

Surface structure and metal epitaxy: STM studies of ultrathin metal films on Au(111) and Cu(100)

D.D. Chambliss, K.E. Johnson, R.J. Wilson and S. Chiang

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099, USA

The scanning tunneling microscope (STM) is an important tool for studying the growth of ultrathin metal structures. The behavior of atoms arriving at the surface determines nanometer-scale structure that is readily measured with the STM. These structural features are important in determining magnetic properties. The variety of structural possibilities is illustrated with the difference between substrate-controlled island nucleation of Ni on Au(111) and diffusion-controlled aggregation of Ag on Au(111). The STM also provides a fairly complete picture of the intermixing that occurs in the early stages of room-temperature growth of Fe on Cu(100).

1. Introduction

The scanning tunneling microscope (STM) is a powerful tool for understanding the structure of magnetic thin films, sandwiches and multilayers. At its best, the STM yields what is almost an atom-by-atom snapshot of a surface. Ideally, taking such a snapshot after growing each layer of a multiple-layer structure would determine accurately the interface roughness and the film thickness inhomogeneity of the finished structure. Of course, interrupting film growth for STM characterization at each step is impracticable. More important, one cannot rely on the simplifying assumption that a layer, once formed, will stay unchanged when the next layer is grown. The goal of the STM work described here is therefore to explore in detail the *atomic processes* of diffusion, island nucleation and intermixing that must be understood to predict with confidence the final structure of a multiple-layer sample. We find that the STM can both resolve old puzzles and lead us to new ones as a result of unexpected behavior.

Growth modes. It is useful to review the relationship of film “growth modes” to the behavior of individual atoms. Bauer’s explanation of the Frank–van der Merwe (FvdM), Volmer–Weber (VW) and Stranski–Krastanov (SK) growth modes in terms of macroscopic surface and interface energies [1] has proved remarkably useful. In metastable structures with metal layers only a few atoms thick, however, kinetic limitations and thermal randomness can yield significant deviations from quasi-equilibrium structures predicted using macroscopic parameters. In particular, many kinds of behavior could be described as “layer-by-layer growth” and yet yield markedly different results.

This is shown schematically in fig. 1, with modes ranging from nearly ideal layer-by-layer (FvdM) growth in (a) to the formation of 3-dimensional islands (VW growth) in (d). In (a), high mobility along terraces and across steps yields layer growth by step flow. Since the step density does not change in this case, reflection high-energy electron diffraction (RHEED) does not display the oscillations often used as a criterion for layer-by-layer growth. Reduced mobility can cause island nucleation, as in (b), for which RHEED oscillations are observed. In (c), deposited atoms move laterally on flat terraces but are unable to cross steps, so they aggregate at the same level on which they land. In this idealized case the frac-

Correspondence to: Dr. D.D. Chambliss, IBM Research Division, Almaden Research Center, K32/802, 650 Harry Road, San Jose, CA 95120-6099, USA. Tel.: +1-408-927-2243; telefax: +1-408-927-2100; e-mail: CHAMB@ALMADEN or chamb@almaden.ibm.com.

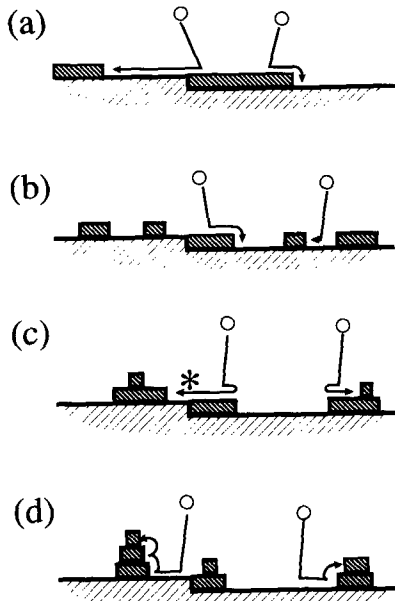


Fig. 1. Atomic motion and growth modes. (a) High mobility "step flow" layer-by-layer (FvdM) growth. (b) Islanded layer-by-layer growth. (c) Simultaneous multilayer growth due to forbidden step crossing. When downward steps are forbidden, a deposited atom may still move from the second-layer level to the first by horizontal motion across the location of a substrate step ("*"). (d) True 3-dimensional island growth (VW growth) requires upward atomic motion.

