Strain Relief at Metal Interfaces with Square Symmetry

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We report a novel mechanism, *internal (111) faceting*, of strain relief at heterointerfaces with square symmetry. The mechanism has been revealed for thin Cu films on Ni(100) by scanning tunneling microscopy. In the first monolayer monatomic chains of Cu atoms are shifting laterally by $1/\sqrt{8}$ lattice constant along $\langle 110 \rangle$ and thereby protrude from the surface layer. With each Cu layer added, the protrusion stripes grow in width by one atom, forming internal $\{111\}$ facets in the Cu film. This picture is in marked contrast to the widely accepted continuum theory of epitaxial growth, which predicts a pseudomorphic film growth up to a critical thickness of 8 monolayers.

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The lattice mismatch between film and substrate material in heteroepitaxial growth leads to strain in the film until the film has adopted its bulk geometry through introduction of strain relieving defects. It is important to understand this strain relief, since the defects influence the morphology and the physical properties of the film. In the widely accepted classical "Matthews picture" the adlayer is thought to remain locked to the substrate up to a finite critical thickness h_c [1–5]. For $h \leq h_c$ the film grows essentially pseudomorphic. For a thickness $h > h_c$ strain is relieved by means of misfit dislocations and associated lattice relaxation. The critical thickness is determined by the elastic constants of both materials and their actual misfit (m). For typical metal-metal systems h_c is found to vary from below 1 Å ($|m| > 10\%$) up to 10–200 Å for small misfits ($|m| \leq 2\%$) [2].

This concept is a continuum model ignoring atomic details of the interface structure. Indeed, it has recently been found to fail in the description of hexagonal close-packed metal interfaces [6–9]. This failure is related to the particular structure of fcc (111) surfaces with fcc and hcp sites of similar adsorption energy. Strain here can easily be accommodated by the introduction of fcc-hcp stacking faults (domain walls). The low energy cost for the formation of misfit dislocations essentially drops h_c to zero or just to the first monolayer [6–9]. On the other hand, the fcc-hcp stacking fault mechanism is symmetrically impossible at square interfaces. For these interfaces many experimental studies have been reported which seem to be in agreement with predictions of the Matthews picture [10]; in particular, an Auger electron diffraction study of Cu growth on Ni(100) seemed to provide quantitative support of the continuum model [11].

In this Letter we demonstrate that at interfaces with square symmetry the scenario of strain relaxation is also more complex than suggested by the simple continuum model and has to account for atomistic details. For Cu films on Ni(100) (compressive strain $m = -2.6\%$) we demonstrate by scanning tunneling microscopy (STM) that beginning from the first monolayer strain is relieved via lateral relaxation of atoms before at about 20 monolayers (ML) bulk dislocations nucleate.

The Cu growth on Ni(100) has been characterized by variable temperature STM; details of the experimental setup have been described in Ref. [12]. The nickel crystal was prepared by Ar^+ ion sputtering and subsequent annealing to 1200 K. The copper films have been grown by thermal evaporation at a background pressure better than 5×10^{-10} mbar and deposition rates of 10^{-3}–10^{-2} ML/s. Sample temperatures during deposition were between 200 and 400 K, i.e., well below the onset of alloying. Some of the STM images have been measured in differential mode, which means that the derivative of the lines of constant tunnel current has been recorded.

The growth of Cu layers on Ni(100) at 350 K is characterized in Figs. 1 and 2. Figure 1(a) shows a Cu film of coverage 0.36 ML; already at this coverage large islands have nucleated and grown on the Ni terraces. A long protruding stripe appearing in the central large island attracts particular attention. The stripe protrudes by about 0.6 Å, has a width of ~6 Å (which is the typical STM-imaging width of a single atom [13]), and traverses the entire island. There is a minimum island size for the formation of stripes which turns out to be of the order of 60–80 Å. Once the islands reach this size there is a high probability for stripes to form. When the first monolayer is filled [Figs. 1(b) and 1(c)], the whole surface is covered by a stripe pattern. The stripes have all the same width and are all running along $\langle 110 \rangle$ with an equal probability for the two orthogonal domains. This pattern is maintained up to coverages of about 20 ML as shown in Fig. 2. Only the width of the stripes grows linearly with the coverage. The density of stripes and their average length, on the other hand, remain constant in this coverage range. There is a further important feature of the stripe pattern. We never observe that the stripes cross each other or coalesce, as demonstrated in all STM images in Figs. 1 and 2.

