Site selectivity in the growth of copper islands on Au (111)

F Grillo1, H Früchtl, S M Francis and N V Richardson
EaStCHEM and School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK
E-mail: federico.grillo@st-andrews.ac.uk

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Abstract. The room temperature deposition of copper onto a Au(111)-(22 × √3) reconstructed surface has been investigated using scanning tunnelling microscopy (STM), up to a copper coverage of approximately 0.7 monolayer (ML). At extremely low coverage (~0.02 ML), preferential adsorption is observed to occur by displacement of gold atoms and incorporation of copper into the top gold layer at alternate herringbone elbows along the ⟨112⟩ directions. Both fcc regions and hcp regions are occupied. With increasing coverage, incorporation of copper continues but copper is also deposited on top of the incorporated copper islands. When full coverage of these islands to monolayer thickness is reached, further deposition leads to preferential growth of those islands located in hcp regions through both the deposition process and migration of copper from other elbows, predominantly those in fcc regions. Eventually, a critical island size is reached above which atomically thick copper islands exhibit a reconstructed surface similar, in essence, to that of the clean gold surface. Models for the initial adsorption mechanism, island formation and the eventual reconstruction of the copper islands are discussed qualitatively in terms of surface strain within the gold and copper surfaces.

1 Author to whom any correspondence should be addressed.
1. Introduction

Ultra-thin adsorbed atomic layers on single-crystal metal surfaces can provide structurally interesting systems in which a delicate balance of forces arises from the lattice mismatch of the adsorbate and the substrate. Because of this mismatch, surface layers are generally stressed and tend to minimize the excess energy by means of surface reconstruction. The phase diagram for the copper/gold system [1] shows that the two metals can form binary solid solutions across the full compositional range, but can also form ordered alloys in the bulk phase, e.g. Cu₃Au, CuAu and CuAu₃. Considering the surface behaviour, gold deposited on Cu (100) is a model system, which forms an ordered surface alloy c(2 × 2) Au/Cu (100). The Cu/Au (111) system has been extensively studied in electrochemical environments. In fact, over the last two decades, it has been characterized by using almost all analytical techniques used in electrochemical surface science [2]. It is a common observation that when copper is deposited on Au (111) electrodes, depending upon the deposition potential, (√3 × √3) R30° or (1 × 1) copper overlayers are formed with no intermixing of the two metals [3]–[5].

Despite the electrochemical interest in the copper/gold system, to the best of our knowledge, few UHV investigations have been reported so far. On the basis of a reflection high energy electron diffraction (RHEED) investigation, it has been reported that, under UHV conditions and at sub-monolayer coverages, copper adsorbs pseudomorphically on Au (111) at 300 K [6]. The Au (111) surface appeared to retain the (22 × √3) reconstruction and the copper overlayer showed a uniaxial compression along the ⟨110⟩ directions for coverages of up to 1 monolayer (ML). Above 1 ML, surface alloying eventually occurred. Macur and Vook [7] suggested a Stranski–Krastanov-like growth mode in which the initial copper deposition is not pseudomorphic; then a smooth copper monolayer formed, followed by strain-free, three-dimensional (3D) growth. The copper lattice was seen to be rotated by ±1.7° with respect to the gold lattice. The second copper layer was characterized by the formation of dislocations, which lie along ⟨110⟩ equivalent directions in the (111) plane and tended to be aligned in adjacent islands. Chang and Carter [8] developed a statistical–mechanical approach for investigating the growth morphology of heteroepitaxial fcc thin metal films on fcc (111) metal substrates, assuming no alloy formation between the two metals. For copper on Au (111), they derived a Volmer–Weber growth type, rather than confirming the experimentally observed Stranski–Krastanov growth [7]. More recently, a combined ion scattering spectroscopy (ISS) and x-ray photoelectron spectroscopy (XPS) study indicated that at room temperature, copper is in or near the subsurface region and the magnitude of intermixing increases with annealing treatments. Supporting density functional theory (DFT) calculations show that copper atoms prefer to segregate subsurface and lie beneath a single layer of gold atoms [9].
In this paper, we report a scanning tunnelling microscopy (STM) study of the deposition of copper on the $(22 \times \sqrt{3})$ reconstructed Au (111) surface. From the lowest coverage, we discuss the early nucleation stage and then describe the evolution of the copper adlayer up to a coverage of about 0.7 ML. We consider the information derived to be of wide significance in revealing, in considerable detail, the role of gold reconstruction in directing the earliest stages of metal cluster growth. This makes this work relevant to those interested in metal-on-metal growth, metal/metal interfaces, network formation based on monodispersed, regularly spaced features and heterogeneous catalysis.

2. Experimental

All experiments were performed in a UHV system (Omicron), having a base pressure better than $10^{-10}$ mbar and equipped with STM and low energy electron diffraction. For the STM study, electrochemically etched tungsten tips were used; all STM images were collected at room temperature and analyzed using the software package WSxM [10]. The Au (111) single-crystal substrate (99.9% purity) was prepared by argon ion sputtering at room temperature and then at 520 K and annealing (800–900 K) cycles until a characteristic $(22 \times \sqrt{3})$ reconstructed LEED pattern and large defect-free terraces in STM were observed. Copper dosing was achieved by electrically heating a high-purity copper wire wrapped around a tungsten filament, yielding a deposition rate of approximately 0.07 ML min$^{-1}$. The nominal coverage was determined from STM images by evaluating the portion of each picture covered by the features (i.e. clusters and islands) observed.

