Lifting of the Au(100) Surface Reconstruction by Pt, Cr, Fe, and Cu Adsorption

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The adsorption and growth of metals on the surfaces of other metals is an important topic for studies of heterogeneous catalysis and bimetallic nanoparticles. The surface structure of these systems impacts nanoparticle growth, catalytic activity, and reaction selectivity. In these experiments, platinum, chromium, iron, or copper were vapor deposited on the reconstructed Au(100) surface. The initial growth of each metal was studied by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). Each of the four metals form anisotropic rectangular islands oriented in the direction of the gold reconstruction rows. The gradual lifting of the surface reconstruction by increased metal coverage is observed, and the reconstruction is fully lifted after 0.5 ML of Pt, Cr, or Fe, or by 3.3 ML of Cu. After the reconstruction is lifted, the island shape changes from rectangular to square, illustrating the effect of surface structure on growth. Second layer islands begin to form before the completion of the first full layer.

Keywords: bi-metallic interfaces; surface reconstruction; scanning tunneling microscopy; surface alloy; catalytic metal surfaces; anisotropic nanostructures.

Introduction

In the field of catalysis, it has been found that bimetallic catalyst systems can have superior activity compared to single metal systems [1-3]. Understanding the structure of these systems is essential. Here, the initial growth of Pt, Cr, Fe, and Cu were studied on Au(100) by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). We present an analysis of the initial growth mode and lifting of the Au(100) surface reconstruction by each of these metals.

These results contribute to our understanding of the surface interactions of bimetallic systems, which are of interest in heterogeneous catalysts and for bimetallic nanoparticles. Structural studies of the initial growth of metals on metal surfaces, particularly with regard to strain and surface reconstruction, provide foundational knowledge for the development of atomistic modeling of structure, surface bonding, and reactivity in surface catalysts and in bimetallic nanoparticle systems. It has been shown that combinations of two metals can offer advantages in catalysis compared to either of the two metals alone [4]. Au-Pt systems have higher catalytic activities, show resistance to coking and CO poisoning, and have other unique properties not present in either metal alone [2, 5]. Au-Cu systems have been shown to improve methanol synthesis [6]. Au-Cr systems are efficient catalysts for alcohol oxidation processes [7]. Au-Fe systems are studied for their unique electronic and magnetic properties [8, 9]. The structure of metals on surfaces also plays an important role in the study of metal-ligand assemblies. Knowing the structure of the metals on the surface by themselves allows for structural comparison with the coordination networks that are formed [10-13].

The growth mode of one metal on the surface of another is also an important consideration in the synthesis of bimetallic nanoparticles [14]. For example, the shape of Au@Ag core@shell nanoparticles, formed by microwave-polyol synthesis [15], depends on the crystal facets expressed by the gold seed. This influence on nanoparticle shape is very important, as the shape of metallic nanoparticles plays a large role in their catalytic reactivity [16, 17]. Surface reconstructions can also play an important role in the growth and function of nanoparticles. Different surface structures, including reconstructions, can change the reactivity and provide different bonding sites for molecules [18]. Fundamental studies of metal growth on single crystal surfaces can add insight into the growth modes and structures observed in the field of metallic nanoparticles.

Prior to this study, real space characterization of Pt and Cu growth on Au(100) in UHV had not been reported. Angle-dependent XPS and LEED studies of Pt on Au(100) have indicated different growth modes: either layer-by-layer (Frank-van der Merwe growth) [19] or nanocrystallites (Volmer-Weber growth) [1], the latter study reporting that Pt lifts the Au(100) reconstruction at coverages above 0.5 ML. Similar disagreements about growth mode also exist for Pt on the Au(111) surface [20-23]. STM studies of Pt [23] and Cu [24] have been conducted at the liquid-solid interface on the unreconstructed Au(100) surface. Previous studies of Fe growth on the Au(100) surface have reported the formation of two dimensional islands growing along the direction of the surface reconstruction rows [8, 25], consistent with the results reported here. Cr growth on Au(100) has been studied by LEED and XPS [9], indicating lifting of the Au(100) reconstruction at sub-monolayer coverages; STM studies have been conducted but only on thicker (>2 nm) films of Cr on Au(100) [26]. The comparison of initial growth modes

for Pt, Fe, Cr, and Cu that we present here, particularly the observation of significantly different growth for Cu, has not been reported previously.