tion of the surface f_n over which the deposited film is n atoms thick depends on average thickness θ as

$$f_n(\theta) = \frac{\theta^n}{n!} \exp(-\theta). \quad (1)$$

This terrace distribution should also yield no RHEED oscillations. (Small oscillations return when atoms change levels by "downward funneling" at island edges [2] or by in-plane diffusion at a substrate step (as at the "*" in fig. 1(c).) The exposed substrate area in eq. (1) is

$$f_0(\theta) = \exp(-\theta). \quad (2)$$

Thus, in this idealization, pinholes always remain whose size and spacing are defined by island nucleation and growth. Fig. 1(d) shows true VW 3-D island growth. The onset of 3-D growth is itself an important subject for STM study [3] but is not dealt with further in this paper.

Reality is more complicated than fig. 1, which omits substrate atom motion, intermixing, and step and cluster motion. Furthermore, real systems represent mixtures of these limiting cases. For example, the barrier to step crossing may be high but not insurmountable. Then atoms landing on a monolayer island might attempt repeatedly to step down, until they succeed, because there is no stable site for them atop the island. If several atoms by chance form a stable cluster atop the island, however, this island nucleus may absorb all subsequent atoms that land on the first layer. Such a situation could yield favorable RHEED oscillations yet leave pinholes through a film several monolayers thick. To make sense out of magnetic measurements on this kind of sample one must examine the structure in detail, with many tools, and not rely on simple characterizations like "layer-by-layer growth".

Relevance to magnetism. The structural details accessible in STM studies are important to magnetic phenomena. An obvious case is the oscillatory coupling between ferromagnetic (FM) materials separated by a spacer whose thickness is varied. The strength of this coupling will depend on the thickness homogeneity and roughness length scale determined when the spacer is grown. A more subtle example is the onset of ferromagnetism in monolayer films. Ferromagnetism will be observed when exchange-connected clusters are large enough that magnetization is stable against thermal fluctuations. This may occur at fairly low coverage for widely spaced islands. If the individual islands are close and therefore small, however, it occurs only when first-layer coverage reaches an appropriate percolation threshold. Overlayer-substrate intermixing may further disperse the magnetic atoms, postponing the percolation to higher coverage.

A final example is found in recent work by Parkin [4,5] on the change in magnetoresistance $\chi = \Delta R/R$ caused by small quantities of Co included at the interfaces in sandwich structures. The results follow

$$\chi(t) = \chi_1 + (\chi_0 - \chi_1) \exp(-t/\xi), \quad (3)$$

where t is the Co thickness and ξ is a length scale close to one atomic diameter. The exponential decay resembles the decrease of exposed substrate in eq. (2). If cobalt grown on a spacer A obeys these statistics, and a FM layer B then covers all exposed areas, then eq. (3) would just be the area-weighted superposition of χ_0 from scattering at A–B interfaces and χ_1 at A–cobalt interfaces. The fitting parameter ξ may differ from a single-layer height either because eq. (2) does not apply exactly or because simple superposition does not describe the scattering exactly.

2. STM results and discussion

Experimental details. The remainder of this paper discusses STM studies of ultrathin deposits

on single-crystal substrates, prepared and studied in a multi-chamber ultrahigh vacuum system that has been described in more detail previously [6]. The single-crystal substrates do not duplicate, of course, all the complexities of samples prepared by evaporation or sputtering; this allows one to determine more precisely the atomic behavior that creates roughness and other structure in films. The first studies examine various metal deposits on Au(111), for which the herringbone reconstruction of the starting surface [7,8] is important in its effects on, and response to, the metal aggregation. Deposits on Cu(100) are less pretty and present a greater challenge because intermixing cannot be ignored. The crystals were prepared by repeated ion bombardment and annealing, and films were evaporated onto a room-

