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Structure and growth of strained Cu films on Ru(0001)

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Abstract

We present X-ray scattering studies of the structure and growth of the heteroepitaxial interface Cu–Ru(0001) between 300 and 870 K. For Cu depositions of between one and two monolayers (ML), a bilayer stripe-phase coexists with domains pseudomorphic to the Ru substrate. At the completion of 2 ML, the stripe-phase wavevector abruptly locks to that of the substrate with a commensurability $\delta = 1/16$ or 1/18, depending on the temperature. Above 2 ML, a cooperative growth process leads to three-phase coexistence, including the bilayer stripe-phase and rotated and unrotated bulk-like Cu islands.

Keywords: Copper; Epitaxy; Ruthenium; Surface stress; Surface structure, morphology, roughness, and topography; X-ray scattering, diffraction, and reflection

Interest in the bimetallic interface Cu on Ru is based on the catalytic properties of the Ru(0001) surface, which supports hydrocarbon conversion reactions [1–3]. The activity and selectivity of these reactions can be enhanced in the presence of Group IB metals like Cu. The enhancement originates, in part, from the modification of the interfacial band structure by the coherent adlayer strain induced at the interface by the Cu–Ru lattice mismatch [4–6]. The study of strain evolution and accommodation is, therefore, central to understanding the properties of bimetallic catalysts.

Cu films adsorbed on Ru(0001) surfaces are among the best characterized bimetallic interfaces known [7–14]. Earlier scanning tunneling microscopy (STM) studies [7,8,10,13] have shown that, following an anneal to 700 K, the first layer of Cu adopts a pseudomorphic structure. This corresponds to a 5.8% expansion of the Cu near-neighbor spacing relative to its bulk value, and implies that the overlayer is strained. At a thickness of two layers, the Cu film is reconstructed to form a uniaxially compressed stripe-phase. Stripe-phases are common in nature, appearing in systems as diverse as high T_c superconductors, liquid crystals and ferromagnetic garnets. In this case, the observed reconstruction is similar to the single layer stripe-phases occurring at other metal–vacuum interfaces [15,16]. The latter consist of a series of linear discommensurations separating regions of the correct fcc-stacking from regions of faulted hcp-stacking. 'Bright-star' and other multilayer reconstructions based on the stripe motif

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have been observed at higher Cu coverages [7,8,10,14]; however, a clear understanding of the transition to three-dimensional growth is still lacking.

In this paper, we describe X-ray scattering studies of the structure and growth of Cu films deposited on Ru(0001) surfaces during deposition and versus substrate temperature. X-ray scattering techniques offer the opportunity to probe the structure of the film and its buried interface in situ over large length scales, and at high temperatures — a largely unexplored regime. Our results confirm the existence of a first-layer pseudomorphic phase, which transforms to a bilayer stripe-phase at coverages above one monolayer (ML). At the completion of 2 ML, the stripe-phase wavevector abruptly locks to that of the Ru substrate with a commensurability $\delta = 1/16$ or 1/18, depending on temperature, and bulk-like Cu(111) islands begin to form. We find that island formation is a cooperative process, in which translational order within the stripe-phase is partially destroyed, and then restored, as the islands nucleate and grow in height. There is evidence of a metastable, partial trilayer, which itself exhibits a stripe-phase reconstruction with $\delta = 1/16$, and which we suggest mediates island growth. Nevertheless, the bilayer stripe-phase persists for Cu depositions of up to 25 ML, consistent with a Stranski–Krastanov growth mode. These results offer new insight into the transition from two- to three-dimensional growth of Cu on Ru(0001), and challenge current theories of metal epitaxy to explain the observed lock-in behavior, the metastable third layer and the multi-phase coexistence.