In the following we discuss a simple model which accounts for the experimental observations. It is motivated by the fact that the compressive strain at the fcc (100)

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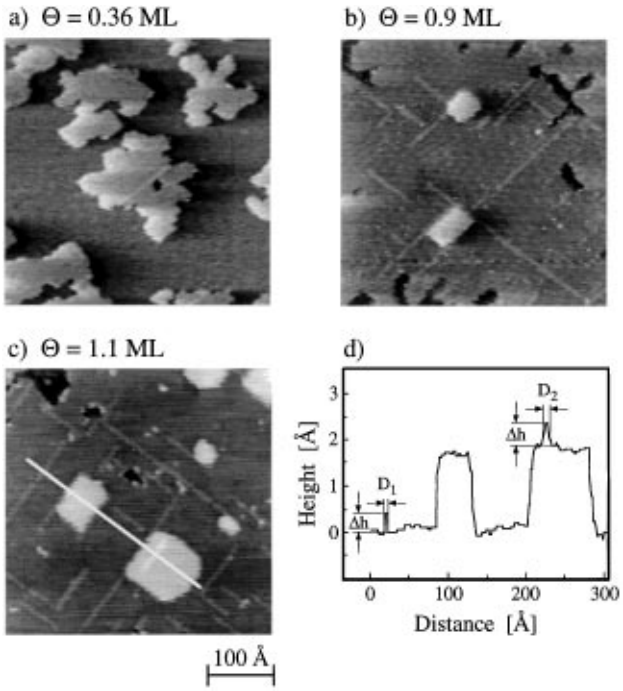

FIG. 1. The growth of Cu on Ni(100) up to completion of the first monolayer. The substrate temperature was 350 K and the deposition rate was 1.5×10^{-3} ML/s. (a) $\Theta = 0.36$ ML, (b) $\Theta = 0.9$ ML, (c) $\Theta = 1.1$ ML, and (d) STM line scan indicated in (c).

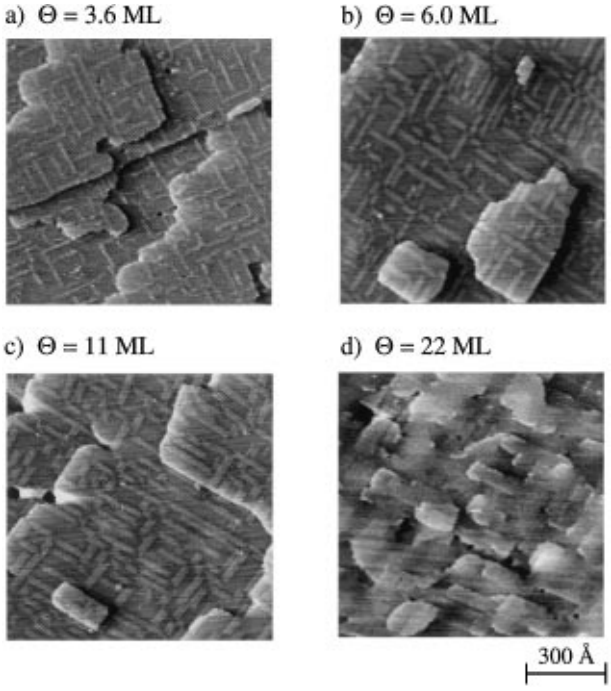

FIG. 2. The growth of Cu multilayer films on Ni(100). The substrate temperature was 350 K and the deposition rate was 1.5×10^{-3} ML/s for $\Theta = 3.6$ ML (a) and $\Theta = 6.0$ ML (b), and 3×10^{-3} ML/s for $\Theta = 11$ ML (c) and $\Theta = 22$ ML(d), respectively.

