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Observation of an adlayer-driven substrate reconstruction in Cu-Pt(111)

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An unusual strain relaxation mechanism has been observed during the growth of ultrathin Cu films on Pt(111) at a substrate temperature of 450 K. After the completion of a pseudomorphic first Cu monolayer, the Pt substrate undergoes a reconstruction which is visible in the pseudomorphic Cu overlayer. Using *in situ* helium atom scattering, interlayer mass transport is observed as ad-atoms are incorporated into the substrate. Scanning tunneling microscopy measurements allow us to label the substrate reconstruction as being similar in nature to the ''star'' network of the reconstructed Pt(111) surface. [S0163-1829(98)52840-8]

Heteroepitaxial growth in systems without an exact lattice match gives rise to strain in the growing film. The magnitude of the strain increases in proportion to the number of layers in the film and ultimately, it determines the maximum thickness of a pseudomorphic structure. A number of mechanisms for strain relief in metal-film growth have been observed recently (see, for instance, Refs. 1 and 2). Dislocation networks and/or reconstructions have been seen in thin growing films, while thicker films often exist as floating overlayers with isotropic relaxation. These observations broadly agree with the expectations from early theoretical models,[3,4] which assume a rigid substrate. The present work explores heteroepitaxial growth on a substrate that is intrinsically less rigid. In particular, the free surface of Pt(111) is subject to a significant tensile stress[5] and shows a tendency to reconstruct.[6] Both theory and experiment draw a direct connection between stress at the free surface and the tendency to reconstruct.[5,6] Our results show an unusual mechanism for strain relief during the growth of copper on a Pt(111) surface. We argue that one of the effects of lattice strain in this epitaxial system is to induce a reconstruction in the substrate.

The experimental work used scanning tunneling microscopy (STM) and helium atom scattering (HAS), which provide information, respectively, on the microscopic structures, *ex situ*; and the *in situ* evolution of the growth. The STM and HAS measurements were performed in two separate UHV systems both with background pressures of less than 2×10^{-10} mbar.

The same Pt(111) crystal with a miscut of less than 0.2° was used in all experiments. For the STM measurements, the sample was cleaned using cycles of argon sputtering at 800 K, annealing at 1100 K, and annealing at 800 K in 1×10^{-6} mbar oxygen atmosphere. A final flash to 1250 K removed the residual oxygen. For the HAS measurements the sample was heated by electron bombardment, and the sputtering temperature was limited to 520 K making slightly longer annealing cycles necessary. Both of the cleaning procedures where judged to result in the same quality of the crystal surface. All STM measurements presented in this paper were performed at room temperature using a home built beetle type STM.[7] The Cu evaporator and the STM were mounted in the same vacuum chamber. Images presented were recorded at tunneling currents of 1 nA and at bias voltages between 0.3 and 0.6 V. The helium scattering measurements were carried out with a 70 meV helium beam produced by supersonic expansion (2% energy resolution) and a spot size of 1 mm^2 on the sample. Experiments were performed with the beam incident at a Cu-Bragg angle so that the variation in the specularly scattered helium intensity during deposition is due to diffuse scattering from step edges and point defects.[8] The scattering geometry and beam temperature were identical for all experiments. A differentially pumped quadrupole mass spectrometer was used to detect the scattered helium atoms. The angular resolution of the system is 0.4°. The deposition rate was typically about 0.01 ML/s with respect to the Pt(111) surface density.

An overview of the different stages of growth is obtained from Fig. 1, which shows the specular He intensity monitored during Cu growth at 450 K. We identify three main regimes, separated on Fig. 1 by points A and B. In the first stage, up to point A, the intensity falls slightly before returning to its initial value at A. This weak oscillation can be related to the step edge roughening during the growth of the first Cu layer. At point A, where the intensity returns approximately to the initial value, the first layer is complete. STM images (not shown) confirm that the growth is pseudomorphic and the first monolayer is complete at point A. These conclusions are in agreement with previous low-energy electron diffraction (LEED) data.[9,10] The behavior up to point A is shown enlarged in the inset of Fig. 1. The period of the oscillation allows the deposition scale to be determined to an accuracy of better than $\pm5\%$. The second stage of growth lies between points A and B. It is characterized by the formation of a threefold strain relief dislocation network and the growth is not in equilibrium on the time scale of the experiment. At the completion of the second monolayer, point B, both STM and helium diffraction show that the dislocation network is fully developed. Experiments, between points A and B, show that when the growth is interrupted some structural relaxation can occur. These structural changes are kinetically limited on the time scale of the experiment. The final stage of growth, after point B, returns

