# Strain Relaxation in Hexagonally Close-Packed Metal-Metal Interfaces

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Scanning tunneling microscopy observations on epitaxial Cu/Ru(0001) show the relaxation of (tensile) lattice strain to occur in four different stages with increasing film thickness, from pseudomorphic to unilaterally contracted to (quasi-)isotropically contracted film structures, with decreasing lattice strain and increasing interface energy. The underlying film layers rearrange during growth. Comparison with other data suggests this scheme to be more generally valid for tensile and, with slight modifications, also compressive strain relaxation in hexagonally close-packed metal surfaces and metal-metal interfaces.

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The effects of in-plane stress on surfaces and heteroepitaxial interfaces are well known. For surfaces, the stress arises from the abrupt termination of the bulk crystal, which results in changes of the bond length in the top layers [1]. At epitaxial interfaces, on the other hand, the lattice mismatch of the two materials involved is the primary source of stress [2]. This can be relaxed either by formation of misfit dislocations [3] or by a reconstruction of the respective layer(s), which leads to periodic commensurate or incommensurate interfaces.

In this Letter we report a scheme of tensile strain relaxation at a hexagonal interface, which has been observed by scanning tunneling microscopy (STM) in thin Cu films on Ru(0001). With growing film thickness we find a sequence of different film structures, labeled mode $A$–$D$, which range from a fully strained pseudomorphic lattice (mode $A$) via two partly relaxed structures (modes $B, C$) to an essentially fully relaxed, bulklike Cu overlayer (mode $D$). We find that the transitions between the different phases in metal heteroepitaxy are not limited to a single (topmost) layer, but can simultaneously involve several layers of the growing film. Hence, in the absence of kinetic limitations, significant reordering of the underlying film layers occurs during film growth to allow the structural transformations. Moreover, the increase in atomic density associated with the progressing relaxation also requires substantial mass transport between the successive underlying layers.

The Cu films were grown by thermal evaporation at pressures below $10^{-8}$ Pa, on a Ru(0001) substrate at temperatures between 300 and 660 K. They show a significant nonuniformity, resulting from kinetic limitations on the one side and the tendency toward thermodynamically favored Stranski-Krastanov growth on the other side. Despite the differences in film morphologies observed for different growth conditions we find essentially the same sequence of relaxation modes $A$–$D$, uniquely determined by the local thickness of the film. This indicates that the relaxation modes are energetically favored rather than kinetically induced.

The STM data were recorded after cool down to 300 K, at bias voltages of 5 to 70 mV and tunnel currents between 2.5 and 40 nA. They are shown in a gray-scale representation, with darker areas representing lower regions. On images containing several terraces each level has been allocated its own gray scale, i.e., the height differences between different terraces have been removed in order to more clearly reveal the vertical corrugation patterns.

For a Cu film with a coverage of 1 monolayer (ML), deposited at 300 K and annealed to 500 K, the Cu is observed to be pseudomorphic to the surface [4], in agreement with earlier findings [5–8]. That is, only the atomic corrugation is resolved, with atomic spacings close or identical to those of the substrate [mode $A$, Fig. 1(a)] and no indication of any long-range modulation.

With increasing thickness, the pseudomorphic state becomes energetically unfavorable, and relaxation of the lattice strain occurs. As a consequence, distinctly different corrugation patterns with characteristic in-plane symmetries are observed. The image shown in Fig. 1(b) was recorded on a Cu film with a nominal coverage of 3 ML, deposited at 550 K and annealed to 660 K. On this image we find areas of different thicknesses and film structures. The local thicknesses in this image, from top left to bottom right, are 2, 3, and 4 monolayers, corresponding to structures $B$, $C$, and $D$, respectively.

