, such as Au/Ru(0001).[24]

Another point to be noted is that triangular Co islands appear on *each* atomic terrace with *two* orientations rotated by 60° with respect to each other. Both orientations are represented with almost equal probability and no significant difference in island size. This finding can be rationalized as follows: Co atoms adsorbed on the Cu(111) surface may reside in a threefold site of fcc or hcp symmetry depending on their relative binding energy. If the difference in energy between both sites for Co/Cu(111) is small (compared to $kT$), roughly equal proportions of fcc and hcp sites will be occupied for the first layer. The initial stacking sequence would then be *ABCa* or *ABCb*, respectively (uppercase letters denote the Cu substrate and lowercase ones the Co layer). Now, if the step edge energy favors the formation of only one type of step, e.g., the $\{111\}$ type, the islands nucleated in the same terrace around Co atoms in fcc or hcp sites have to be triangular and display the observed rotated orientations. Furthermore, in order to keep the step edge orientation, they will continue the growth with stacking sequences of *ABCabcabca* and *ABCbacbacb*, respectively. Note that these two equivalent ways of stacking (111) planes are twin-related fcc, but will mimic the pseudohexagonal symmetry of diffracted beams characteristic of hcp symmetry (see below).

The argument above is consistent with two other experimental observations: first, the report of triangular islands of Co on Ru(0001) with identical orientation in each terrace changing orientation when changing to the next terrace.[18] This result indicates that one type of step edge is preferred. Furthermore, the *ABAB* hcp stacking of Ru(0001) then forces the flipping of step microfacet, and thus triangle, orientation in alternate atomic terraces. The second report concerns Fe on Au(111).[25] In that case, for 0.5 ML of Fe, triangular islands 1 ML high alternate orientation in going along the "herringbone" reconstruction of Au(111), which is known to consist of regions where Au atoms sit in fcc and hcp stackings, respectively.[25]

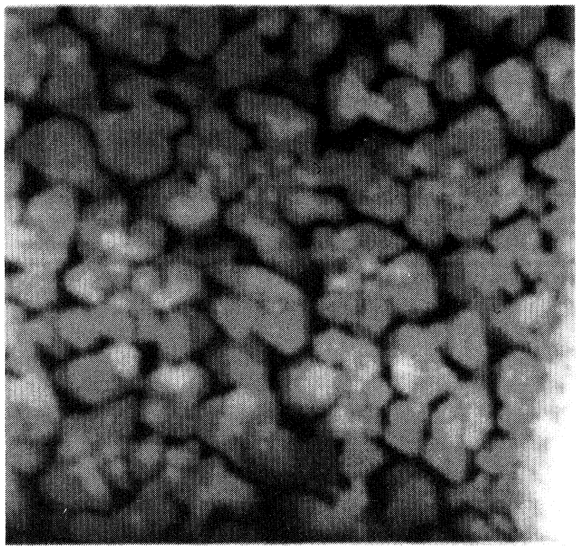

FIG. 3. Topograph of 5 ML of Co grown at RT on Cu(111), taken at $I$ =1.3 nA and $V$ =1.9 V. Image size is 1200×1200 Å$^2$.

An important consequence of the formation of twinned bilayer islands is that a domain boundary exists even in the first layer, which may impede the coalescence of the islands during subsequent growth of the Co film. This is illustrated in Fig. 3, which visualizes the surface after deposition of 5 ML of Co at RT on Cu(111). The film is composed of flat-top crystallites with lateral sizes (100–150 Å) almost identical to those obtained for 0.6 ML. The grain boundaries between crystallites are still preferentially oriented along high-symmetry directions of the substrate and amount to 25% of the imaged surface. Their apparent depth is 8–12 Å, i.e., they reach down to the substrate. This image proves that the initial double-layer islands grow vertically without coalescing into a uniform film. The energy dependence of the LEED pattern from this surface shows clearly the hexagonal symmetry expected for hcp Co (0001). We believe that, in the coverage range explored here, it is the presence of domain boundaries in the initial nuclei (twinned fcc crystallites), which causes the symmetry of the LEED pattern to transform from threefold to sixfold during the growth of Co and not the change to the hcp Co bulk structure. Only thicker Co/Cu(111) films display some hcp fraction as detected by XRD.[13] The crystallites of Fig. 3 are, in summary, fcc twins (111) oriented and epitaxial with the substrate but the mesoscopic morphology of the film is *granular*, with extended grain boundaries between crystallites.

The presence of twin-related orientations seems to be intrinsic to the growth of Co on Cu(111) under UHV conditions. Both orientations nucleate independently and play an important role in subsequent growth by yielding grain boundaries between Co crystallites. These grain boundaries probably persist during the growth of Cu on top of the Co film because Cu will grow twinned on the twinned Co overlayer. Since there is no reason for the grain boundaries to coincide from Cu to Co layers, the next Co layer may contact the first one in several places forming magnetic bridges. We suggest that these defects may be responsible for a direct ferromagnetic coupling between adjacent Co layers which may obscure the AF coupling in Co/Cu superlattices grown by MBE on Cu(111).[8–10]

In summary, we have demonstrated the following for Co/Cu(111).

The growth is *not* layer by layer. In fact, the first monolayer of Co does not wet the substrate; it rather grows in the form of bilayer islands. This finding explains a puzzling discrepancy between angular-resolved photoemission data[26] and density of states calculations,[27] whereby the experiments show the absence of a theoretically predicted shift of the Co minority band when increasing the Co coverage from 1 to 2 ML.

The 2 ML high islands do *not* coalesce at higher deposited coverages (up to 5 ML) producing a flat, uniform, and continuous film. The islands grow in height with almost the same lateral dimensions producing an epitaxial and crystalline, but granular, film.