In this work, we use STM and XPS to study the growth of Pt, Cr, Cu, and Fe on the Au(100) surface. We demonstrate that each of these metals grows in flat nanoislands, which are rectangular in shape and oriented with the surface reconstruction rows. Second layer growth begins before completion of the first layer. In each case, the surface reconstruction is gradually “lifted” as coverage of the ad-metal increases until no evidence of the reconstruction remains above 0.5 ML of the ad-metal.

Experimental Methods

All experiments were performed in an ultra-high vacuum (UHV) system ($< 5 \times 10^{-10}$ Torr). One chamber contains the scanning tunneling microscopy (STM) system (SPM UHV 750, RHK Technologies). A separate but connected chamber contains an X-ray photoelectron spectroscopy (XPS) instrument (Mg/Al dual anode X-ray source XR-50 and electron energy analyzer PHOIBOS 150, SPECS GmbH) and a third connected chamber contains the electron beam evaporator for metal deposition. These chambers are interconnected allowing preparation and characterization of the samples without exposure to air.

The reconstructed gold (100) single crystal surface (Princeton Scientific) was prepared by repeated cycles of thermal annealing at 500 °C and argon ion sputtering at a sample temperature of 200 °C. Platinum (99.95% pure rod, Goodfellow), copper (99.99% pure rod, Goodfellow), and iron (99.95% pure rod, Goodfellow) were vapor deposited onto the surface using an electron beam evaporator (QUAD-EV-S Mini e-beam

Evaporator, Mantis Deposition Ltd.). Chromium (99.995% pure chips, Sigma-Aldrich) was vapor deposited from an aluminum oxide crucible using the same evaporator. XPS spectra were used to verify the cleanliness of the surface before deposition and to measure the surface coverage. To calculate their coverage, ad-metal intensities were compared to a previously determined single monolayer C 1s intensity for an organic film on the same Au(100) surface [27]. Au 4f intensities were also compared between experiments in case of detector intensity changes. A more detailed description of XPS coverage determination can be found in the Supporting Information.

The STM images were all acquired at room temperature using tunneling currents between 0.2 and 0.4 nA and bias voltages of 0.8 to 1.2 V. The tungsten STM tips were prepared by electrochemical etching. The microscope was calibrated using images of terephthalic acid on Cu(100), which has been well characterized [28, 29]. Image analysis was performed using the WSxM software [30]. Background subtraction was performed using global plane subtractions and/or line-by-line linear flattening. No smoothing or other image processing filters were used on the STM data.

Results and Discussion

Anisotropic Nanoisland Formation of Pt, Cr, and Fe

At low coverage (0.05-0.15 ML), Pt, Cr, and Fe form anisotropic, rectangular islands Au(100) surface (Figures 1a-1c). The long axis of the islands is parallel to rows from the hexagonal c(26×68) surface reconstruction of the Au(100) [31], which are

clearly imaged by the STM. The reconstruction rows are a physical corrugation of the topmost Au atom layer of around 0.2-0.3 Å (measured by X-ray reflectivity) [32] or 0.47 Å (calculation) [33]; we measure the corrugation to be 0.39 ± 0.12 Å by both STM and non-contact atomic force microscopy in our study and measure the spacing between the corrugation rows to be 1.35 ± 0.04 nm. This distance is consistent with previously reported values [8].

STM line profiles across the islands measure island heights of 2.48 ± 0.14 , 2.40 ± 0.15 , and 2.45 ± 0.13 Å for Pt, Cr, and Fe respectively, which are each slightly larger than the 2.24 ± 0.11 Å height of the Au step edges. These height profiles indicate that the islands are only one atomic layer thick (Figure 2), but do not show a significant trend with nearest neighbor distance (Table 1). The surface reconstruction row corrugation is imaged through the metal islands at low coverages. As the coverage is increased to ~0.3-0.4 ML, the number and size of the islands increases, but they retain their rectangular shape (Figures 1 and 3). STM images in a prior study [26] also found one atomic layer thick Cr islands; those islands had round shapes, likely due to the 300 °C annealing treatment performed during Cr film growth.