The well-known uniaxial relaxation mode $B$ [5] consists of double lines running along ⟨120⟩. The pattern has a periodicity of ~43 Å along ⟨100⟩. High-resolution data (Fig. 2) confirm the structural correspondence between this relaxation and that of the reconstructed Au(111) surface [9,10]: Both surfaces exhibit soliton walls separating fcc and hcp stacked regions. In the walls the surface atoms occupy slightly higher bridge sites, which appear brighter in the image. Figure 2 also reveals the lateral displacement of surface atoms along ⟨120⟩ of 0.8 Å, associated with the transition from fcc to hcp sites. The walls thus act as one-dimensional misfit dislocations [5]. For double-layer Cu/Ru(0001) films, 18 Cu (surface) atoms

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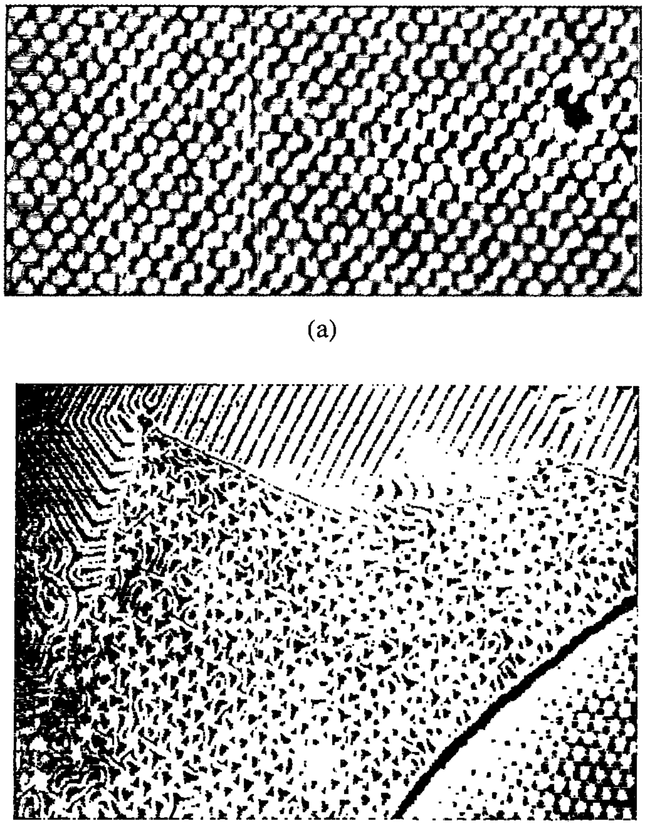

FIG. 1. STM images of two differently thick, annealed Cu films illustrating the corrugation patterns characteristic for the different relaxation modes. (a) Fully strained, pseudomorphic lattice (mode *A*) observed on a 1 ML film (image size 7.7 nm × 40 nm); (b) relaxation of the lattice strain in modes *B* (local thickness 2 ML, top), *C* (local thickness 3 ML, middle), and *D* (local thickness 4 ML, bottom) for thicker films. This image was recorded on a film with a nominal thickness of 3 ML (image size 193 nm × 115 nm).

cover 17 Ru substrate atoms along ⟨100⟩. On average, the film has almost exactly assumed the Cu lattice constant across the double lines, i.e., the lattice strain imposed by the 5.5% misfit between the Cu and Ru lattices is almost completely relaxed along that direction. Along the double lines, however, the lattice is in registry with the Ru(0001) substrate and under tensile stress.

Interestingly, for Cu/Ru(0001) we have never observed any longer range order of the double lines, comparable to the chevronlike "herringbone" pattern formed on Au(111) [10,11]. Instead, large domains of three different orientations are formed. In both arrangements the lattice strain is relaxed more isotropically on a large scale [12]. On a local scale, however, it is relaxed in one direction only—along the double lines the elastic strain is still present.