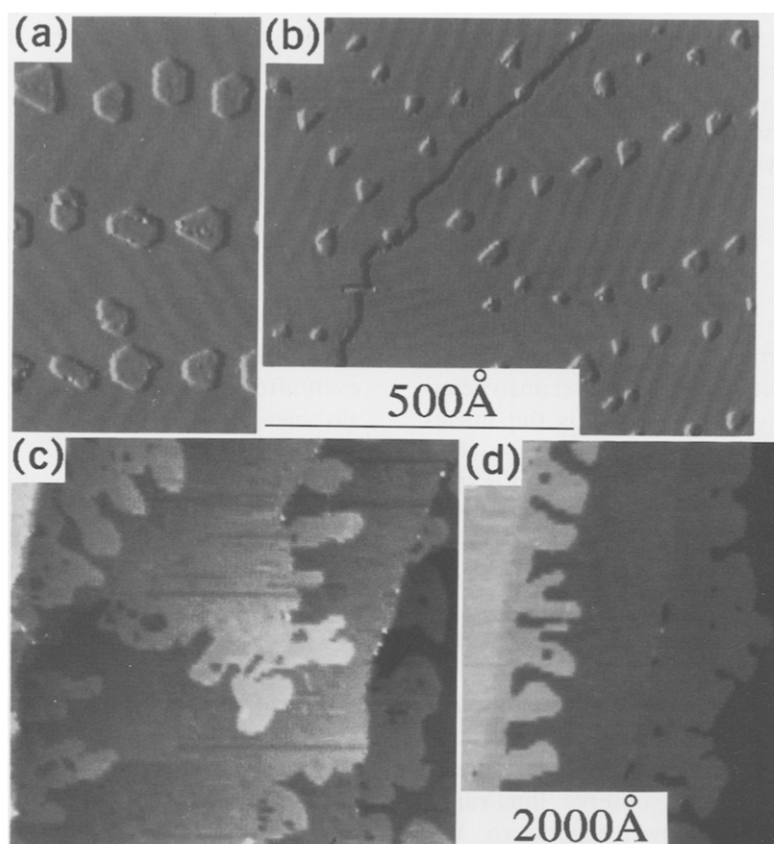


Fig. 2. STM images of metal deposits on Au(111). (a) Submonolayer Ni forms islands at “elbows” of reconstruction. Images (a) and (b) have been numerically differentiated to show both islands and reconstruction ridges. Length scale in (a) is similar to (b). (b) Fe islands at elbows. (c,d) Ag fingerlike growth against lower sides of steps.

temperature substrate. Further experimental details are provided elsewhere [7,9–11].

The coverage of deposited metal in monolayers (ML) is usually determined in a straightforward and accurate way from STM observations. The wide step spacings of our substrates (often 1000 Å) allow original steps to be distinguished from those created by island growth. The coverage is simply the total atomic volume that has been added atop the original surface, comprising islands and deposits at steps. If one can discern the original step locations (as for Ag on Au(111)) or can choose a region where almost all growth is in islands (as for Ni on Au(111)) the coverage is typically accurate to better than ± 0.02 ML. Some uncertainty remains because island boundaries are not sharply defined and because local coverage will vary statistically from image to image as a result of atom diffusion and aggregation. Step heights are also measured accurately. Piezoelectric parameters are calibrated accurately for macroscopic translations and step heights on well-understood crystal surfaces are used to check against changes in these parameters over time. In typical results some uncertainty remains due to noise, step rounding with blunt tips and “piezo creep”.

Ultrathin metal films on Au(111). The variability of ultrathin film growth is seen when different metals are deposited on the reconstructed Au(111) surface. Most remarkable is the nucleation of regularly spaced island arrays when Ni is deposited [9] (fig. 2(a)). Similar nucleation is seen for Fe [10,12,13] (fig. 2(b)) and for Co [12]; while Ni and Fe form monolayer islands, the Co forms as bilayers [14]. The long-range ordering is caused by nucleation at “elbow” sites in the “herringbone” reconstruction of well-annealed Au(111). These sites are the locations of dislocations of the surface lattice [9,13]. It is not yet known whether the island arrays possess any unusual magnetic properties, but at coverages where the islands remain separate one might observe long-range magnetostatic ordering at low temperature. The ordered nucleation might also define the magnetic grain structure of thicker films on Au(111). These results suggest that relatively minor surface

features (in this case, bends in misfit dislocations) can contribute in important ways to the ultimate texture of an ultrathin film.