Figure 1. A series of STM images showing increasing Pt coverage. (a) 0.05 ML, (b) 0.1 ML, (c) 0.15 ML, (d) 0.3 ML, (e) 0.4 ML, and (g) 0.5 ML, where the reconstruction goes from being unperturbed in (a) to fully lifted in (f). Insets in each panel show a zoomed in view, from the same image in the panel, of the reconstruction lifting in regions of the surface between the metal islands. Each sample was annealed for 10 minutes at 170 °C.

Figure 2. Zoom in STM images of Pt (a), Fe (b), and Cr (c) islands. An average of 10 parallel line profiles taken across the islands are provided in (d), (e), and (f) for Pt, Fe, and Cr respectively. The reconstruction rows can be seen clearly, even through the ad-metal islands.

Lifting of the Surface Reconstruction

As the metal coverage increases up to 0.5 ML, regions on the surface can be seen where the reconstruction is partially lifted (Figures 1 and 3). That is, there are fewer reconstruction rows at each increasing coverage step. At low coverages, the presence of the reconstruction varies significantly across the surface, *i.e.*, the reconstruction is lifted locally around the ad-metal nanoislands above a certain critical size (about 10 nm long). This effect of a critical island size is likely due to an energetic competition between (a) the strain of small metal island growth on the reconstructed surface that would favor a transition to the unreconstructed surface and (b) the strain of the local grain boundary that would result from a mismatch at the boundary of a local unreconstructed region surrounded by reconstructed surface atoms. The former effect would scale proportionally

with the island area, while the latter effect would be proportional to the length of the island perimeter (proportional to the square root of the island area). The size of the island has to be large enough that the energy gain from lifting the reconstruction becomes thermodynamically favorable to overcome the high energy of the boundary. There is also likely a significant kinetic barrier to lifting the reconstruction, even at coverages where this transition might be favorable in a localized region. We would expect to see earlier transitions to lift the reconstruction if we annealed the surface, but this would simultaneously lead to significant sintering of the islands into much larger islands and makes the comparison to smaller islands impossible.

The reconstruction is fully lifted at a coverage of 0.5 ML Pt (Figure 1f), consistent with a prior LEED study [1]. Fe and Cr are also found to lift the Au(100) reconstruction after reaching a similar coverage of about 0.5 ML (Figures 3e and 3f).

STM images of Pt, Fe, and Cr show a striking difference in the shape of the metal islands that are present on the reconstructed Au surface (rectangular) compared to those on the un-reconstructed surface (square). The islands are rectangular on the reconstructed surface, presumably due to the anisotropy in the surface from the reconstruction rows. Interestingly, on the quasi-hexagonal reconstructed Au(100) surface, we do not observe hexagonal island shapes, but instead see rectangular island shapes; this would be consistent with a square atomic packing in the islands, which may have an epitaxial relationship to the reconstructed top layer of Au that parallels the interface between the top Au layer and the Au layer below. Islands on the non-reconstructed surface have a square shape (average aspect ratio ~ 1), as expected for isotropic, epitaxial 2D growth on an FCC (100) surface (square symmetry); this is illustrated in the histogram of length to

width aspect ratio of Pt islands at four different coverages (Figure 4). In this analysis “length” is always measured in the direction parallel to the reconstruction rows and “width” is measured in the perpendicular direction. When the Pt islands are measured at 0.1 or 0.3 ML (before the reconstruction is lifted), the length:width ratios range from 1-4, with an average of about 2. When the Pt islands are measured at 0.4-0.5 ML or above (after the reconstruction is lifted), the length:width ratios are distributed around one, indicating square islands (Figure 1f). This shift in metal island shape is observed for all of the metals studied and is most likely due to the corresponding change in gold surface structure: the anisotropic nature of the reconstruction rows favor adatom diffusion in one direction and lead to rectangular island shapes, but without the reconstruction, square islands are observed. Similar anisotropic growth has also been observed in related systems, such as Au deposited on Pt(100) [34] and Au deposited onto Au(100) [35], as well as in studies of organic adsorbates [36, 37].