For Cu films with a height of three layers a characteristic isotropic pattern (mode *C*) is observed, consisting of corrugation lines in a triangular arrangement [Figs. 1(b) and 3]. The occurrence of U-shaped double-line terminations similar to those observed on Au(111) [10], or even of double-line pairs at the corners of some triangles (Fig. 3, arrow), indicates that there is a close relation between these corrugation lines and those in the double-layer Cu film. That assignment is further corroborated by atomic resolution data (not shown). Hence these lines also represent domain boundaries separating areas with fcc and hcp stacking. Similar to the unilaterally relaxed mode *B* structure the fraction of the surface occupied by the two stacking types differs, again signifying a different stability of the two stacking types. In this case, however, the domain boundaries intersect, forming protruding stars with Cu atoms in on-top positions at the intersection. The energetic costs for these stars must be sufficiently low to make these structures more favorable than the striped mode *B* phase, where domain boundaries do

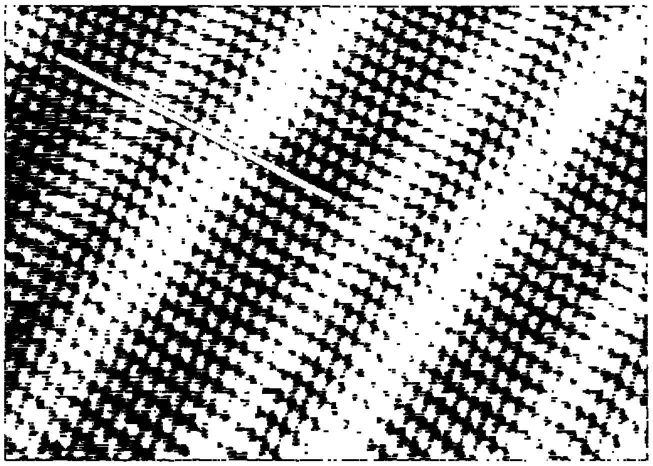

FIG. 2. High-resolution STM image (9.5 nm × 6.5 nm) of the unilaterally contracted "striped" phase (mode *B*), with double-line misfit dislocation, on a 2 ML film (⟨100⟩ is marked).

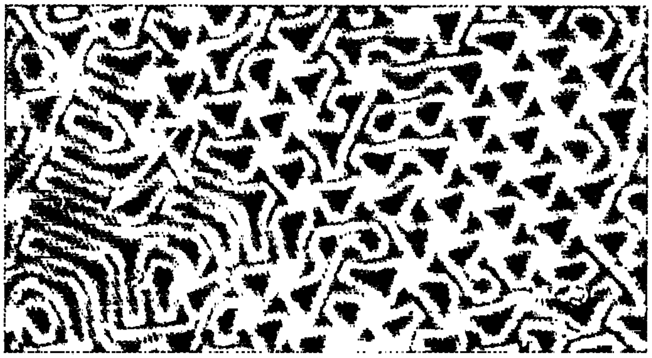

FIG. 3. STM image of the two-dimensional triangular relaxation mode (mode *C*, Cu thickness 3 ML). At the "white stars" the atoms occupy on-top sites at the interface; the arrow marks small double lines in the pattern similar to those in the mode *B* structure of a 2 ML film, indicating that the white corrugation lines have the same origin as the double lines in the latter structure, i.e., the atoms locally occupy bridge sites (image size 70 nm × 40 nm).

not intersect. Networks of similar type were reported previously to form on alkali-covered Au(111) surfaces [12], and the characteristic protrusions were also observed, as minority defect species, on clean Au(111) [10] and on Pt(111) during homoepitaxy [13].

The threefold symmetry of the corrugation pattern is clear proof that the unilateral lattice contraction observed for a two-layer film has been removed. A corrugation pattern of threefold symmetry cannot be formed by stacking an isotropically contracted Cu layer (threefold symmetry) on top of the unilaterally contracted two-layer film (twofold local symmetry). Hence the structure of the underlying two-layer film has been changed by—and during—the deposition of the third layer. If we exclude a rearrangement of the Ru substrate lattice, this can be achieved by different ways of film restructuring: (i) by forming a triangular type second layer on a pseudomorphic first Cu layer, (ii) by a rearrangement of both underlying Cu layers leading to a structure transition located at the Cu-Ru(0001) interface, (iii) by forming a pseudomorphic double layer with a triangular third layer on top, and (iv) by partial strain relaxation in two or more structural transitions. Since the double-layer film already shows partial strain relief, it is not reasonable that the third layer would induce it to become pseudomorphic. Instead the third layer tends to reduce the relative influence of the substrate and allows more strain relief in all layers, which rules out possibility (iii). The last possibility also appears to be energetically less favorable, leaving (i) and (ii) as the most feasible structures. A definite decision between (i) and (ii), i.e., whether the structure transition occurs at the Cu-Ru(0001) interface or between a pseudomorphic first Cu layer and the partly relaxed second Cu layer, is not possible on the basis of the present data.

