The growth of ultra thin Cu-films on Pt(111), probed by helium atom scattering and scanning tunnelling microscopy

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Abstract

The growth of ultra thin Cu films (up to 25 ML) on Pt(111) at a substrate temperature of 340 K has been investigated using helium atom scattering (HAS) and scanning tunneling microscopy (STM). In the first monolayer the growth is 2D-pseudomorphic with nucleation at step sites. No reconstruction of the substrate is observed. Diffusion limitation along the step edges leads to the formation of branched island structures which coalesce leaving randomly distributed holes (on average 30 Å in diameter) as revealed by STM measurements.

Keywords: Atom–solid scattering and diffraction – elastic; Copper; Diffusion and migration; Growth; Low index single crystal surfaces; Nucleation; Platinum; Scanning tunneling microscopy

1. Introduction

Metal-on-metal growth can be viewed as a competition between, on the one hand, energetic factors favouring a structure that minimises the free energy of the whole system and, on the other hand, kinetic factors that control and limit the rate of the various diffusion processes. In this paper we report the results of experiments on the heteroepitaxial growth of Cu on Pt(111) at 340 K, from the submonolayer regime up to 25 ML. The main emphasis is on the microscopic nucleation and diffusion processes occurring during the growth of the first monolayer.

Cu/Pt is a noble metal system with 8% lattice mismatch and negligible bulk diffusion at 340 K [1]. Growth on Pt(111) can result in a partial incorporation of adatoms forming a reconstructed phase to minimise the substrate inherent tensile surface stress. Such behaviour has been observed, at elevated temperatures, during both homoepitaxial [2] and heteroepitaxial (e.g. cobalt) growth [3]. In contrast, silver, which has a larger atomic volume than platinum, forms a first pseudomorphic adlayer when completed and the tendency towards incorporation in the Pt(111) surface is inhibited [4,5]. In the Cu/Pt system studied here, the smaller atomic volume of copper could favour reconstruction of a mixed Cu/Pt surface layer as a means to relieve both the intrinsic surface stress and the lattice strain in the growing copper film. However, the exact nature of this strain relief and the point at which it sets in will depend on both the interaction with the substrate and the interaction between the adatoms. Our results show no
reconstruction during the growth of the first copper layer at a growth temperature of 340 K. The growth in the first layer proceeds pseudomorphically, and is dominated by diffusion along surface steps, which controls both the initial nucleation of copper islands and the subsequent development and coalescence of the islands.

2. Experimental methods

The STM and HAS measurements presented in this paper were performed in two UHV systems both with background pressures of less than $2 \times 10^{-10}$ mbar. The same Pt(111) crystal with a miscut of less than 0.25° 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 $1 \times 10^{-6}$ 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 cleaning procedures resulted 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 [6]. Both the Cu evaporator and the STM are mounted in the same vacuum chamber. After each experiment the sample was cooled, the first image typically being taken within 15 min of the end of deposition. Images presented were recorded at tunneling currents of 0.1 nA and at bias voltages between 0.8 and 1.2 V.

The HAS was carried out with a 70 meV helium beam produced by supersonic expansion (2% energy resolution) and directed onto the sample, covering an area of 1 mm². A differentially pumped quadrupole mass spectrometer was used to detect the scattered helium atoms. The angular resolution of the system is 0.3°. The deposition rate was typically about 0.01 ML s⁻¹ with respect to the Pt(111) surface density. It was calibrated to an accuracy of approximately 15% from He intensity oscillations during layer-by-layer growth found in a different experiment. The experiments reported here were carried out with the beam incident at a Cu Bragg angle so that the drop in intensity during deposition is due mainly to diffuse scattered from step edges and point defects [7].

3. Results and discussion

Fig. 1 shows the specular in-phase He intensity monitored during Cu growth at 340 K. The He intensity curve provides information about the change in surface morphology in real time as the film is growing. A high specular intensity arises from a mirror-like surface, while steps and adatoms reduce the intensity, as does any atomic scale corrugation on a growing layer [7]. The absence of any oscillations in the He intensity curve presented here points to a 3D growth mode. However the fact that the curve is not simply exponentially decaying indicates that other processes are also taking place.