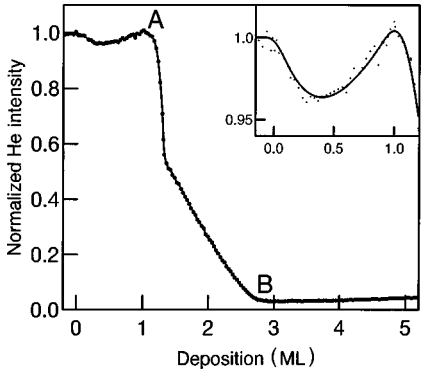

FIG. 1. Specular helium intensity as a function of Cu deposition. The substrate temperature was 450 K. The inset shows an expanded view of the behavior up to point A, where the first monolayer completes. The sudden change in slope at this point has been used to calibrate the horizontal time axis in units of Pt monolayers.

to equilibrium, in the sense that interrupting the growth does not lead to further relaxation. Kinetically limited growth is only observed between points A and B. In the ''thick-film'' regime, after point B, the kinetics increasingly resemble those of homoepitaxial growth on Cu(111).[11,12] Growth occurs by step flow and the He intensity rises as the corrugation from the dislocation network is buried and an incommensurate overlayer is created.

The main emphasis of the present work is to discuss the behavior between points A and B and, in particular, to argue that the mechanisms occurring during the kinetically limited region of growth include a reconstruction of the Pt(111) substrate. Figure 2 shows the results of experiments where the growth is interrupted at various points, with the sample temperature maintained at 450 K throughout. The dashed curve shows the time dependence during the growth stage (as in Fig. 1) and the full curves show the time dependence of the specular helium intensity after growth is interrupted.

Before point A and after point B there is no change in intensity when the growth is interrupted; the growth occurs in quasiequilibrium. Between A and B the intensity varies after the growth is interrupted. The behavior is similar in all cases and corresponds to reordering, which gives an initial,

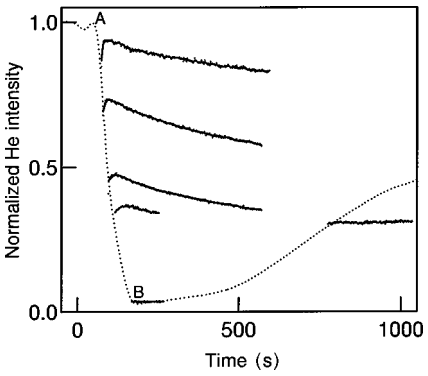

FIG. 2. Change in specular He intensity as a function of time after interruption of growth at various depositions. The dotted curve shows the intensity change during uptake (Fig. 1 and the full lines show the intensity variation following interruption of growth at approximately 1.1, 1.2, 1.5, 1.6, 2.5, and 12 ML). The substrate temperature was held at 450 K throughout the experiment.