surface is highest in the close-packed ⟨110⟩ direction. Therefore, intuitively it could be expected that chains of atoms are squeezed out from the adlayer and create protruding stripes. Because of the square symmetry, these stripes have to form with equal probability in both ⟨110⟩ directions, perpendicular and parallel to the substrate step edges. The simplest way to generate such stripes is to shift Cu atoms from their fourfold hollow site to the twofold bridge site (see Fig. 3, coverage 1 ML). Such a bridge site atom has a reduced number of nearest neighbors in the substrate, but it gains binding energy in the adlayer. There are two nearest neighbors below and, in addition, four lateral neighbors with a binding length which is only about 10% larger. More importantly the protruding atoms gain lateral freedom of expansion and the film can partially relieve its strain. Obviously this lateral freedom of expansion is overbalancing the lowered binding energy.

Figure 3 shows the model for the generation and the growth of the protruding stripes up to a coverage of 3 ML. The height Δh is constant for all coverages. Considering the simplest case of a hard sphere model, one obtains $\Delta h = 0.4$ Å for the growth of Cu on Ni. The width D depends on the coverage; i.e., for 1 ML the stripes are exactly one atom wide, for 2 ML two atoms, and so on. The atoms filling the stripes (light colored) are relaxed, while the atoms between the stripes which are situated at the hollow sites (dark colored atoms) are essentially pseudomorphic as we discuss later. In our model the density of the stripes and their length distribution is determined by the monolayer configuration. The subsequent growth stabilizes the pattern of stripes by the creation of internal {111} facets along the stripes and {110} facets at both ends. This is energetically favorable because the strain relaxation takes place by the formation of the highly stable close-packed {111} facets.

The *internal (111) faceting* model [14] is in quantitative agreement with our experimental observations. This is demonstrated in Fig. 4 summarizing the quantitative data analysis of the stripe pattern as a function of film thickness. The first graph shows clearly that the height of the stripes is constant for all coverages. The height Δh was found to be 0.6 ± 0.1 Å, which is in fair agreement with the simple hard sphere model ($\Delta h = 0.4$ Å) [15]. The linear dependency of the width of the stripes on the coverage is demonstrated in the second graph of Fig. 4. The horizontal lines indicate the stepwise growth of the width D as expected from our model. This behavior is also evident in the STM line scan shown in Fig. 1(d). In crossing a step edge, going from one Cu monolayer to the second Cu layer, it is observed that the stripes are exactly one atom wider on the bilayer than on the monolayer. It should be noticed that we have plotted corrected stripe widths in Fig. 4, taking into account the finite imaging width of the STM tip [13].

Above monolayer coverage the density of stripes is constant, $(8.0 \pm 1.4) \times 10^{-4}$ per substrate atom, independent of film thickness. In the submonolayer range a critical island size for formation of stripes exists which is of the order of 60–80 Å corresponding to about 30 atomic dis-

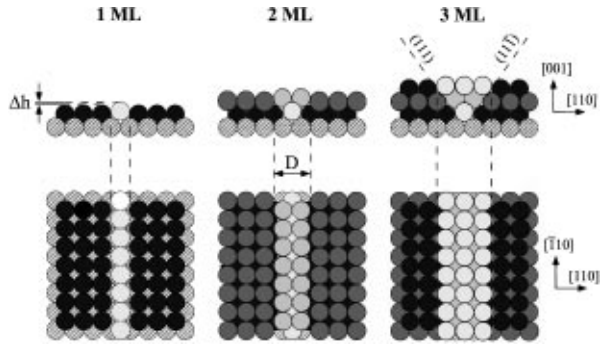

FIG. 3. The *internal (111) faceting* model describing the appearance of the protruding stripes at the Cu/Ni(100) interface. The figure shows the side view and the top view for the coverages of 1, 2, and 3 ML. The shaded circles represent the substrate atoms (Ni). The "dark atoms" (Cu) are placed at the four-fold hollow sites in the pseudomorphic geometry. The "light atoms" (Cu) form the stripes and are placed at the two-fold bridge sites in the first layer. As indicated for the coverage of 3 ML, {111} facets are formed along the stripes.

tances. The first islands reach this size at coverages of ~0.25 ML. With increasing coverage more and more islands attain the critical size and more stripes are formed, finally saturating at monolayer coverage. We may speculate that above the critical size relaxation at the island step edges is no longer sufficient for the strain release of the pseudomorphic islands, and Cu chains are squeezed out of the adlayer.