DFT calculations were performed using VASP code [11] with the PW91 functional [12], the projector augmented wave (PAW) method using appropriate pseudopotentials included in the VASP package [13], a Monkhorst-Pack grid consisting of 15 $k$-points in each surface direction in the Brillouin zone and an energy cut-off of 500 eV, corresponding to 36.75 Ryd. The Au (111) surface was modelled as three layers of a $3 \times 3$ slab and the topmost layer was allowed to relax, with the bottom layer atoms kept fixed at the ideal bulk positions. A vacuum slab equivalent to four metal layers was used to separate the metal slabs in the $z$-direction. All total energies were extrapolated at 0 K.

3. Results and discussion

Clean Au (111) shows a hexagonal surface, which reconstructs at room temperature into the well-known $(22 \times \sqrt{3})$ superstructure [14, 15]. The Au (111) $(22 \times \sqrt{3})$ reconstruction is generated by a unidirectional compression along the $\langle 110 \rangle$ directions of the top gold layer, accommodating 23 top layer gold atoms in 22 bulk lattice atomic spaces. The resulting superstructure cell, about 6.3 nm long, is comprised of areas with $hcp$ and $fcc$ stacking regions separated by ridges, discommensuration lines, organized in pairs. These discommensuration lines run in a zigzag pattern characterized by $\pm 120^\circ$ bends, the elbows. This so-called herringbone structure is comprised of bridge sites, where the transition between $hcp$ and $fcc$ coordination occurs, and is raised with respect to the surrounding areas by about 0.02–0.03 nm [15]. The shorter separation, between two ridges constituting a pair and encompassing an $hcp$ region, is about 2.4 nm and constant. This makes the regions of $fcc$ stacking approximately 65% wider than those of $hcp$ stacking. The pairs of discommensuration lines give rise to two distinct structures at the elbows. One of the lines is ‘pinched’ at the elbow,
while the partner line bulges at the adjacent elbow. The discommensuration line is ‘pinched’ when the orientation of the bridge site, occupied by the surface gold atoms, remains the same around the elbow and is ‘bulged’ if the orientation changes by 120°. Along the zigzag of a given discommensuration line, elbows are alternately pinched and bulged. This gives rise, in one case, to the *hcp* region becoming wider at the elbow and the *fcc* being narrower, as along the row of elbows marked by the arrow A in figure 1(a).

However, in the adjacent rows of elbows (arrow B in figure 1(a)), the *fcc* regions become wider and the *hcp* regions narrower instead. These regions of closest approach between the two discommensuration lines are indeed regions of higher local strain in the surface gold layer, which contains ~4% more gold atoms than the corresponding bulk (111)-plane and hence are the most reactive. It has been calculated that even though the *fcc* sites are more stable by only 2 meV with respect to the *hcp* sites [16], the discommensuration lines have an energy content 182 meV higher. The actual highest energy points are anticipated to be the ones corresponding to the kink sites at the ±120° bends along the ridges [17].

The initial step following copper deposition to low coverage, about 0.02 ML, is shown in figure 1(a), where dark features appear between every pair of ridges that create a narrowed elbow of the (22 × √3) reconstruction, i.e. where the pinched ridge is on the outside of the pair of ridges and the bulged ridge on the inside. To highlight this, a white dashed line, which follows an *hcp* stacking domain, has been drawn in figure 1(a) as a guide to the eye. Copper deposition occurs exclusively in the narrowed regions at the elbows, such that along the A rows along the ⟨211⟩ directions (figure 1(a)), deposition is in the *fcc* stacking regions, whereas along the B rows, it occurs in *hcp* stacking regions. Clearly, it is not the stacking that determines the preferred nucleation site but rather the local arrangement of gold atoms in the vicinity of the elbows. More detailed characterization of the regions of deposition shows that the density of copper atoms in these newly formed structures is highest adjacent to the bulged discommensuration lines and rather lower towards the pinched lines; this is shown by the asymmetry of the main feature defining the copper cluster in the line profile shown in figure 1(b). We therefore conclude that the most favoured location for the nucleation of the copper deposition is in the vicinity of those gold atoms where the change in bridge site orientation occurs. A model of the Au (111) surface (22 × √3) reconstructed, including the copper adsorption sites, is shown in figure 2.

At this stage, the clear and characteristic (22 × √3) reconstructed LEED pattern in which the hexagonal first-order spots are surrounded by the lower intensity diffracted spots generated by the (22 × √3) superstructure observed during crystal preparation became broad and less resolved but retaining a hexagonal pattern overall.