Very different behavior is found when a different metal, Ag, is deposited. In this case almost no islands are formed, presumably because less-reactive Ag atoms have smaller binding energies at the elbow sites. The Ag atoms instead diffuse across the terraces and aggregate on the lower sides of steps [7]. This forms fingerlike aggregates (figs. 2(c,d)) because Ag atoms that have been incorporated into the deposit do not diffuse along the step to reach the lowest energy configuration, nor do they often step down from the second layer to the first. Nonetheless, second-layer growth is rare because an atom landing atop an Ag finger can escape by crossing the Ag/Au boundary at which the finger started, as marked in fig. 1(c) with “*”. The shapes differ significantly, however, from the simple fractals expected for pure diffusion-limited aggregation [15] and reported recently for Au on Ru(0001) [16]. The different behavior here is due to interaction with the Au(111) reconstruction [10]. This system, considered one of the simplest layer-by-layer growth metal systems, displays surprising complexity when examined at a nanometer length scale. Indeed, the long-range diffusion of Ag and the suppressed step crossing cause some large (1000×1000 Å²) exposed Au patches to remain even after 1 ML deposition [7] despite the otherwise nearly perfect layer-by-layer growth.

Fe on Cu(100). Fe deposition on Cu(100) is studied primarily because the Cu(100) surface lattice stabilizes Fe in the face-centered cubic (FCC) structure [17,18]. Deposition at room temperature does not yield simple layer-by-layer growth, however, and uncertainty about the true growth behavior has persisted to the present. Forward-scattering anisotropies in Auger electron diffraction (AED) [19] and X-ray photoelectron diffraction (XPD) [20] at submonolayer Fe coverages show that many Fe atoms are covered either by Fe or Cu atoms. This was interpreted to indicate Fe agglomeration into bilayer or thicker islands [20]. Furthermore, Auger Fe/Cu peak ratio curves plotted against Fe deposition cali-

brated with Rutherford back-scattering appear to show breakpoints at 2 and 4 monolayers but not at 1 or 3, which was interpreted to show sequen-

tial growth of *bilayers* [21]. Several experiments indicate, however, that the actual growth is more complex. CO adsorption experiments show that