An important experimental observation is the fact that stripes neither cross nor coalesce at all coverages below 20 ML. This behavior is easy to understand in the internal faceting model. There are two domains of bridge sites on the square fcc (100) surface depending on the direction of the stripes. At their potential junction, two orthogonal stripes are always separated by $1/\sqrt{8}$ of a lattice constant (i.e., $1/2$ nearest neighbor distance) rendering crossing impossible. Coalescence is also unlikely as the distance between two parallel stripes is given by the lattice constant of the Ni substrate and the merging of two stripes would block further transverse relaxation. Therefore, at higher coverages one can find neighboring parallel stripes which have a smaller width than the other stripes at the same image (not shown here). Only at high coverages close to 20 ML, where almost all of the surface is covered by relaxed stripes, neighboring as well as orthogonal stripes merge and thereby form bulk dislocations [see Fig. 2(d)].

The density of the stripes, their mean length, and the exponential length distribution do not markedly vary by the change of the deposition rate (10^{-3}–10^{-2} ML/s), substrate temperature (200–400 K), coverage (1–17 ML), or film annealing up to 900 K. These quantities seem to be of universal character. Therefore, we conclude that the network of stripes is determined by the strain due to the lattice mismatch and not by the growth kinetics.

In Fig. 5 the internal (111) faceting model is compared to the experimental data of Chambers *et al.* [11].

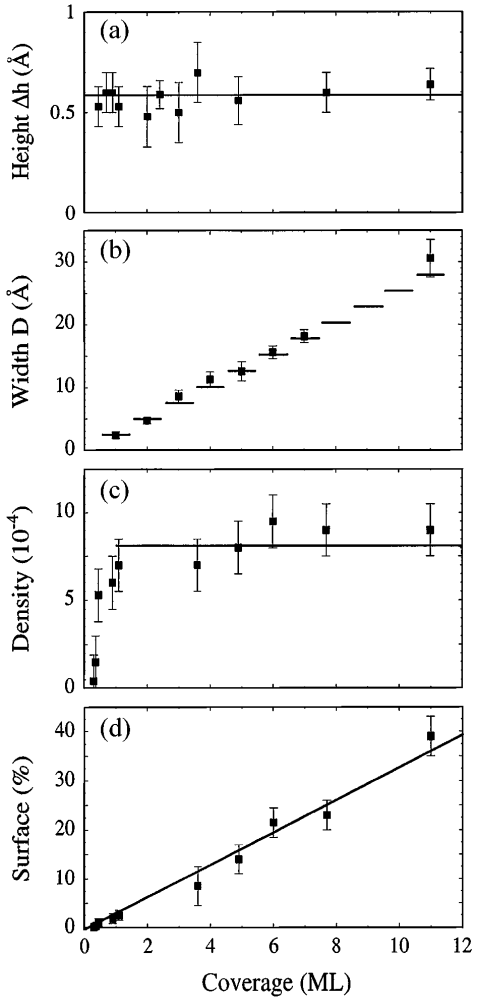

FIG. 4. Quantitative analysis of the pattern of protruding stripes observed on Cu/Ni(100). Plotted are the height Δh (a), width D (b), density of stripes (c), as well as the total surface area covered by stripes (d); all quantities as a function of Cu coverage.

These authors had studied the growth of thin Cu films on Ni(100) by Auger electron diffraction (AED) and compared their data with the predictions of the continuum model of Matthews and Crawford [4] (thin solid line). The continuum model predicts a critical thickness of $h_c = 14.8$ Å ≈ 8 ML. Up to this thickness Cu should grow pseudomorphic. Only at coverages above 8 ML the film should relax its strain spontaneously by the formation of bulk dislocations. Chambers *et al.* interpreted their experimental data as confirmation of the continuum model.