Similar dark features were previously observed in a study of nickel deposition on Au (111) and were attributed to substitutional nickel atoms [18]. A two-step nickel nucleation mechanism onto the herringbone elbows was proposed: in the first step, mobile nickel adatoms displace gold atoms via a place exchange process; in the second step, the substitutional nickel atoms act as nucleation sites, trapping further nickel atoms diffusing on the surface. Eventually, a gold–nickel alloyed island forms [19]. On the basis of surface-free energies and heats of sublimation values, a similar mechanism is also thought to occur for the addition of iron and cobalt, but has been disregarded for other metals, such as aluminium, silver and, indeed, copper [18]. Nevertheless, in contrast with the predictions [18], figure 1 provides substantial evidence that, already at room temperature, the onset of copper deposition/incorporation occurs by gold atom displacement at areas close to but outside the bulged discommensuration line of the (22 × √3) reconstruction, with islands then developing in the adjacent narrowed region, regardless of whether this is
Figure 1. (a) STM topography showing the initial copper adsorption/incorporation stage. The dark areas at the Au (111) \((22 \times \sqrt{3})\) reconstruction elbows are attributed to copper atoms undergoing a place exchange process with gold atoms. The white dashed line over \(hcp\) stacking regions is a guide for the eye, clearly showing that along this line elbows are alternately populated by copper atoms. The white oval indicates an area of substitutional incorporation of copper atoms, whereas the white arrow points to a feature attributed to a small cluster of copper atoms within this area. Coverage is about 0.02 ML. A contrast enhancement filter has been applied for clarity (apparent height difference between the lowest and the highest point is 0.06 nm); the black arrow labelled A shows a row of adsorption sites located in \(fcc\) regions, whereas along that marked B, adsorption is in \(hcp\) regions \((80 \times 42 \text{ nm}^2, -1 \text{ V}, 0.78 \text{ nA})\); in the inset, the fuzziness at the step edge is due to gold atom condensation \((32 \times 40.5 \text{ nm}^2, -1 \text{ V}, 0.79 \text{ nA})\). (b) Line profile along the blue arrow in (a): (i) indicates a bulged elbow, (ii) the maximum density of copper atoms and (iii) a pinched elbow. (c) Line profile as in the inset of (a) showing an apparent step height of about 0.22–0.23 nm.
characterized by fcc or hcp stacking. Gold atom displacement is in line with the observation that the energy content of a Cu–Cu bond (168 kcal mol$^{-1}$) is only slightly smaller than Cu–Au (179 kcal mol$^{-1}$) and Au–Au (184 kcal mol$^{-1}$) (energy contents for the bulk phases [20]), thus the place exchange mechanism does not require a large energy expenditure. The region over which substitution occurs, as indicated by the white oval in figure 1(a), covers an area of about 3–4 nm wide, but consists of smaller features about 0.35–0.5 nm wide, as indicated by the white arrow in figure 1(a). The latter features are attributed to very small clusters comprising not more than a few copper atoms. This image corresponds to a coverage of approximately 0.02 ML.

We propose that in this very first step, each copper atom replaces a single gold atom in the first layer, eventually forming a single layer thick, 2D island of copper. The gold atoms, after being displaced from their original positions by the copper atoms, undergo rapid diffusion over the terrace and eventually reach a step edge, where they are seen to condense. This is a dynamic process revealed by the fuzzy appearance of the gold step edge, as shown in the inset of figure 1(a) and the corresponding line profile in figure 1(c) showing an apparent step height of about 0.22–0.23 nm, in good agreement with the calculated step height on Au (111) of 0.236 nm.

The dark appearance (i.e. lower electron density detected via STM) of the copper atoms can be tentatively explained in terms of the values of the workfunction for the two metals.
(4.93 eV for Cu (111) [21] and 5.35 eV for Au (111) [22]). In agreement with electronegativity differences, this difference in workfunction will result in a local redistribution of electron density from copper to gold, leading to lower electron density in the vicinity of copper atoms. Sham et al [23, 24] and Kuhn and Sham [25] demonstrated that, although a charge compensation electron transfer is likely to occur, a net but small charge flow onto gold is the result of such a charge compensation mechanism. Recently, dark features seen with STM after deposition of copper onto a Pt (111) substrate were attributed to copper atoms incorporated into the first platinum layer, after comparison with DFT-simulated STM images [26]. This result supports our interpretation of the dark features observed. The value of the workfunction for Pt (111) is 5.80 eV [27] and therefore larger than that for Cu (111) and indeed even Au (111), thus likely increasing the electron density redistribution effect and making the difference in contrast more evident in the case of copper on Pt (111). However, this criterion alone may not be sufficient for explaining this phenomenon of dark features representing incorporation of copper into the gold layer, since it was also observed [28] for systems in which the adsorbate (111) workfunction (Au) is approximately the same as that of the substrate (Ni (111), 5.35 eV [29]).

Since differences in apparent height in STM might be due to a combination of electronic effects and real topographic differences, a geometrical contribution should perhaps also be taken into account. To gain further insights into the dark areas seen on STM, we performed DFT calculations for different configurations of a copper atom located on or into the first layer of a $3 \times 3 \times 3$ gold slab. In this instance, it is not necessary to take into account the reconstruction of the gold surface, which would require the use of a larger slab and considerably more computational power, since the purpose is to discuss the appearance of the embedded copper atom in an STM image. After initial relaxation of the Au (111) slab, one gold atom of the topmost layer was substituted by a copper atom (initially moved away from the position of the replaced gold atom) and the modified system allowed us to relax once more. Relaxation shows the tendency of the copper atom to move laterally to an equilibrium position corresponding to the ideal lattice position for a gold atom in the $(x, y)$-plane, but also to sink towards the second gold layer in the $z$-direction. After relaxation, STM images were calculated according to the Tersoff–Hamann approximation [30] in which the tunnelling current is considered to be proportional to the projected integrated local density of states in the direction normal to the surface, $z$, at the position of an ideal tip, assumed to be an s-type wave function, in an energy range between the Fermi level and the voltage bias experimentally applied. A constant current STM image can be calculated and compared to the experimental observations. At low charge density contours, where the tip is sufficiently distant from the surface to avoid major perturbation of the electronic structure, the copper atom incorporated into the Au (111) topmost layer appears as a dark feature (figure 3(a)).