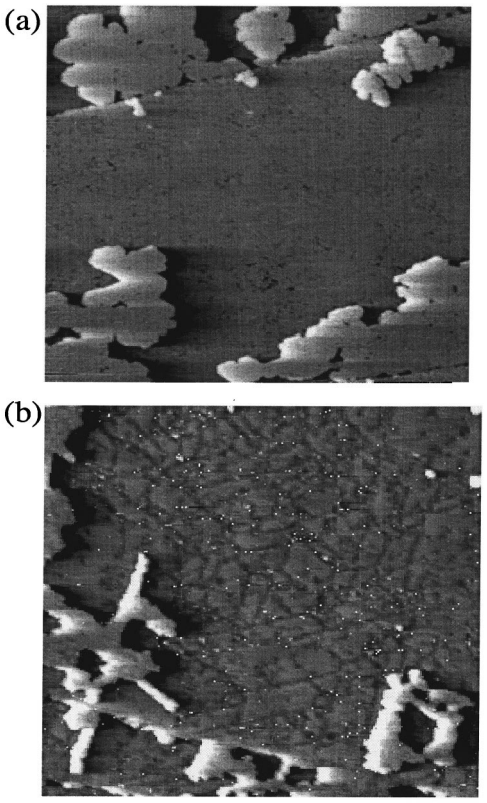

FIG. 3. (a) STM image, 1440 Å$\times$1440 Å, taken after approximately 1.3-ML Cu deposition at a sample temperature of 450 K. After deposition the sample temperature was cooled to room temperature as quickly as possible. (b) STM image for a similar deposition to (a). The position on the sample is slightly different, but the image area is similar. For this experiment the sample was held at 450 K for 210 s after the growth was interrupted, before it was cooled to room temperature. There are clear differences in the morphology of the second-layer islands (the bright regions) in (a) and (b), furthermore the first Cu layer in (b) exhibits dark lines which are attributed to the onset of a reconstruction in the substrate. Islands of the second Cu-layer in (b) have a fragmentary structure which is directly related to the alignment of the dark lines in the first layer.

rapid rise in intensity, taking a few seconds, followed by a much slower decrease. The observation of kinetic limitation indicates that new and slower mechanisms of mass-transport are active in the narrow window between A and B.

It was not possible to investigate all points of the reordering using *ex situ* STM; however, two important stages have been identified by experiments where growth was interrupted and the sample maintained at 450 K for specified times before quenching to the observation temperature of 300 K. Figure 3 shows STM images following growth of approximately 1.3–1.4 ML. Second layer islands are the brighter regions in these figures. For Fig. 3(a), the sample was quenched immediately. The time taken for this process corresponds roughly to that of the respective intensity maxima after growth interruption shown in Fig. 2. Figure 3(b) shows results for a delay of 210 s before the sample was quenched. A comparison of Figs. 3(a) and 3(b) shows a significant change in the island morphology. Initially the islands, which are the second growing layer, are compact and rounded, Fig. 3(a). They