Figure 5 shows clearly that the AED data are much better described by the *internal (111) faceting* model than by the continuum model. Using the *internal faceting* model and the STM data we have calculated the mean values of the transverse lattice expansion. The fraction of the relaxed stripe volume is determined by adding up the stripe coverage in the individual layers as determined by the measurements shown in Fig. 4(d). The relative weight of the individual layers for the AED experiment has been

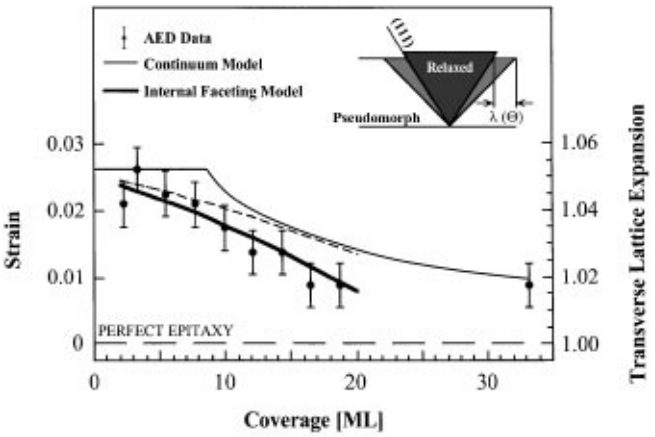

FIG. 5. Comparison of the *internal (111) faceting* model (thick solid and dashed line) and the continuum model of Matthews and Crawford [4] (thin solid line) with the Auger electron diffraction data of Chambers *et al.* [11] (filled circles). Dashed line—only copper in the stripes is fully relaxed. Thick solid line—copper in the stripes and close to the stripe boundary relaxed ($\lambda = 0.2\Theta$).

accounted for by the simple ansatz $I = I_0 \exp(-\Theta/\Theta_0)$ using an attenuation factor of $\Theta_0 = 7$ ML. Assuming the stripe atoms are fully relaxed and the copper between the stripes is pseudomorphically grown, one obtains the dashed line in Fig. 5. However, it is likely that the copper close to the stripe boundary is not perfectly pseudomorphic but partially relaxed. It is reasonable to assume (see the inset in Fig. 5) that the additional relaxation at the stripe boundary, $\lambda(\Theta)$, depends linearly on the coverage. With $\lambda(\Theta) = 0.2\Theta$ (in atomic distances), we obtain the thick solid line in Fig. 5 which is in excellent agreement with the data of Chambers *et al.* This implies that most of the copper between the stripes is pseudomorphic and the film relieves its strain gradually in a layer-by-layer fashion.

It is noteworthy that our model also explains the moiré fringes seen many years ago in transmission electron micrograph images of Cu films on Ni(100) [16] that until now were not understood [11]. The copper in the stripes is relaxed while the surrounding Cu matrix is essentially pseudomorphic with the Ni substrate. This difference in lattice structure between relaxed Cu on one hand and pseudomorphic Cu and Ni substrate, on the other hand, naturally explains the appearance of moiré fringes in the transmission electron microscopy (TEM) images [17].

Finally, we want to point out that the stripe pattern at the surface substantially influences the nucleation and thus the growth mode of the Cu film. The protruding stripes act as diffusion barriers and heterogeneous nucleation centers [18]. This is evident in Figs. 1(b) and 1(c). The islands in the second monolayer nucleate preferentially at stripes and have a more regular shape compared with the islands in the first monolayer. In particular, the enhanced nucleation density is responsible for the almost perfect layer-by-layer growth up to 20 ML [19].

In conclusion, we have shown that the relaxation of lattice strain at interfaces with square symmetry can be much more complex than expected. The continuum approach completely fails to describe the strain relief scenario at the Cu/Ni(100) surface. We are convinced that this failure is not the exception [20]. Atomic scale surface probes like STM give unprecedented microscopic insights in growth phenomena as shown here and will continue to provide unexpected results. Atomistic details need to be considered in appropriate modeling of interfacial structures.

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