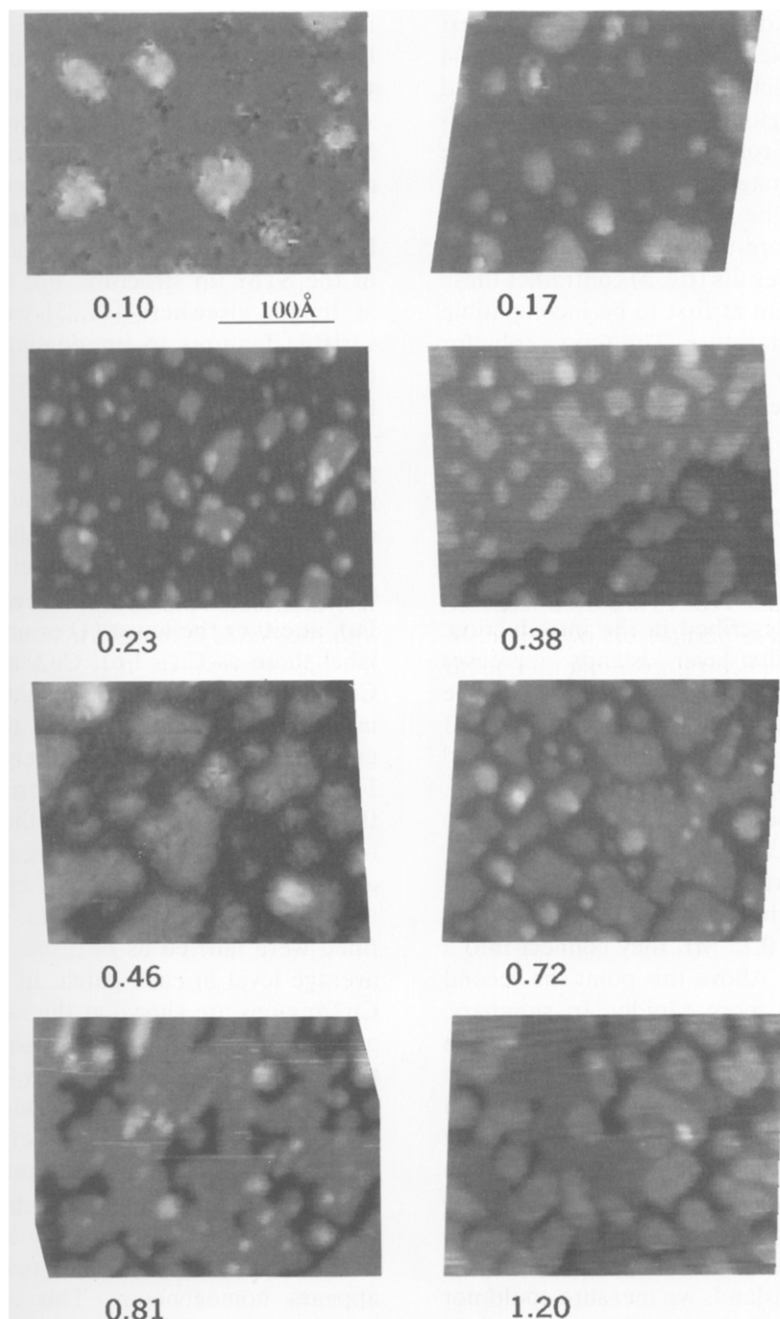


Fig. 3. Island nucleation and growth for Fe on Cu(100) (300 K). Coverage in ML is marked below each image. Almost all islands are of monolayer height. The island number density increases until island coalescence dominates. As noted in the text, Fe patches in Cu surface appear sometimes as small bumps (as in 0.17 and 0.23 ML images) or as depressions (as in 0.10 and 0.53 ML images).

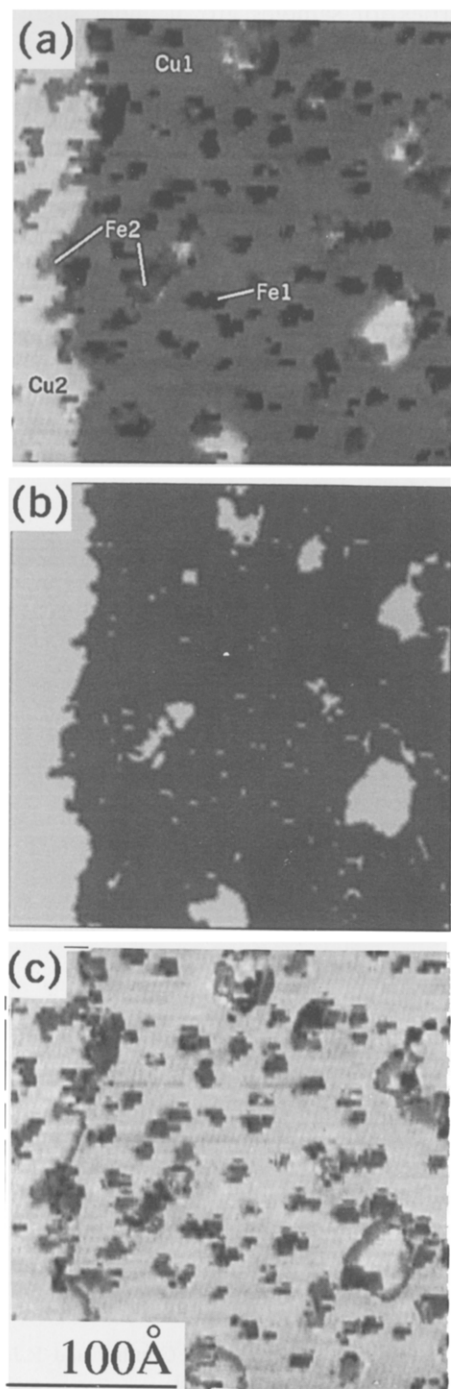
many Cu atoms are still exposed after 2 ML of Fe deposition [20]. RHEED [22], medium-energy electron diffraction (MEED) [23] and helium-atom scattering (HAS) [24] show a rapid decrease in specular intensity during deposition of the first monolayer and simple oscillations begin only at 4 or 5 ML. The diffraction results are interpreted to indicate initial agglomeration of Fe into multi-layer islands [23]. From these conclusions, one might expect STM images at coverages below and just above 1 ML to be dominated by islands (or deposits at steps) more than 1 layer high.