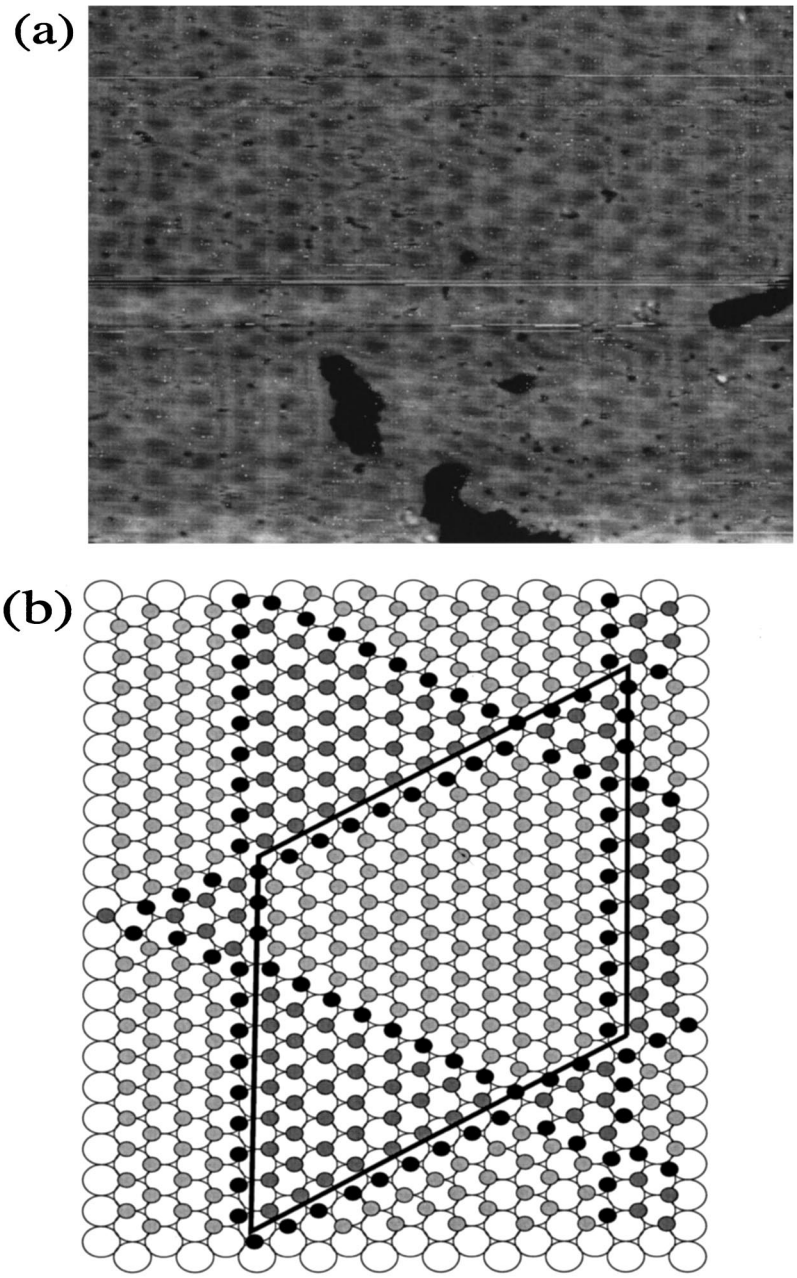

FIG. 4. (a) STM image, 480 Å$\times$480 Å, of the surface close to point B in Fig. 1, where the second monolayer completes. This image shows the threefold network of domain boundaries arising from a reconstruction of the Cu overlayers. The surface orientation is $[\bar{1},1,0]$ upwards and $[1,1,\bar{2}]$ right. (b) Atomic model for the threefold network of domain boundaries imaged in (a). The surface orientation is similar. Open circles represent underlayer atoms in a hexagonal structure. Filled circles represent atoms on high-density domain boundaries. These atoms are more nearly twofold coordinated with substrate atoms and are imaged as bright lines in (a). The two kinds of shaded circles represent threefold coordinated atoms: light shading predominates and corresponds to fcc coordinated atoms; darker shading represents hcp coordinated atoms.

develop into more fragmentary structures with fine linear protrusions and bridges, Fig. 3(b). Also the area occupied by the islands in the final state is significantly less than in the initial state, Fig. 3(a). This last observation, in conjunction with the notion that new mechanisms of mass transport have opened up, suggests that atoms are being transferred from the surface layer to lower layers in the system.

The other new feature which has developed on the surface shown in Fig. 3(b) is the darker lines in the first Cu layer. The lines have a width of 24 ± 2 Å and are 0.3 ± 0.1 Å deep. They intersect at 60° and 120° angles and are oriented along the directions $[\bar{1},\bar{1},2]$,$[\bar{1},2,\bar{1}]$,$[2,\bar{1},\bar{1}]$. We attribute these darker lines to the onset of a reconstruction in the Pt substrate, rather than some feature in the exposed Cu layer, for the following reasons. We have shown the lines are associated with an increase in density in the lower layers as adatoms are removed from second-layer islands. An increase in density of the first Cu layer implies, however, that some Cu atoms would have to occupy sites higher than the ideal layer spacing. Thus, a simple topograph would indicate bright regions, as observed, for example, in the double-line reconstruction of (111) surfaces of the $5d$ metals Pt and Au.[6,13,14] Since we observe dark lines in the first Cu layer, the Cu atoms in the first layer cannot be occupying higher sites. It follows that the reconstruction must be in a lower layer; that is, in the Pt substrate. The dark features we observe presumably arise from spectroscopic rather than topographic effect.[15,16] The fact that the lateral extent of the dark features and the crystallographic orientations correspond with those observed in the reconstruction of a free Pt(111) surface[6] supports the idea that the reconstruction in the present case has a similar structural basis. Apart from the dark lines indicating the substrate reconstruction, the image of the first copper layer is featureless and we conclude that, at this stage, it remains pseudomorphic with respect to the reconstructed substrate.