The X-ray scattering experiments reported here were carried out on beamline X22C at the National Synchrotron Light Source. Monochromatic X-rays of 8.0–10.5 keV were focused to a spot of about 1 mm^2 using a bent, cylindrical mirror and a Ge(111) double crystal monochromator. The Ru(0001) crystal had a diameter of 6 mm and a thickness of 1.5 mm. Its surface orientation was polished to within 0.1° of the crystallographic (0001) plane, which itself exhibited a bulk mosaic width of about 0.05°. The surface preparation involved sputtering at 300 K with 1 keV Ar ions followed by repeated cycles of oxygen annealing

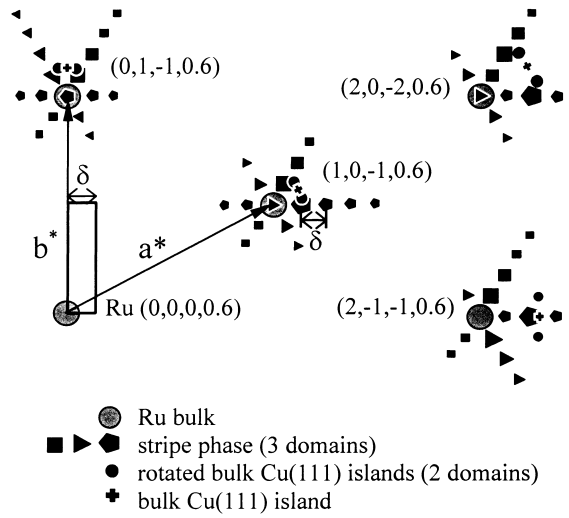

Fig. 1. Schematic diffraction pattern for Cu coverages greater than 2 ML and temperatures ≥570 K, where stripe-phase and island structures coexist. The symbols are described in the text.

to remove carbon [17,18]. The sample was subsequently annealed [19], and checked for surface contamination using Auger electron spectroscopy. Cu was evaporated onto the Ru surface using a resistively heated Knudsen cell. The deposition rate was calibrated from oscillations of the X-ray reflectivity observed at the (0001) position, and set at about 0.1 ML min^{-1}.

The surface diffraction pattern obtained in the present experiments for Cu depositions between 2 and 25 ML is shown in Fig. 1. Each symbol indicates a rod oriented parallel to the surface normal direction along which the scattered X-ray intensity is distributed. The large, gray circles locate crystal truncation rods (CTRs) [20], which arise from the hcp Ru substrate. CTRs are indexed with the in-plane substrate lattice periodicity and pass through the bulk Bragg reflections. Squares, triangles and pentagons in Fig. 1 originate from the surface reconstruction, which has a periodicity different from the substrate. Each symbol reflects one of the three equivalent rotational domains of the stripe-phase, which form on the underlying hexagonal substrate. The largest symbols correspond to primary reflections and the smaller to satellites from higher-order Fourier components. The separation between the primary and higher

order peaks is the commensurability δ, which defines the shorter side of the surface unit cell (shown by the rectangle in Fig. 1).

The simplest interpretation of the observed diffraction pattern is in terms of a two-layer, uniaxial modulation of Cu chains along the [100] direction. In matrix notation, the real space super-structure unit cell is $\{(1/\delta, 0), (1, 2)\}$, where the lattice constants are given by $\boldsymbol{a}_{\mathrm{Cu}} = (1/\delta)\boldsymbol{a}_{\mathrm{Ru}}$ and $\boldsymbol{b}_{\mathrm{Cu}} = \boldsymbol{a}_{\mathrm{Ru}} + 2\boldsymbol{b}_{\mathrm{Ru}}$. From an analysis of the intensities (to be presented elsewhere), we infer that the uniaxial modulation of the Cu chains causes a transverse displacement of top-layer Cu atoms from hcp-sites (of the Ru substrate) to fcc-sites as one travels along the [100] direction, thereby producing stripes. Between stripes are dislocation regions in which Cu atoms reside in quasi-bridge sites. Second-layer Cu atoms are only slightly out of phase with first-layer atoms, which preserves the stripe motif in the bilayer. It follows from this that the modulation of the Cu chains increases the Cu layer density by an amount δ relative to the pseudomorphic monolayer, and relieves the strain along the [100] direction.

