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A structural model and mechanism for Fe epitaxy on Cu(100)

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Abstract

A structural and mechanistic model for initial room temperature Fe epitaxy on Cu(100) is presented, based on scanning tunneling microscopy data. Changes in Fe atom attachment kinetics with coverage θ yield several growth regimes: Fe incorporation into the surface by atomic exchange with Cu ($\theta < 0.2$), growth of first-layer Fe islands ($0.2 < \theta < 0.7$), and simultaneous layer-1 and layer-2 growth ($0.7 < \theta < 2$). These results reconcile qualitative disparities in previous interpretations of experimental results.

The unanticipated complexity of structures resulting from metal epitaxy on single-crystal metal substrates has necessitated careful reevaluation of previously proposed models. The structural evolution of face-centered cubic (fcc) Fe epitaxy on Cu(100) has remained contentious despite investigations with many surface sensitive techniques. An accurate model must account for seemingly contradictory experimental results, as well as explain the growth mechanisms and driving forces that generate the surface structures. Continued interest in the relationship of film structure to the perpendicular and in-plane magnetization in nearly fcc Fe films [1-5] underscores the need for an understanding of the growth at different temperatures. Low-energy electron diffraction has shown that deposited Fe maintains approximately the fcc structure of the Cu

structure by a martensitic transformation [7]. Medium-energy electron diffraction (MEED) [8] and helium atom scattering (HAS) [9], techniques sensitive to mesoscopic topography, indicate three stages of room temperature (RT) growth: an initial decline in intensity, interpreted as Fe agglomeration; above $\theta \approx 4$ ML a recovery of intensity and 1 ML period oscillations, considered laverby-layer growth; and a final intensity drop at the fcc-bcc transition. The initial "agglomeration" stage has received considerable attention. A CO titration technique [10] showed a significant fraction of the exposed surface consists of Cu after Fe deposition of up to 2 ML. Forward scattering anisotropies for Auger electrons [11] and X-ray photoelectrons [10] indicated some Fe atoms are covered even at $\theta = 0.1$ ML [12]. Calibrated Auger breakpoint measurements suggested bilayer growth [13], which was the prevailing interpretation until contradicted by scanning tunneling mi-

substrate for coverage θ up to 10–14 monolayers

(ML) [6]; after deposition of additional Fe the

overlayer reverts to the body-centered cubic (bcc)

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croscope (STM) measurements [14–16]. It is now known that intermixing of Fe at the Cu substrate occurs upon the initial deposition, as first suggested by STM measurements [14] and since confirmed by low-energy ion scattering (LEIS) [17].

In this paper we describe the structure and atomistic mechanisms for the initial RT growth of Fe on Cu(100). Our model, shown in Fig. 1, is based on the layer filling behavior measured in STM images of many samples, and on the morphological changes and compositional variations observed in these images. Its salient features are initial intermixing at the substrate-overlayer interface, followed by simultaneous growth into the first two layers. Thermodynamics, in particular the significantly higher surface free energy of fcc Fe than of Cu [18], explains the driving force for minimizing the exposed Fe surface, but the resulting structure is ultimately determined by the RT kinetics. We present the first model that simultaneously accounts for the persistence of exposed Cu, the covering of Fe atoms, and the observed topography.

An ultra-high vacuum preparation and STM system was used [19]. After cycles of cleaning by Ar^+ bombardment and 900 K annealing, the Cu(100) crystal surface consisted mainly of atomically flat, defect-free terraces > 200 Å wide. Prior to deposition the sample was cooled to within 25°C of RT; for depositions not at RT, conductive heating or cooling was used. All STM images were acquired at RT. Fe was deposited from well outgassed 99.998% pure wire heated by electron bombardment, typically at 1 ML in 80 s. Auger electron spectroscopy (AES) was used to monitor



Fig. 1. Schematic representation of surface cross section after RT deposition. Solid represents Fe and hatched regions Cu. Arrows denote initial location of (100) substrate surface. (a) At 0.05 ML deposited Fe exists principally in substrate inclusions. L1 islands are Cu. (b) 0.3 ML Fe adds to edges of islands and nucleates new islands. (c) 1.0 ML. Simultaneous growth in first two epitaxy layers. (d) 2.0 ML. First two layers nearly complete; L3 growth has begun.

sample contamination; typical C contamination was < 0.2%, low enough to have no measurable effect on images. Fe coverage was determined by three techniques: AES intensity ratios; exposure, measured with an ion gauge in the Fe flux; and quantitative analysis of the STM images. Images were taken at constant current and are displayed using a height-keyed gray scale.