This is in line with results obtained for other systems [26]. Thus, considering the position of the copper atom with respect to the topmost gold layer after relaxation, its size (the copper radius being smaller than that of gold by about 0.03 nm) and its appearance in the simulated STM image, we conclude that the dark features experimentally observed should be attributed to copper atoms incorporated into the first gold layer. Significantly, and in contrast, a DFT calculation on a copper atom adsorbed on the topmost gold layer, regardless of the adsorption site, shows that copper appears as a protrusion brighter than gold (figure 3(b)).

The calculation of a complete (potential energy) versus (reaction coordinate) diagram for the place exchange mechanism and related configurations is under investigation and will be presented elsewhere [31].

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After further copper addition, the favoured substitutional sites become saturated, and small, circular, now bright, copper islands grow at all those elbows of the herringbone reconstruction previously characterized by Cu/Au place exchange (figure 4(a)). The growth of on-top copper builds therefore on the initial nucleation sites shown in figure 1(a), remaining at this stage in the narrowed regions at the elbows regardless of the fcc or hcp stacking. Close scrutiny of these regions shows that adjacent to the bright areas are darker regions, attributable to newly incorporated copper but now in the adjacent widened elbow, i.e. on the inside of the bulged ridge; this effect is more pronounced in B-type rows, where the new dark features now appear in the fcc stacking regions, than in rows of A-type, where they would be in hcp regions. In agreement with the values for the cohesive energy for copper (about 3.53 eV) and for gold (about 3.78 eV) [8, 32], with increasing coverage, instead of mixing with gold to form a bulk alloy, copper islands appear to enlarge, doing so in a distinct manner (figure 4(b)). This evidence for asymmetry between the A and B rows, i.e. islands initiated in hcp rather than fcc regions, is continued in the next stage of island growth. Now, growth is largely limited to those initial islands found in hcp regions (B-type rows) and occurs across the hcp and immediately adjacent fcc regions, leading to a ‘D’-shaped feature. Of the 32 largest, triangular-shaped islands shown in figure 4(b), 28 are based on the elbow narrowing in hcp regions (B-type rows) and only four are based on initial islands at the elbow narrowing of fcc regions (A-type rows).

Interestingly, the larger island shown in figure 4(a) is also an fcc-based island. It is of particular significance that, although all narrowed elbows are populated by initial substitutional copper atoms (figure 1(a)) and then by small islands (figure 4(a)), further growth, even in the hcp regions, is limited to only about 9% of the elbows. It is the growth of these islands, rather than the initial nucleation, that then dominates with increasing coverage. As well as the same shape, the majority of the islands appear to have the same orientation of triangle determined by the direction of the initiating elbow, which is likely due to the confining effect of the underlying corrugation during the growth process, i.e. indicating that islands growth in hcp regions is far more favourable than that of the ones residing in fcc regions. In figure 4(c), islands grow and exhibit a reconstructed surface. The apex of the triangle pointing in the direction of the elbows becomes much more rounded becoming more ‘D’-shaped than triangular, although the

Figure 3. Simulated STM images of a copper atom (red spheres) in (a) or on (b) the topmost layer of an Au (111) substrate (yellow spheres) within a $3 \times 3$ surface unit cell.
Figure 4. STM topography showing the evolution of the copper overlayer with increased coverage: (a) about 0.025 ML, small bright clusters form on the \((22 \times \sqrt{3})\) reconstruction elbows where incorporation had previously occurred \((88 \times 88 \text{ nm}^2, -1.26 \text{ V}, 1.1 \text{ nA})\); (b) about 0.062 ML, some evolve into triangular-shaped islands favouring those in B rows where the initial incorporation is in hcp sites; the white oval indicates an island that has not yet grown \((178 \times 178 \text{ nm}^2, -0.91 \text{ V}, 1.2 \text{ nA})\); (c) about 0.18 ML, islands grow, become more 'D'-shaped and show a reconstructed surface \((170 \times 170 \text{ nm}^2, -1.2 \text{ V}, 0.88 \text{ nA})\); (d) about 0.36 ML, islands start to merge (white oval); at this stage some copper condensation on step edges is also observed as indicated by the white arrow \((210 \times 210 \text{ nm}^2, -1.2 \text{ V}, 0.81 \text{ nA})\); the inset shows the reconstruction occurring on an island (derivative of the topography, \(32 \times 40 \text{ nm}^2, -1.2 \text{ V}, 0.85 \text{ nA}\)). (a–c) Contrast enhancement filter applied for clarity.