We turn next to a description of the phase behavior observed for the strained Cu films on Ru(0001) during growth. Longitudinal scans of the primary stripe-phase reflection for one of the rotational domains were taken during Cu deposition and as a function of substrate temperature (as shown in Fig. 2a for 720 K). For Cu coverages below 1 ML no super-structure peaks were observed, consistent with the presence of pseudomorphic domains. Above 1 ML the stripe-phase peak appears and grows in intensity with increasing Cu coverage. Its wavevector remains constant, or increases slightly, and corresponds to an average compression of the Cu layer by about 5.8%. Near completion of the second layer, the stripe-phase peak abruptly shifts to a larger wavevector and locks to a commensurate value with $\delta = 1/16$ (6.25%). This wavevector corresponds to a stripe-phase superstructure with 17 Cu atoms for every 16 Ru atoms along the [100] direction. The shift in wavevector at the completion of two layers implies an additional compression of the average Cu–Cu spacing along the [100] direction by only about 0.02 Å. It is reminiscent of the density

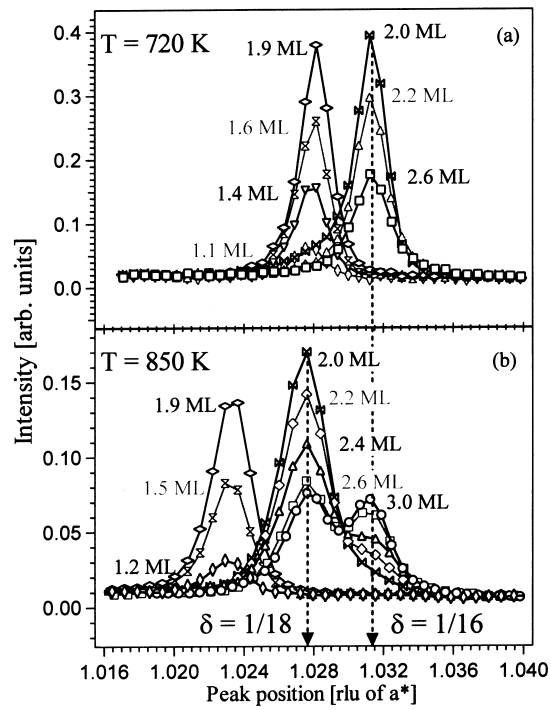

Fig. 2. Scans of the principal $\mathrm{Cu}(1+\delta/2, \delta/2, -1-\delta, 0.15)$ stripe-phase reflection as a function of coverage at (a) 720 K and (b) 850 K. The abrupt incommensurate–commensurate transition at 2 ML and the two- and three-layer stripe-phase peaks are illustrated.

changes observed at layer completion in isotherms of noble gases adsorbed on graphite surfaces, which in some cases are also accompanied by an incommensurate–commensurate transition [21].

Similar results were obtained at higher temperatures; however, above 720 K the primary stripe-wavevector locks with $\delta = 1/18$, as shown for 820 K in Fig. 2b). This corresponds to a superstructure with 19 Cu atoms for every 18 Ru atoms. There is, in addition, weak scattering with $\delta = 1/16$. Between 2 and 3 ML, the peak at $\delta = 1/16$ grows in intensity at the expense of the peak at $\delta = 1/18$, but then disappears above 3 ML. We suggest that at this temperature the scattering with $\delta = 1/16$ corresponds to a metastable, three-layer reconstruction, as will be discussed in more detail below.

The dependence of the primary stripe-phase wavevector on Cu deposition is summarized for five different temperatures in Fig. 3. The peak

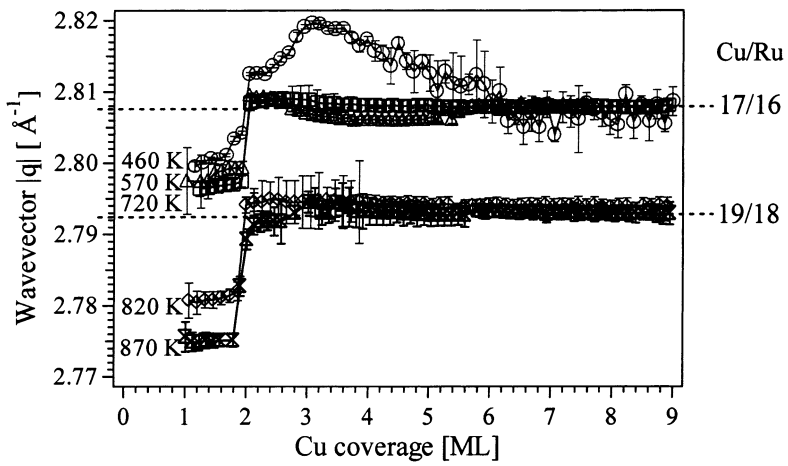

Fig. 3. Position of the stripe-phase wavevector versus Cu coverage and substrate temperature. The fractions 17/16 and 19/18 represent the $q_{(100)}$ projections with reference to the orthogonal lattice system of the stripe-phase. The metastable phase that locks with $\delta = 1/16$ is not shown.