The average relaxation of the Cu lattice in mode *C* (periodicity ~61 Å, average nearest neighbor distance 2.61 Å) amounts to 3.7% relative to the Ru(0001) substrate, leaving the Cu lattice expanded by 1.9% in average in comparison with Cu(111). There is still some in-plane stress present in the film. In addition, there are still significant local distortions in the Cu lattice. The in-plane stress must vanish completely as the film thickness further increases. Ultimately, the overlayer is expected to become bulklike, at the expense of forming an (in)commensurate internal interface. Indeed, for thicknesses in excess of three layers the Cu film surface shows the quasihexagonal corrugation pattern of such an interface (Fig. 4, local thickness 4 ML). The periodicity of 49 Å agrees perfectly with the Cu-Ru lattice mismatch of 5.5%, i.e., the Cu overlayer lattice has practically assumed its bulk lattice constant. A similar result has been obtained in an earlier low energy electron diffraction study [6]. The structure in the STM image is practically identical with the moiré pattern expected from a hard-sphere model, including a rotation of the Cu(111) lattice with respect to the Ru(0001) substrate by ~1°. Similarly, as for the three-layer film, the underlying film has to rearrange during deposition of the fourth layer to induce this corrugation pattern. Even for these thick films the corrugation, which again must originate at a depth of several layers, is evident on the surface. Thus, the film lattice undergoes out-of-plane distortions as a consequence of the relaxation at the interface.

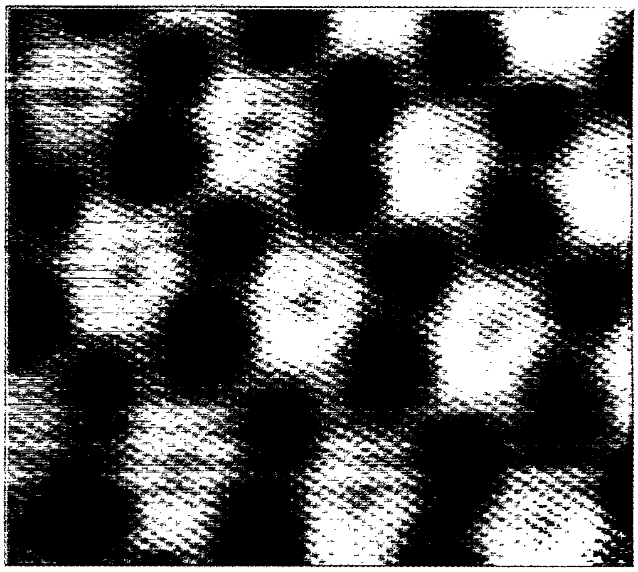

FIG. 4. Atomic-resolution STM image (17.2 nm × 14.1 nm) of the fully relaxed, quasihexagonal structure of a film with 4 ML (local) thickness (mode *D*), forming an (in)commensurate interface with the substrate. The Cu(111) overlayer has the Cu bulk lattice constant and is slightly rotated (1°) with respect to the substrate.