back edge of the triangle defined in this way remains straight. At this stage, seeding clusters can no longer be seen and, confirming the difference in reactivity between A-type and B-type adsorption sites, only one out of the 34 islands is an island based on an A-type adsorption site.
row. Eventually islands become more irregular in shape and merge, as indicated by the white oval in figure 4(d). Some copper condensation on the lower side of the Au (111) step edges is also evident now (white arrow in figure 4(d)). The very well resolved and sharp appearance of these steps makes them clearly distinguishable from the ones where the displaced gold atoms initially accumulate (inset of figure 1(a)). It is worth noting that the copper layer condensed on the step edges does not appear to expand as rapidly as the copper islands, suggesting a difference in reactivity between the two configurations. Thus, further deposited copper preferentially adds to an island already formed around the herringbone elbow on the terraces, rather than condensing onto a gold step edge.

The energy of adding an atom of copper to a copper step edge has been calculated to be very similar for \{111\} and \{100\} faceted steps, 0.26 and 0.27 eV, respectively \[33\]; therefore a (nearly) regular hexagonal island shape would be expected. A possible explanation for the ‘D’ shape is perhaps due to interactions with the underlying Au (111) surface. Molecular dynamics/Monte Carlo-corrected effective medium (MD/MC-CEM) calculations \[34\] show that, for Au (111) homoepitaxial growth, condensation on fcc \{111\} faceted steps (0.25 eV) is more favourable than on the hcp ones (0.28 eV); the activation energy for adding a gold atom to a \{100\} faceted step is 0.26 eV instead. Because of the reported values and in agreement with the observation that the majority of growing islands are located on hcp sites, we argue that this is the most likely configuration in which the newly formed copper islands accommodate.

LEED patterns collected at the different coverage stages show progressive fading of the \((22 \times \sqrt{3})\) pattern and broadening of the integer order spots. No extra diffraction spots related to the adsorbed/incorporated copper could be seen; this suggests that the copper lattice might be aligned or misaligned by only a very small angle with respect to the gold lattice, as previously reported \[7\].

Island size distributions for coverages ranging from about 0.02 ML to about 0.2 ML are presented in figure 5. The distributions were normalized to an area of 150 \times 150 \text{nm}^2 and were all fitted with Gaussian functions. The normalized results are summarized in table 1. For coverages up to about 0.02 ML, the average size of the initial areas modified by the adsorption/incorporation process (figure 5(a)) is about 1.73 \text{nm}^2. The narrow full-width at half-maximum (FWHM) of the curve in figure 5(a) indicates a high degree of similarity between the islands, which on average are separated by 6.41 \text{nm}: a value in good agreement with the periodicity of the elbows in the herringbone reconstruction. For three times the dosing time, the coverage nearly doubles (figure 5(b)), even though the island density stays almost constant within the experimental error. At this stage, the copper islands show a different appearance: the original apparent depressions are substituted by protrusions with adjacent depressions. Protrusions are on average 1.82 \text{nm}^2 wide, whereas depressions have an average area of only 0.33 \text{nm}^2 (table 1 shows an evaluation of both depressions, on the second row, and protrusions, on the third row, and the sum of the two, fourth row). We ascribe this different appearance to more copper substituting for gold first, having the effect of enlarging the dark areas, then starting to condense on top of the substitutional sites, without covering them completely; the copper second layer appears as a protrusion. Thus, the total feature footprint increases to about 2.41 \text{nm}^2 and the average nearest-neighbour island distance decreases. Beyond this coverage, the island size grows with the coverage; now the FWHM increases, indicating that a more heterogeneous island topology is present.

Following the initial growth at every narrowed elbow, the total number of islands within a given area shows a dramatic decrease with increasing coverage and the average island distance
increases. In this situation, some of the islands increase in size, predominantly those in hcp elbows, and are thought to destabilize the copper nucleated into vicinal, particularly fcc, elbows sites, which then undergo rapid diffusion and eventually condense preferentially into a close-by island, indicating also that, at this stage, the trapping of an incoming atom at an island is higher than that of a substitutional site or that of a newly condensed layer at a step edge. After the nucleation stage, which occurs via a place exchange mechanism, as already discussed, all of these observations are consistent with island growth via an Ostwald ripening process, where a small number of larger islands are more energetically favoured than a large number of smaller islands; therefore small islands tend to disappear and large ones to grow.

On the basis of the growth observed, we propose the following mechanism for island formation. (i) Substitution/incorporation of copper into alternate pinched herringbone elbows

Figure 5. Island size distributions normalized to a 150 × 150 nm² area for coverage ranging from about 0.02 to 0.2 ML.
Table 1. Normalized island size distribution results\textsuperscript{a}.

| Coverage (%) | Mean number of features | Mean size distance (nm) | Size (nm\(^2\)) | FWHM (nm\(^2\)) | Feature type | Based upon STM image |
|--------------|-------------------------|-------------------------|------------------|------------------|--------------|---------------------|
| 1.69         | 178                     | 6.41                    | 1.73±0.08        | 1.66±0.26        | D            | 1a                  |
| 0.66         | 165                     | 0.33±0.01               | 0.48±0.03        | 0.66±0.26        | D            | 4a                  |
| 1.75         | 189                     | 1.82±0.11               | 1.47±0.25        | 1.95±0.39        | P            | 4a                  |
| 2.41         | 6.0                     | 2.15±0.11               | 1.95±0.39        | 4a               |              |
| 6.24         | 39                      | 13.92                   | 58.92±1.25       | 15.84±2.71       | P            | 4b                  |
| 18.06        | 34                      | 21.35                   | 115.99±3.86      | 84.89±8.91       | P            | 4c                  |