positions were extracted from fits of longitudinal scans to Gaussians. In each case, the stripe-phase peak appears at about 1 ML and grows in intensity with increasing deposition. The initial wavevectors appear incommensurate with the Ru(0001) substrate and decrease with increasing temperature. At 2 ML Cu coverage there is a shift of the stripe-phase wavevector to a commensurate value. For temperatures below 760 K the wavevector locks with $\delta = (1/16) \pm 0.003$, whereas at higher temperatures it locks with $\delta = (1/18) \pm 0.002$. It follows that the stripe-wavevector locks to that of the Ru(0001) substrate at all temperatures between about 460 and 900 K. The temperature dependence of the lock-in wavevectors probably reflects the in-plane thermal expansion coefficients of the two lattices, which differ by about a factor of three.

A striking feature of the present results is the appearance and growth of bulk-like Cu(111) islands for depositions above 2 ML. Evidence for the islands is shown by the filled circles and crosses in the diffraction pattern of Fig. 1. These positions correspond to Bragg reflections of bulk Cu(111) islands with two preferred orientations. One orientation is aligned to the symmetry directions of the Ru substrate and the other is rotated by $\sim 0.9°$. Island formation is illustrated in Fig. 4, which shows the integrated intensities and inverse correlation lengths (widths) of the island and stripe-phase peaks at 720 K, plotted versus Cu coverage. Qualitatively similar results were obtained at other temperatures. As seen from the open circles in Fig. 4a, the stripe-phase peak grows quickly between 1 and 2 ML, then reaches a maximum and decreases. The decrease is associated with the appearance and growth of the rotated islands (open squares). At the same time, the full widths of the stripe-phase peaks exhibit a pronounced maximum, whereas those of the rotated and unrotated islands decrease to a minimum (see Fig. 4c). This implies a loss of translational order in the stripe-phase with the average domain size decreasing from ~ 800 to ~ 400 Å, concomitant with the growth of the islands to an average size of at least 150–200 Å. Between 2.8 and 3.5 ML the integrated intensities of all three reflections grow together, with the peak of the rotated island increasing by nearly a factor of ten. In addition, the wavevector of the islands relaxes to the bulk value (implying that the lattice constants reach their bulk values) (Fig. 4b), and the average stripe-domain phase recovers its original correlation length of ~ 800 Å. Above 3.5 ML the stripe-phase intensity slowly decreases, consistent with gradual replacement by bulk islands. This implies that the stripe-phase is not present at the island–Ru interface.

The development and growth of Cu islands is, therefore, a cooperative process in which each