As depicted in Fig. 1a, the first Fe deposited at RT exchanges with substrate Cu atoms and forms inclusions in the outermost substrate layer (L0), the ultimate density of which reaches 28 ± 5 per $(100 \text{ Å})^2$. The displaced Cu atoms form firstlayer (L1) islands or form somewhat rough deposits at step edges. Figs. 2a and 2b illustrate the typical STM imaging of the Fe inclusions. The Fe inclusions in L0 and at edges of L1 islands often appear in STM images as patches, usually depressions, with indistinct boundaries and apparent depth or height weakly dependent on bias [14]. This non-topographic imaging mode is variable and tip dependent, yet is observed for nearly all our samples with $\theta < 0.2$. The origin of this chemical sensitivity of the tunneling junction is unclear. The contrast is specific to small Fe clusters in the substrate and at edges of L1 islands, and is not observed for larger Fe islands at higher coverage. Similar chemical contrast has been reported for alloy crystals [20].

The total area of patches in L0 and at L1 island edges agrees with the quantity of deposited Fe, and with the amount of Cu aggregated in L1 in islands and at steps, within a 15% error inherent in assigning boundaries. Thus, as depicted in Fig. 1, little or none of the Fe penetrates deeper into the bulk than L0. Deposition at elevated temperature yields somewhat larger substrate inclusions, while, as shown in Fig. 2c, low-temperature (LT) deposition at 100 K inhibits Fe exchange with the Cu substrate even when annealed to RT. Subsequent annealing to 420 K activates the exchange and Fig. 2d shows the presence of Fe inclusions. While LT deposition suppresses intermixing, the resulting surface is rougher than a RT deposit: $\theta = 2.8$ ML deposited at LT and annealed to RT yielded a surface with Fe growth above layer 3 (L3) $\sim 20\%$ of that in L3; for RT the comparable value is ~5%. At lower coverages, annealing temperatures sufficient to smooth these rough surfaces activate exchange with the substrate.

For RT deposition beyond 0.2 ML, many small islands are observed in L1 (Fig. 3a), and most Fe atoms aggregate in L1 rather than exchange with Cu in L0. The number density of islands, plotted in Fig. 4a, increases markedly until islands coalesce. In regions between large coalesced islands,

the small newly formed islands of Fe nucleate at a density roughly equal to that of the underlying Fe inclusions. The accelerating island nucleation for $0.1 < \theta < 0.4$, which is not compatible with classic nucleation and growth models, is explained below considering the Fe-Cu heterogeneity of the surface.

The comparatively large Fe regions that aggregate in L1 do not display the strong Fe-Cu



Fig. 2. STM images of Fe inclusions. (a), (b) 0.05 ML deposited at 1 ML in 800 s. $V_{sample} = -0.7$ V. Dark areas in terraces are the inclusions. L1 Cu islands are bright areas. (c) 0.2 ML deposited at 120 K, annealed to RT. Fe observed only as multilayer islands with no evidence for the formation of inclusions. $V_s = -0.2$ V. (d) Same sample annealed to 420 K, activating exchange of Fe with substrate Cu. ~ 0.03 ML Fe now present as inclusions. $V_s = -0.3$ V.





Fig. 3. Representative images of epitaxial layer filling. (a) 0.68 ML; $V_s = -0.5$ V. (b) 0.82 ML; $V_{sample} = -1.5$ V. (c) 2.0 ML; $V_s = -0.3$ V.

contrast in STM images observed in L0 for lower coverage. L1 heterogeneity can be seen clearly, however, in the changes induced by O_2 exposure (Fig. 5). The Fe periphery of L1 exhibits strong corrugation with a quasi-hexagonal lattice spaced 3.2 ± 0.3 Å, consistent with hexagonal planes in bulk FeO, and with FeO on Pt(111) observed using STM [21]. The Cu component at the core is unaffected, and covers $17 \pm 4\%$ of the surface. This suggests Fe inclusions make up $17 \pm 4\%$ of L0.