\textsuperscript{a}In the ‘Feature type’ column, D indicates depressions and P protrusions.

occurs within the first gold layer and is limited by the elbows size. (ii) When this critical size is reached, at increased coverage, further copper atoms both condense over the substitutional copper increasing the islands size and exchange for gold, creating a narrow strip of substitutional area around the islands. (iii) At higher coverage, the addition of copper to an already formed island is energetically far more favourable than a small island incorporated into the first gold layer. When compared to the larger islands, the adsorbed/incorporated smaller islands are inherently more unstable because of their smaller curvature radius, thus inducing a higher 2D vapour pressure. In this situation, Morgenstern \textit{et al} [35] showed that a larger number of free atoms (2D gas) on the substrate are present nearer the smaller islands. This creates a composition gradient leading to 2D diffusion of the free atoms from smaller to wider islands. As a net effect, one island enlarges and incorporates the adjacent small clusters, causing the nearby elbows to lose copper; the empty sites are likely filled up by relaxation of the gold surface layer atoms. (iv) Condensation on clean elbows no longer occurs and atomically thick islands expand. The mechanism proposed suggests a dependence of the copper sticking probability with coverage and a higher sticking probability for copper to condense onto copper than onto gold.

In figure 6, diagrams of an island growth sequence are shown and compared to the respective STM images, as follows. Nucleation sites (a), which appear as depressions, are followed by the formation of islands, which appear now as protrusions adjacent to depressions, on almost all of the nucleation sites (b). Figure 6(b) shows also an island that has already grown to an appreciable size; the island is almost perfectly triangular, with a flat top surface, most likely (111) oriented, and that is surrounded by a darker area. The latter is ascribed to substitutional copper atoms. Initially as the islands grow, they do not show any reconstruction. However, at the next stage shown in figure 6(c), islands expand along a \langle 211 \rangle direction and are characterized by a straight discommensuration line, parallel to the edge along a \langle 110 \rangle direction. This line, which originates and terminates on the island edge in the proximity of the herringbone reconstruction, reveals that the topmost layer has a higher atomic density with respect to the underlying layer; a second line on the island is also seen. This second line, characterized by \pm 120° angle bends, does not appear to merge with any of the gold surface corrugation lines. At this stage, adjacent substitutional sites can no longer be observed.

Finally, in figure 6(d), the straight discommensuration line along a \langle 110 \rangle direction and a further pair of lines on the island are visible. These lines comprising a pair are once
Figure 6. Diagrams and STM images showing the formation and evolution of an island (see text for details): (a) $31 \times 29$ nm$^2$, $-1.0$ V, $0.78$ nA; (b) $33 \times 32$ nm$^2$, $-1.26$ V, $1.1$ nA; (c) $31 \times 29$ nm$^2$, $-1.25$ V, $0.75$ nA; and (d) $41.5 \times 33$ nm$^2$, $-1.2$ V, $0.84$ nA.

again characterized by $\pm 120^\circ$ angle bends but are now continuous with the herringbone reconstruction, when reaching the step edge. No distortion of the gold ($22 \times \sqrt{3}$) reconstruction can be seen around the copper islands. These islands are characterized by brighter lines reminiscent of the discommensuration lines on the clean Au (111) surface; however, they have distinctive differences, as will be shown later. When adding copper to gold, because of a large lattice mismatch between the Cu (111), 0.256 nm, and the Au (111), 0.288 nm, epitaxial growth of the copper layer is not expected to occur and stress is introduced into the system. In order to relieve the stress induced by the lattice mismatch, the copper layer undergoes a uniaxially compressed reconstruction. We observed that this reconstruction readily occurs, even in islands as small as about 10 nm$^2$. Assuming that an island consists of copper atoms only, arranged as in a (111) plane of an fcc crystal lattice, this corresponds to about 150 atoms. When a critical island size is reached, a raised line, which is interpreted as copper atoms residing in bridge sites, appears on the island edge parallel to a $\langle 110 \rangle$ direction, therefore a close packed one. In order to relieve further stress, the island then develops along a $\langle 211 \rangle$ direction edge; a pair of raised discommensuration lines eventually appears. MD simulations by Lei and Tang [36] have predicted that there is a critical size that the copper islands need to reach in order to relieve the stress created by the lattice mismatch. In this theoretical study, when a small copper island, comprising less than 43 atoms, is added to an Au (111) surface, some of the copper atoms occupy fcc sites and others hcp sites, but the stress is not yet sufficient.
to induce the transition of copper atoms from one coordination site to another. However, for increased islands size, when the number of atoms reaches the critical number 43, the stress is high enough that the transition of copper atoms from one coordination site ($fcc/hcp$) to the other ($hcp/fcc$) along the $\langle 211 \rangle$ directions can occur. The prediction of the appearance of this particular discommensuration line is in agreement with the presence of raised lines over the islands that we experimentally observed and described in detail in figure 6, although the critical island size for this reconstruction is somewhat larger (about 150 atoms) than that predicted by Lei and Tang [36]. In the final configuration, copper atoms occupy both $fcc$ and $hcp$ sites.