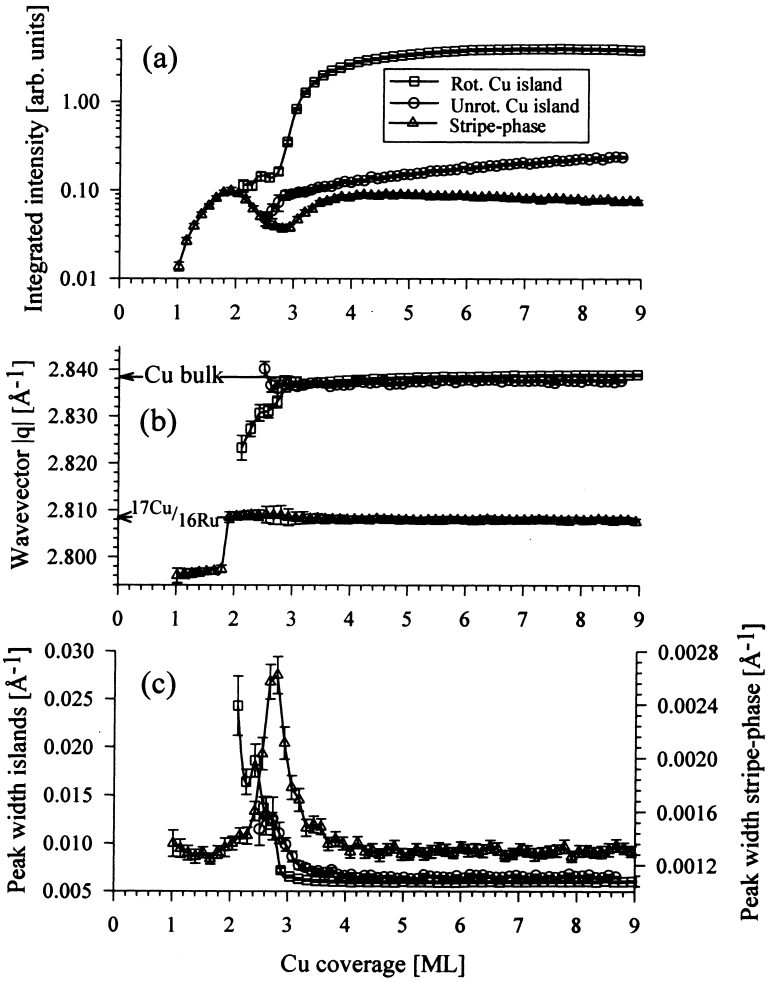

Fig. 4. Dependence on Cu coverage at 720 K of: (a) integrated intensity of the stripe-phase (triangle) and island (rotated: square, unrotated: circle) reflections surrounding the Ru(1, 0, −1, 0.6) CTR; (b) stripe-phase and island wavevectors; (c) inverse correlation lengths. The island wave vectors were determined at the (1, 0, −1, 1) reflections of bulk Cu expressed in a hexagonal system.

phase eventually maximizes the extent of its translational order. Since the stable stripe-phase reconstruction is limited to two Cu layers, the data suggest that the rotated island heights increase steadily with increasing deposition, up to 25 ML at least. This is characteristic of a Stranski–Krastanov growth mode [9,12], and implies the existence of a partial third layer, which feeds Cu atoms to the growing islands. Evidence for the existence of such a layer is given by the metastable stripe-phase with $\delta = 1/16$ observed at and above 760 K (see Fig. 2b). Separate measurements of oscillations in the X-ray reflectivity during growth support this interpretation at all temperatures, and suggest the possibility of two- and three-layer stripe-phases with $\delta = 1/16$ below 760 K. To our knowledge, such an evolution among stripe and island phases during growth has not been previously observed, nor theoretically proposed.

No direct evidence has been found at any temperature for the multilayer "bright-star" and trigonal structures, which have been clearly observed by STM [7,8,10,13,14]. This may result, in part, from the short-ranged translational order

exhibited by these structures, making them difficult, although not impossible, to detect with high-resolution X-ray scattering techniques. We believe it is more likely that these structures form from the metastable third layer noted above, and depend on temperature and deposition history. This underlines the importance of conducting growth experiments during adlayer deposition and at fixed temperature.

We conclude by summarizing the observed phase behavior. For coverages between 0 and 1 ML the interface structure is pseudomorphic with $\delta = 0$. Between 1 and 2 ML domains of bilayer stripe-phase form in coexistence with the pseudomorphic domains. Above 2 ML three stable phases coexist, including rotated and unrotated bulk-like Cu(111) islands and a commensurate stripe-phase reconstruction — the latter with a wavevector locked either to $\delta = 1/16$ or 1/18. The development and growth of the bulk islands is a cooperative process, involving temporary loss of translational order in the stripe-phase domains and a metastable, partial third layer. These results clearly point to the importance of competing interactions at the Cu–Ru(0001) interface. In this case, the energy gained by denser Cu packing, whether in the bilayer stripe-phase or in the bulk-like islands, is balanced by the resulting misfit of the Cu and Ru lattices. This leads to the higher-order commensurate states in the reconstruction, and to the small rotation of the islands. Finally, we note that while the phase behavior found for temperatures below about 500 K is qualitatively similar, the observed structures are relatively disordered, with correlation lengths smaller by nearly a factor ten at 300 K.

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