The actual STM results (fig. 3) contradict these expectations and seem at first to be incompatible with results in the literature. The topography for Fe exposures below 1 ML is dominated by 1-layer-high islands (height $(1.7 \pm 0.2 \text{ \AA})$). Some second-layer growth is seen in the form of small islands atop larger 1-layer islands, but up to 0.75 ML it accounts for less than 10% of the area covered by islands. The second-layer islands are small compared with the first-layer islands on which they stand, as expected for accidental island nucleation as described in the introduction. The number of first-layer islands increases steadily up to about 0.4 ML deposition, with the typical island spacing decreasing from 80 Å at 0.1 ML to 25 Å at 0.4 ML. This continued island nucleation up to a fairly high coverage is unusual, since the first islands to form usually tend to absorb the arriving atoms and suppress further nucleation. With further deposition the number of islands decreases because growing islands coalesce, until at about 0.75 ML they connect into a percolating network. Above this point the second layer starts to grow more rapidly. In summary, the topography by itself disproves models in which Fe bilayers or thicker layers cover much of an undisturbed Cu(100) surface. Instead it suggests a tendency toward FvDM growth in which atomic motion on terraces and across steps is possible but limited. It is clear, though, that the topography alone, interpreted simplistically, does not give the whole story.

In particular, the islands we measure could not account for the forward scattering observed in AED and XPD [19,20], if they are Fe islands atop an undisturbed Cu surface. One must conclude

that many Fe atoms actually lie below the original Cu(100) surface, having exchanged places with surface Cu atoms. In other words the islands contain many Cu atoms that have popped out to make room for Fe atoms. The compositional inhomogeneity of the surface can in fact be seen with the STM, in a way that is not fully understood. At coverage below about 0.25 ML the STM images contain not only topographic islands of well-defined height, but also smaller features which can appear as slight bumps or (less often) holes, depending mostly on uncontrolled aspects of the STM tip structure. For reasons discussed at length elsewhere [11,25] we attribute these variable features to (predominantly) Fe patches that lie in the plane of the neighboring Cu surface.

For some tip conditions the boundaries of these patches have been observed with near-atomic resolution, as is seen in fig. 4(a). The different apparent heights in the data allow regions of the sample to be identified as either "unaltered" (presumably Cu) or altered by inhomogeneity (i.e., Fe), at either the lower (1) or upper level (2). We label these as Cu1, Fe1, Cu2, and Fe2. Fe1 and Cu2 are the darkest and lightest parts of the image, but Cu1 and Fe2 are difficult to distinguish because the apparent height change at the Fe patches in this image is variable and close to the height of a Cu step. With the data of fig. 4(a), boundaries were defined using a slope threshold, and in a few cases apparent errors due to data noise were corrected by hand. Patches thus defined were labeled as Fe1, etc., according to the average level in each patch. In fig. 4(b) Fe2 and Cu2 regions are shown at the same height, 1.8 Å above Fe1 and Cu1. The remaining height variations (fig. 4(c)) mainly show the composition variations, but they also include some inaccuracies due to noise and edge effects near island boundaries. Despite some uncertainty in the details, specific quantitative and qualitative conclusions are clear. The patches have well-defined irregular shapes, while the rest of the surface appears homogeneous. This suggests that Fe atoms have tended to segregate instead of forming a random alloy. This is consistent with the low solubility of Fe in bulk Cu. The patches are



smaller and closer (25 Å apart) than the islands (80 Å) at this coverage. These length scales are determined by the behavior of Fe and Cu adatoms, respectively, and thus should be different. (Different length scales for islands and for inhomogeneity, comparable to those here, have been measured for Fe on Au(100) using LEED spot profiles [26].) Next to each island is found at least one Fe patch in the surface, so the patches appear to be important in nucleating islands. Fe patches tend to be larger at steps and island edges, and a few islands appear to consist mainly of first-layer Fe.