The copper island apparent height is approximately 0.15 nm, a value much smaller than the one expected either for a Cu–Cu (0.208 nm) or an Au–Au (0.236 nm) monatomic step on the respective (111) planes. Since the nucleation sites, corresponding to copper atoms embedded within the first gold layer, appear initially as depressions (figure 1(a)) and then evolve into islands appearing as protrusions without any appreciable change in size (figure 4(a)), we are inclined to think that the copper islands are two atomic layers thick, the first one of which is partially incorporated into the gold surface layer.

Even though copper and gold are reported to be miscible in every ratio [1] and Au/Cu and Cu/Au bilayers show interdiffusion of the two metals in the interfacial region after annealing to about 670 K [7, 37, 38], Au–Cu intermixing at room temperature seems to be unclear. In fact, it has been ruled out for up to 5 ML of gold on Cu (111) [21, 39], but a Cu–Au surface alloy forms readily in systems such as c(2 × 2)-Au/Cu (100) [40], Au/Cu/Au (110) [41] and (4 × 1) Cu$_3$Au (110) [42]. Moreover, during vacuum deposition, no intermixing is predicted to occur at 0 K, but deposition at higher temperatures (300 K and above) or at high incident kinetic energies may favour it [36]. In our case, the preparations were carried out at room temperature and, as already clarified, we ascribed the dark STM features observed on the (22 $\times$ $\sqrt{3}$) reconstructed gold surface elbows to copper atoms undergoing place exchange with gold atoms; therefore a certain limited and local degree of copper incorporation into the first gold layer occurs. However, we are inclined to rule out the formation of a solid solution or ordered alloy, which elsewhere were deduced from changes in the topography ([19, 43] and references therein), since by adding more copper to the system, the islands grow, reconstruct with raised discommensuration lines over an atomically flat area and eventually merge into a new layer. We therefore speculate that, even though a small amount of copper is incorporated into the first gold layer, mixed composition within the islands and then the adlayer seems not to occur. Recently, high-resolution transmission electron microscopy (TEM) studies [44, 45] have shown that a copper–gold alloy, prepared on amorphous carbon films by vacuum evaporation of the two metals and post-annealing to about 820 K, appears as domains of mixed composition both disordered and ordered, the latter characterized by linear features of variable spacing, dictated by the alternation of pure gold and pure copper rows. Similar features were produced by annealing a multilayer coverage preparation to about 760 K.

For a coverage of about 0.7 ML, figure 7(a) shows an area of the surface where at least four different terraces, labelled as A, B, C and D, are recognizable. The top part of the image, as well as the bottom left and right corners, shows the typical Au (111) (22 $\times$ $\sqrt{3}$) reconstructed surface; all of these areas belong to what appears to be the same copper-free terrace (A). Over it, at the centre of the image, an almost defect-free layer (B) with a different pattern is visible ‘less than’ one atomic layer higher. This pattern comprises pairs of brighter ridges, which proceed in parallel for several nanometers, mainly along the (211) directions. This seems to agree with the observation of an overall hexagonal LEED pattern with diffuse first-order spots.
Figure 7. (a) STM topography showing copper reconstructed terraces on the Au (111) \((22 \times \sqrt{3})\) reconstruction, about 0.7 ML, with key features identified: (i) a pair of raised lines that splits when approaching the step edge; (ii) ridges of the top terrace merging with the ones on the bottom terrace; (iii) ridges running not in pairs; (iv) pairs creating closed loops; (v) gold–copper step; (vi) copper–copper step; A, B, C and D indicate different terraces \((240 \times 240 \text{ nm}^2, -1.23 \text{ V}, 0.8 \text{ nA})\); and (b) line profile as indicated in (a).

When in the proximity of a step edge, the pairs appear to split into two ridges; one of the two ridges follows the step edge, whereas the other one either follows it in the other direction or terminates normal to it (figure 7(a), i). When the corrugation follows the step edge, the direction of the ridge can be off registry with respect to the original directions. In most cases,
the line perpendicular to the step edge proceeds onto the next terrace and ‘merges’ with the
corrugation of the reconstruction present on that terrace (figure 7(a), ii), indicating that the
adlayer reconstruction is influenced by the underlying reconstructed layer. On the left side, an
area where the ridges are not paired but individually run randomly along off registry directions
is also present (figure 7(a), iii). The ridges have an apparent corrugation of (0.040 ± 0.005) nm
with respect to the darker areas, while the separation between two ridges enclosing hcp domains
is approximately (1.66 ± 0.02) nm; this distance is generally maintained when the ridges are
parallel and not crossing. The separation, however, increases corresponding to ±120° angle
bends and when two pairs merge. On the copper terrace (terrace B) the overall periodicity
is larger than on the clean gold (terrace A), with the fcc regions much wider and the hcp
regions perhaps slightly narrower than on clean gold; this might correspond to a weaker uniaxial
compression in the copper layer. As a consequence the bulges in the elbows are considerably
more distinct and in the extreme become a 120° bend into the third ⟨211⟩ direction. In turn, this
gives rise to more changes in direction in the ridges and to triangular closed loops, which are
equivalent to three bulged discommensuration lines (figure 7(a), iv).