These observations can be rationalized within the description of strain relaxation put forward by Frank and van der Merwe [3], where the film structure is described as a subtle balance between the strain energy required for elastic distortion of the overlayer to match the substrate and the interface energy associated with forming a relaxed, nonpseudomorphic interface. The structure of the respective Cu films, for different local thicknesses, the dimensionality of the in-plane contraction, and, qualitatively, the amount of lattice distortions and interface energies are compiled in Table I. The elastic strain energy increases proportionally with the thickness of the film. For very small thicknesses, e.g., for monolayer films, the elastic energy is often smaller than the energy required for forming a relaxed interface, and a pseudomorphic film structure results. For very large thicknesses, the energy associated with in-plane distortions becomes very high and complete relaxation of the strain must occur, even if that requires the formation of an energetically unfavorable, internal (in)commensurate interface (*D*). In the two intermediate modes *B* and *C*, with periodic misfit dislocations in one or two dimensions, the interfaces are lower in energy than the commensurate interface *D*, while the film lattices still contain significant residual elastic distortions.

The subtle balance between the interface energy and the elastic strain energy thus successively stabilizes a series

TABLE I. Compilation of the different modes for strain accommodation, showing the (local) Cu film thickness of their occurrence, their dimensionality, and, qualitatively, the amount of lattice distortion upon relaxation and interface energy.

| Mode | (Local) Cu film thickness (ML) | Dimension of relaxation | Lattice distortion | Interface energy |
|---|---|---|---|---|
| *A* | 1 | ··· | + + + | ··· |
| *B* | 2 | 1 | ++ | + |
| *C* | 3 | 2 | + | ++ |
| *D* | >3 | 2, isotropic | ··· | + + + |

of different interface structures. As the thickness and therefore the strain energy associated with in-plane lattice distortion increases, the structures contain successively decreasing residual in-plane distortions: for strain (mode *A*) → one-dimensional relaxation (mode *B*) → triangular isotropic relaxation with appreciable residual strain (mode *C*) → isotropic relaxation with virtually no in-plane strain (mode *D*). On the other hand, these structures occur at the expense of the formation of interfaces with increasing energy cost.

Such a sequence of structures describes a framework which appears to be generally applicable to metal epitaxy on hexagonal surfaces. Examples of this scheme have been observed for other epitaxial systems with negative [14] and, with slight modifications, also with positive misfit [15,16]. Omission of structures of this sequence with increasing film thickness, which is frequently observed, can be understood within this general picture as a consequence of the layer dependent, relative sizes of the intralayer interactions and the corrugation of the interface potential. For example, for Co and Ni, which have a −7.2% and a −7.8% mismatch with Ru(0001), respectively, the pseudomorphic structure of the monolayer film (mode *A*) turns directly into isotropically contracted structures (mode *D*) for double-layer and thicker films, signifying a larger reduction in the corrugation of the interface potential as compared to Cu/Ru(0001) [14,17].

For systems with a positive misfit the situation is slightly different in that the steeply increasing repulsive Morse potential more effectively prevents the film from compression. For Au/Ru(0001) with a +6.25% misfit, e.g., the hard core repulsions within the adlayer are such that a pseudomorphic structure is not even possible in the monolayer film. Instead this shows a unilateral (expansive) relaxation (= mode *B*), followed by an isotropically relaxed, triangular structure (= mode *C*) for the double-layer film and an isotropic, uniformly relaxed structure for local film thicknesses in excess of two layers [15]. In the case of Ag/Pt(111) [16], on the other hand, the corrugation of the Ag adsorption potential is sufficient to force the monolayer film into a pseudomorphic structure, which is compressed by 8.9% with respect to Ag(111). The bilayer film then assumes a (metastable) unilaterally expanded structure (= mode *B*) after deposition at room temperature, which transforms into a triangular phase upon annealing.

The effect of modifying the relative sizes of intralayer interactions and interface potential corrugation can, e.g., be observed in the case of Au(111). This surface is known to reconstruct into a mode *B* structure with a 4% contraction of the topmost layer. In the presence of a dilute, mobile alkali adlayer the Au surface layer transforms into mode *C* [12].

In conclusion, based on STM characterization of growing Cu films on a Ru(0001) substrate we have deduced a scheme for the relaxation of (tensile) lattice strain, which agrees with other available experimental data and provides a consistent picture for strain relaxation in close-packed hexagonal metal surfaces and metal-metal interfaces. The structural transformations of the film often require a rearrangement of existing film layers during growth of the next layer.

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