From these observations we assemble a model for the first stage of deposition, which accounts for the observed island growth and the observations found in the literature. Fe atoms land, diffuse on the surface, and exchange places with Cu atoms, driven by an energy term related to the higher surface energy of Fe than of Cu. Fe atoms form patches either because the Fe–Cu exchange is easiest at other Fe atoms or a step, or because Fe atoms move within the surface after the initial interchange. At first, most Cu atoms released by exchange travel to step edges, with incorporation being possible from above or below. The Fe patches offer sites for island nucleation, since it is energetically favorable for a growing island to cover Fe rather than Cu. The production and expansion of these nucleation sites is why new islands continue to form with increasing coverage. Fe atoms that land atop Fe patches, or reach there by diffusion, can also form first-layer islands there. The first deposited Fe, then, gets covered rapidly by Cu or Fe, which accounts for electron forward scattering. In a sense, bilayer islands do form, but they are embedded one layer deep in the Cu surface. True second-layer growth

Fig. 4. Topography and composition of 0.1 ML Fe on Cu(100). (a) STM data with a sharp boundary at each Fe patch. Labels Cu1, Fe1, Cu2, Fe2 indicate typical Cu and Fe regions on lower and upper levels. (b) Approximate topography derived from (a). Pixel-size false “islands” and gaps in true islands are errors in semiautomatic height determination from (a). (c) “Composition” image equal to (a) minus (b). Dark patches (i.e., apparent holes) are interpreted as Fe patches in Cu substrate of islands.

is uncommon because an Fe atom landing on a Cu island is readily incorporated into the island. Some second-layer islands may form atop first-layer Fe growth. This may be why second-layer islands tend to be found at the edges of islands, where first-layer Fe is found, not near the centers, where the mathematics of diffusion and absorption at steps would predict.

After 1 ML of deposition, more than half of the exposed surface probably consists of Cu. Further Fe deposition presumably continues to promote Cu atoms to higher levels, though the details change as the film texture and the underlying atomic composition evolve. While most or all of the Cu atoms are eventually covered, the effects of initial intermixing persist at least to 4 ML in the form of small height variations, ≈ 0.2 Å high, with size and spacing similar to that of Fe patches at 0.1 ML. This may be related to the streaking observed in LEED [27,28]. The changes in composition and in nanometer-scale surface structure could dominate the diffraction intensity results, obscuring oscillations that might be predicted on the basis of topography alone [23]. It is not surprising, then, that diffraction oscillations appear only after several ML of deposition has presumably buried almost all Cu atoms.

These results for Fe on Cu(100) teach important lessons about epitaxy. The intermixing that occurs here is very different from interdiffusion at a solid–solid interface. Indeed, processes that occur only at surfaces, such as adatom diffusion and aggregation, play such a central role in film structure that when films of different orientation (such as (100) and (111) texture) display different magnetic properties, a structural difference associated with growth behavior must be considered as an explanation. We also see the value of using seemingly redundant structural probes so that a false assumption implicit in the interpretation of one probe (here, the assumption that the substrate is undisturbed) is likely to be discovered.

3. Conclusion

The complexity of metal-on-metal growth presents problems and possibilities. A few param-

eters like surface free energies and adatom diffusivities cannot fully determine the structure that arises from growth. It is thus not surprising that different laboratories can get different magnetic properties for samples grown under slightly different conditions. With local probes like STM it is possible, however, to determine the details of growth and understand more clearly which are the essential variables to control. We can hope that this knowledge can lead us not only to approach more closely the ideal structures we have tried to grow for years, but also to conceive of and produce new nanometer-scale structures made possible by the rich variety of atomic behavior on surfaces.

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