In agreement with the apparent step height measured on the islands, the apparent step
height between terrace A, showing the clean Au (111) herringbone reconstruction, and terrace
B, showing the copper reconstructed layer, is about 0.15 nm (figure 7(a), v, and line profile
in figure 7(b), v). This is once again consistent with the presence of a copper double layer
comprising a second copper layer grown over the first substitutional copper atoms, which are
partially incorporated into the first gold layer.

The new pattern observed after copper deposition is therefore due to the reconstruction of
the second copper layer, suggesting that the first copper layer is pseudomorphic. The actual step
height measurement is, however, likely to be affected by the difference in workfunction of the
two metals, the partial incorporation of the copper layer into the gold layer and electronic effects,
as previously discussed. The difference in apparent height between the two top terraces, B and
C, exhibiting the more corrugated pattern (figure 7(a), vi, and cross section in figure 7(b), vi) is
about 0.21 nm, a value in agreement with the Cu (111) step height, indicating that a third and
narrower copper terrace, C, accommodates on top of the second one (a further copper terrace,
D, can be seen on the right side). In this case, the measurement is not affected by electronic
effects, since a copper layer sits on another copper layer and the underlying gold influence can
be regarded as constant. This way of determining the presence of a third copper layer is also
consistent with the way in which Vestergaard et al [46] inferred the presence of two atomic layer
thick gold islands on Ni (111).

Del Pópolo et al [47] performed microcanonical molecular-dynamics simulations within
the embedded atom model in order to explore the behaviour of a not necessarily commensurate
1 ML of copper on Au (111). After equilibrating their system at about 300 K using a set of
potentials derived from Foiles et al [48], they obtained a final structure in which the copper
monolayer is compressed, leading to the generation of holes and incommensurate domains,
which is qualitatively very similar to the topography we show in figure 6. They also add that
the compression of the top layer is caused by the shorter lattice parameter for the bulk copper
overlayer and that the Fourier transform of the averaged atomic densities was represented by a
hexagonal pattern with very diffuse spots, in good agreement with our LEED observations.

The corrugation pattern inevitably calls for comparison to the Au (111) \((22 \times \sqrt{3})\)
reconstruction and can be tentatively explained in similar terms: along the close packed
directions, one extra copper atom is thought to sit over one less gold (111) atomic space.
Similarly, if the bright ridges can be attributed to transition regions between fcc and hcp coordination sites, because of stability reasons, the hcp stacking regions should be localized in the narrower area between the ridges and the fcc regions anywhere else, since the fcc stacking structure is likely to be inherently more stable.

When compared to the herringbone reconstruction, the copper reconstructed layer shows ridges running once again along the \( \langle 211 \rangle \) directions and a rougher average corrugation. It is also characterized by a higher fcc/hcp stacking site ratio and an increased number of defects, in particular closed loops and split corrugation lines that occasionally run randomly on the terraces. Other metal-on-metal systems, such as Cu/Ru (0001) [49, 50] and Ag/Pt (111) [51], are reported to behave in a similar way, i.e. showing an adlayer that reconstructs in a similar manner to the one described earlier, in order to relieve the strain due to the lattice mismatch. In these cases, a first layer of the added metal grows pseudomorphically on the substrate and a second layer unidirectionally reconstructs. During this investigation, the presence of a copper double layer was derived mainly by considering the growth mechanism and it was also observed that the reconstruction of the second copper layer occurs for a coverage far less than 1 ML, without lifting the underlying reconstruction already present upon the gold surface.

The sub-monolayer copper adlayer is stable upon annealing up to about 650 K, when it appears to dissolve into the bulk gold crystal and a clean and regular \((22 \times \sqrt{3})\) reconstruction reappears under STM imaging and LEED analysis.

4. Conclusion

STM shows that the onset of copper adsorption occurs via a place exchange mechanism at specific sites identified as the narrowed regions within the highly reactive elbows of the Au (111) herringbone reconstruction, irrespective of hcp or fcc stacking. With increasing coverage, there is a preference for growing those islands initiated in hcp regions and with a growth scheme compatible with the Ostwald ripening process. Islands eventually coalesce and evolve into a partially incorporated double layer when approaching the monolayer regime. When a critical island size is reached, to relieve the stress induced by the lattice mismatch, the new layer reconstructs in a herringbone-like fashion. Different events occur at step edges: firstly the displaced gold atoms condense on them expanding the terraces; copper condensation is then seen. Islands on terraces appear to grow faster than the layer nucleated at step edges. Overall, copper appears to grow on Au (111) in a Frank–van der Merwe fashion; however, the appearance of a further copper layer is seen before completion of the previous one.

The details revealed by our UHV study have allowed a deep appreciation of the role of the Au (111) herringbone elbows, not only in the very early stages of cluster formation, during which gold atom substitution dominates and both hcp and fcc elbows are targeted, but also in the next stage, during which growth in the vicinity of hcp elbows is preferred.

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