These observations are in complete contrast with the results for Co/Cu(100),[16] where a rather uniform layer-by-layer growth approaching ideality (except for the first layer) has been observed. We believe that the morphology of Co/Cu(111) unraveled here holds the clue to the difficulty in detecting AF coupling in Co/Cu superlattices grown by MBE along the (111) direction.

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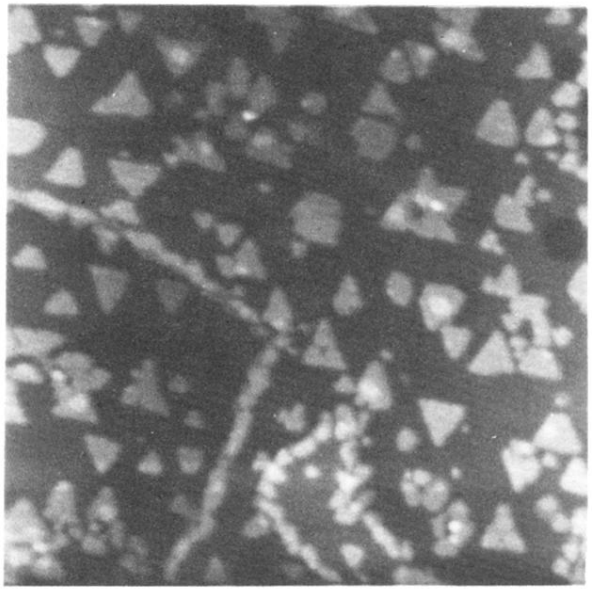

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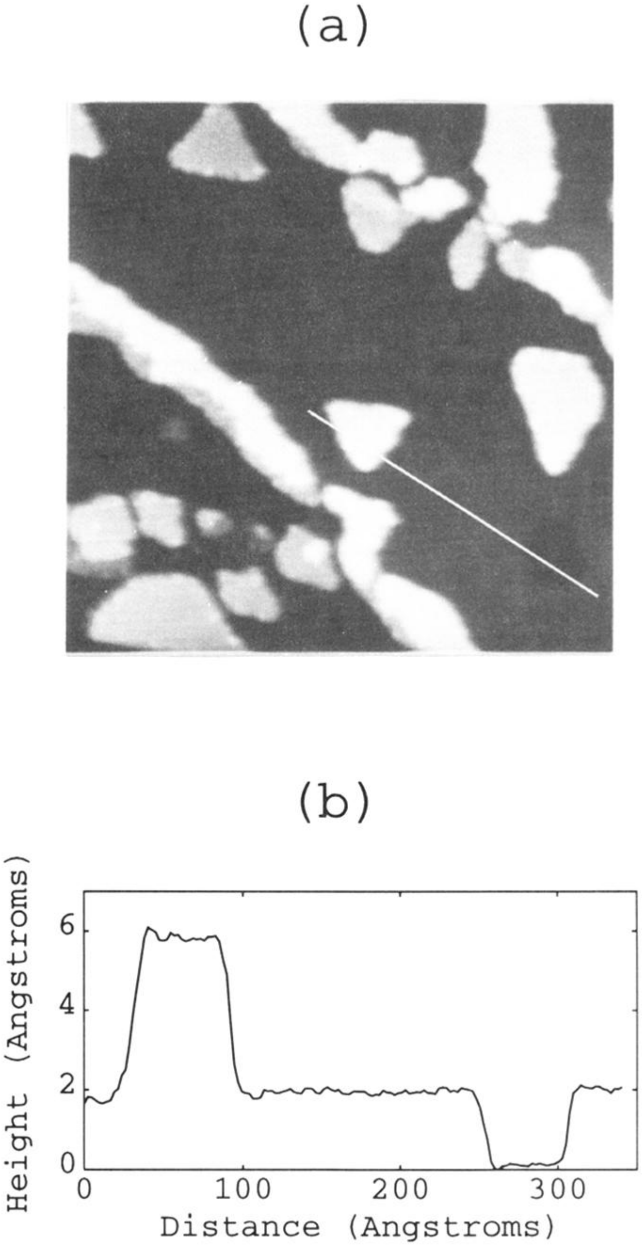
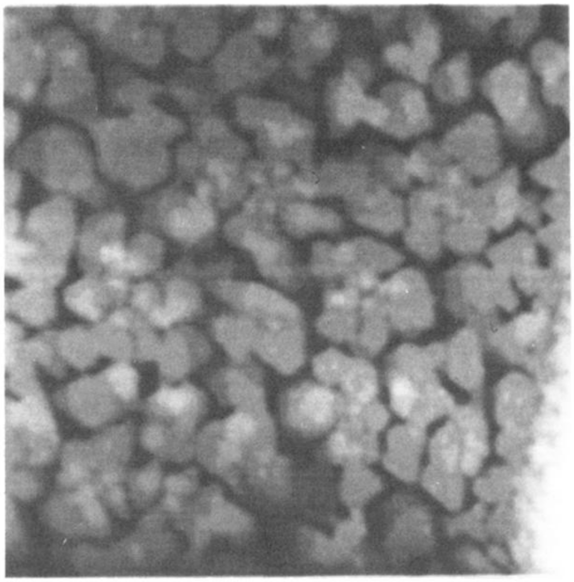


FIG. 2. (a) Topograph of 0.6 ML of Co/Cu(111) recorded at $V = -2.7$ V and $I = 0.8$ nA. The size of the image is $515 \times 515$ Å$^2$. (b) Profile along the line indicated in (a).



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