The complex structure summarized in Fig. 1 occurs as a result of non-equilibrium growth in

which mobile deposited Fe atoms are trapped by several processes: adhesion to steps and islands; joining of two Fe or Cu adatoms to nucleate an island; metastable trapping atop an Fe inclusion; and incorporation into L0 by exchange with a Cu surface atom. The kinetics changes as reactive sites are created or covered over and different processes become dominant. In the intial stage, most Fe atoms are absorbed into L0, driven by the Fe-Cu surface energy difference $\Delta \gamma \approx 0.5$ J/m^2 [18], and L1 islands consist largely of Cu released by exchanges. The positive heat of mixing Q for Fe in Cu (roughly +40 kJ/mol, esti-



Fig. 4. Quantitative image analysis of Fe epitaxy. (a) L1 and L2 island number density. (b) Epitaxial growth, by layer. In both plots curves are guides only and vertical lines indicate percolation threshold.

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mated from the solubility at 1340 K [22]) makes incorporation of new atoms easier beside Fe atoms already in L0 than at pure Cu sites, so Fe-Cu "intermixing" occurs as discrete inclusions rather than as a random alloy. Q also favors nucleation of Fe islands in L1 atop the Fe inclusions in L0. Thus, the availability of many inclusions after $\theta = 0.2$ causes an accelerating nucleation of L1 islands (Fig. 4a) and aggregation of most Fe into L1. This qualitative description is confirmed by a quantitative analysis using rate equations [23].

Another change, the increase in L2 growth at $\theta = 0.7$ in Fig. 4b, occurs upon percolation of the L1 aggregate. L2 growth is nucleation limited: most adatoms landing atop an L1 island without a preexisting L2 island will not survive long enough to encounter other adatoms and form a new L2 island, before being incorporated into the L1 island. Still, a few adatoms do survive long enough to form some L2 islands. Given the flux F and typical island size for these samples, this implies a

long adatom lifetime on islands (> 25 ms), so a step, approached from above, must be highly reflective (>99%). After L1 percolates into a connected network, adatoms will sample a large area in this lifetime (instead of the same area, repeatedly) and are likely to find and attach to an L2 island. Then only atoms landing on exposed L0 surface add to L1; this slower filling of L1 is reflected in the L1 curve of Fig. 4b as a slope decrease from nearly 1 to 0.3. Further L2 island nucleation is suppressed after percolation (Fig. 4a) by the more effective absorption of adatoms by L2 islands than by downward steps. As is the case for L1 islands on L0, L2 islands form preferentially over the Fe component of L1, near the periphery of L1 islands. After percolation, an adatom's diffusive trajectory is presumably confined mainly to the (connected) Fe regions and avoids the Cu regions near the centers of what had been separate islands.

Previous experimental results reflect the changes in morphology during growth described









here. The break in AES intensity ratios at 2 ML [13] detects he simultaneous near-completion of L1 and L2, 1 ut does not indicate layer composition or inter nediate surface structure. The very early multi-layer growth observed by XPD [10] and AED [1] indicates the covering of Fe inclusions by L1 slands. Cu remains exposed in part because of (u segregation in the atom exchange process, but mostly because L1 completion is delayed; me surable holes persist beyond $\theta = 2$ ML (Fig. 4b. For comparison with past and future experiments, at $\theta = 1.0$ ML our model estimates 0.35 ± 0.06 ML of exposed Cu, and $0.35 \pm$ 0.06 ML and 0.08 ± 0.4 ML of Fe covered by one and two layers, respectively. The main features of MEED intensity variations [8] are also reproduced well ty applying kinematic diffraction theory to our S [M data [23].

Models of simple epitaxial growth predicated on a quasi-quilibrium and an abrupt boundary between components are clearly inadequate to describe R7 deposition of Fe on Cu(100). The surface energies and the heat of mixing drive the formation or inclusions and their covering by the next layer, but equilibrium even on a 30 Å scale is not reached at RT. Significant experimental quantities such as the extent of Fe-Cu intermixing are governed by adatom kinetics, which is controlled by the evolving surface morphology. Previous ext erimental conclusions relying on narrow structural evidence and simplified growth models could not describe the resulting complexity accurately. STM images alone also do not provide a complete picture of composition and structure, b it in conjunction with other structure measurements and composition sensitive techniques, STI4 has provided the means to unite seemingly contradictory interpretations with a real space pictu e of atomic structure. The clarification of the atomic processes involved, and their morphologi al consequences, should permit a quantitative reexamination of data and resolution of the long standing controversy over this system. This work was supported in part by the Office of Naval Research (N00013-89-C-0099).

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