We now turn to the surface structure at B, in Fig. 1. We identify this point as being close to the completion of the second monolayer. There is an abrupt change in the slope and it is the point at which the specular spot profile in helium diffraction shows a clearly defined threefold structure. Large scale STM images (not shown) indicate that second-layer growth completes before growth of the third layer commences and, at the point of completion, a higher resolution image, Fig. 4(a), shows a surface covered by the threefold network of domain walls. Analysis of the specular peak profile in HAS indicates that the threefold structure has a three fold superlattice with a period of 34.9 ± 0.5 Å, in agreement with the period of 35 ± 2 Å between the domain walls determined from Fig. 4(a). The structure is similar to that observed in growth at 340 K (Ref. 17) and is consistent with high-density domain walls, where atoms occupying bridge sites separate regions of hcp from fcc-coordinated atoms. Figure 4(b) shows an atomic model for the threefold network of domain walls that is consistent with both the STM image, Fig. 4(a), and the helium diffraction spot profile. A similar structure, but with low-density domain walls, has been suggested for the related Ag/Pt(111) system.[2] The density of atoms in the surface follows from the superlattice size and is 9% greater than the underlying hexagonal mesh.

Using the structural model, Fig. 4(b), for the surface at the point where the second monolayer completes, it is possible to compare the surface density of atoms with measurements of the amount of material deposited. The structural model shows, as mentioned before, that a reconstructed overlayer contains 9% more atoms than the substrate. Simple scaling from Fig. 1, using point A as the completion of one pseudomorphic layer, gives 2.77 ± 0.10 ML (weighted mean of several runs) as the amount of Cu deposited up to point B, with respect to the unreconstructed Pt(111) surface. We can demonstrate that mass transport into the Pt(111) substrate must have taken place since, if it had not, a maximum excess of 0.18 ML can be accommodated in the reconstructed Cu film (2 layers of 9% greater density). The most likely scenario is one where copper atoms are incorporated in the substrate to facilitate the density increase as the substrate reconstructs.

In summary, the growth of copper on Pt(111) at 450 K commences with a pseudomorphic first layer. In the submonolayer regime, between one and two monolayer, the growth is more complex and involves kinetically slow processes that are linked to a reconstruction of the substrate. The substrate reconstruction, involving incorporation of Cu atoms, is the first stage of strain-relief in the Cu/Pt(111) system. Alloy formation has been reported in Al growth on Pt(111).[18] The one-way mass transport observed in the present work is fundamentally different. The driving force for the substrate reconstruction in the present case is related to the release of strain energy rather than having its origin in entropic factors and/or heats of solution.

Our observation of an adlayer-driven substrate reconstruction gives an insight into the role of tensile stress in the reconstruction of free surfaces. Three effects need to be included in a complete description of surface reconstructions: first, a requirement for shorter bond-lengths in the surface layer; second, an appropriate energy change for incorporating additional atoms into the surface layer; and third, weak interlayer bonding, which allows the disruption of bonds between surface and bulk, as the surface reconstructs.[5] Only the first two energetic factors can be addressed through calculations of surface stress and surface energy.[19] In the present experiments, the tensile stress at the free surface is removed since the outermost Pt atoms are in a bulklike environment, completely surrounded by atoms. Instead, there is a tensile stress applied to the outermost Pt atoms by virtue of the lattice strain in the pseudomorphic copper overlayer. In this respect our observations differ from those of Grütter and Dürig,[14] who observe a reconstruction of the free Pt(111) surface in response to adsorbed Co atoms. Tensile stress is present at the free surfaces of simple and transition metals,[5] yet only a minority of such surfaces reconstruct. We observe a substrate reconstruction, in response to the lattice strain of the overlayer. The character of that reconstruction, judged by its geometric characteristics and atom density, is similar to those of the free surface reconstruction. Both observations suggest that an important factor in the reconstruction of the $5d$ metals, Ir, Pt and Au, must be the ease of disrupting interlayer bonds.

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