Up to a coverage of 1 ML the intensity decreases uniformly. This is followed by a more dramatic decrease after the onset of the second layer. Passing a coverage of ~1.4 ML a further change in slope occurs. At 3 ML, the specular intensity reaches a minimum. A spot profile analysis of the specular helium peak in this regime shows the formation of

![Image](image_url)

Fig. 1. The specular helium intensity monitored at a Cu Bragg angle. The horizontal axis shows the amount of Cu deposited, calibrated relative to the Pt(111) surface density. The main curve shows the intensity as a function of coverage up to 25 ML. The inset shows the first 2 ML of the main graph magnified.
a 3-fold corrugation pattern. By comparison with STM data the pattern can be identified as a strain-relieving dislocation network leading to a 0.3 Å corrugation on the second layer (Fig. 2). Hence, the reduced specular intensity can be attributed to the atomic corrugation created by this atomic superstructure of the second layer. As the film thickness increases further, the growth kinetics resemble those of a Cu(111) bulk-like surface. The He intensity rises as the superstructure is buried and the corrugation disappears. Further details will be published in a forthcoming paper [8].

The remaining part of this paper will concentrate on the growth of the first monolayer. The growth structure in this regime is in quasi-equilibrium. This was confirmed by the observation of a constant specular He intensity for several minutes after deposition of 0.25 ML. Room temperature STM images showed no sign of substrate reconstruction and HAS diffraction experiments, keeping the substrate at 340 K after deposition, revealed no diffraction features. We conclude that a substrate reconstruction does not take place at this temperature.

Interpretation of scattering data in the first monolayer region (magnified in the inset of Fig. 1)

Fig. 2. Image (48 × 48 nm²) of a 2 ML Cu film grown at 340 K showing the formation of a strain relieving dislocation network.

Fig. 3. (a) Image (960 × 960 nm²) of 0.25 ML Cu on Pt(111) deposited at 340 K presented as illuminated from the left. (b) Image (480 × 480 nm²) of 0.85 ML Cu on Pt(111) deposited at 340 K, revealing the existence of small holes in the first Cu layer. The image is shown as illuminated from the right. The inset (0.8 ML Cu, 24 × 24 nm²) highlights the holes. Both images are shown with descending substrate steps pointing "downhill" towards bottom of page.
is facilitated by additional information provided by large scale STM topographs presented in Fig. 3. In both images the absolute surface height decreases from the top to the bottom of the image (direction of down-steps of the Pt substrate).

After deposition of 0.25 ML (Fig. 3a) the Cu adatoms have formed branched islands mainly nucleated on lower terrace step edges. Island nucleation at step sites reflects a large diffusion length for Cu adatoms on the substrate; however, the branched island shapes show restricted diffusion of adatoms along the island perimeters once they are condensed at the edge of an island. There is no preferred orientation of the growth direction. The width of the island branches is of the order 100–200 Å which is comparable to the widths found for Au growth on Ru(0001) [9–11] and Ag growth on Pt(111) [12] around room temperature.

The growth morphology at 0.85 ML is shown in Fig. 3b. At this coverage, almost all of the original substrate step-sites are occupied by copper atoms. Nevertheless, the line of the substrate steps is preserved in the topograph. Thus, the majority of this type of step have copper atoms on both the upper and lower terraces. We call these Cu–Cu steps. The absence of nucleation at Cu–Cu steps implies that growth is taking place at other sites, which must have copper on the upper terrace and Pt on the lower (Cu–Pt steps). It follows that the binding energy at a Cu–Pt step must be higher than at a Cu–Cu step.

The fact that no second layer islands are visible in Fig. 3b shows that adatoms arriving on the Cu film can escape easily and incorporate at the growth front of the first layer. There are three possible mechanisms: first, crossing a Cu–Pt step with incorporation on a vacant lower terrace site; second, crossing the line of a pre-existing substrate step from the Cu island to a vacant Pt terrace; third, crossing a Cu–Cu step along the line of a former substrate step. The last case can be ruled out since large barriers to step crossing are known to exist for homoepitaxial growth of Cu(111) [13].

Atomic resolution STM images show that the first Cu layer is pseudomorphic [14], in agreement with previous LEED data [15,16]. However, closer inspection of Fig. 3b (inset) reveals the presence of holes, about 30 Å in diameter with a density between $5 \times 10^{-5}$ and $1 \times 10^{-4}$ holes Å$^{-2}$. Similar holes have been observed after growth of Cu films on Ru(0001) [17]. They originate from growing islands which have not completely coalesced. The holes are still visible as the second layer is forming. This is because their area is so small that there is a higher probability of adatoms meeting on Cu-covered terraces and forming homogeneously a new second layer nucleus than of them filling a hole. The holes disappear upon annealing to 800 K [14] due to the onset of alloying. The holes explain the absent oscillation in the He-intensity during first layer growth. They act as diffuse scatterers [7] and hence prevent the He intensity from reaching its initial value at completion of the first monolayer.

References