Figure 3. STM images of Fe (left column) and Cr (right column) at increasing coverage on Au(100). The coverage of Fe or Cr is indicated in the panel label. Reconstruction rows of Au(100) are imaged across the surface at 0.1 ML of either metal, but fewer reconstruction rows are observed as coverage increases (panels c and d), and the reconstruction is fully lifted by ~0.5 ML (panels e and f).

Figure 4. A histogram showing the length:width ratios of Pt islands on Au(100) at increasing Pt coverage. “Length” is always measured in the direction parallel to the Au(100) reconstruction rows. For 0.1 ML, $N = 182$ with a total surface sampling of $125,000 \text{ nm}^2$; for 0.3 ML, $N = 123$ with a total surface sampling of $78,125 \text{ nm}^2$; for 0.4 ML, $N = 139$ with a total surface sampling of $62,500 \text{ nm}^2$; and for 0.5 ML, $N = 168$ with a total surface sampling of $78,125 \text{ nm}^2$. The dotted lines represent the island area weighted means for each coverage by color.

For each metal, second layer islands begin to form before the completion of the first layer. This growth mode was hypothesized for Cr based on LEED, angle-resolved photoemission, and work-function measurements [9], and also for Pt on Au(100) [19].

When we estimate the apparent coverage of the metal nanoparticles from the STM data, we find for each of these three metals that the apparent coverage in STM is higher than the coverage calculated from XPS (Figure 5). While some of this effect may be due to exaggerated particle sizes in STM images due to tip size (tip convolution effects), there

may also be some contribution due to surface alloying within the nanoparticles, so that the apparent size of the particles includes some volume occupied by Au atoms. This effect has been observed to varying degrees in prior studies of Fe growth on Au(100) [8, 25], Fe on Cu(100) [38], Cr on Au(100) [9, 26], and Au on Pt(100) [34].

Figure 5. A graph showing apparent coverage as imaged by STM vs. coverage calculated from XPS intensity. Pt is shown in red, Fe in green, Cr in blue, and Cu in purple. The black line indicates where the apparent STM coverage would equal the calculated XPS coverage.

Growth of Cu on Au(100)

The growth of Cu on Au(100) was found to differ significantly from the metals discussed above in several ways. The aspect ratio of the 2D Cu islands is significantly larger than for Pt, Cr, or Fe (Figure 6). At 0.3 ML coverage, the average area of Pt, Fe, and Cr islands are 17 nm², 19 nm², and 47 nm², respectively; Cu islands are significantly

larger (243 nm^2), indicating that the diffusion energy barrier is significantly lower for Cu than for the other three metals.

Figure 6. A series of STM images showing increasing Cu coverage. (a) 0.15 ML, (b) 0.3 ML, (c) 0.6 ML, (d) 1.2 ML, (e) 2.4 ML, and (g) 3.3 ML, where the reconstruction goes from being unperturbed in (a) to fully lifted in (f).

The difference between the apparent STM coverage and the coverage determined by XPS (Figure 5) is the most significant for Cu and deviates in the opposite direction compared to the other metals studied. The apparent coverage of Cu measured by STM is

noticeably lower than the coverage measured by XPS. This indicates that the area covered by Cu islands is smaller than expected due to some diffusion of Cu atoms into the Au. The idea of Cu mixing into the Au can also be seen in Figures 6d-6f, where the coverage of Cu does not appear to be greater than 1 ML, and it is difficult to see the increase in coverage between each image. According to bulk binary phase diagrams, Cu is the most prone (of the four metals studied) to formation of a solid solution in Au [39-42], showing bulk alloying behavior near room temperature, which is consistent with the enhanced Cu-Au mixing observed in our system. The low temperature used in this study (room temperature) likely limits the solvation to the top surface layers so that the Cu still contributes significantly to the XPS signal. The other three metals alloy with Au at much higher temperatures, above 200 °C. Also, since the experiments presented here were conducted at room temperature, there may be significant kinetic limitations to alloying.

Cu growth is significantly different from the three other metals studied in that (a) coverage determined by XPS measurements is significantly higher than that from STM experiments, indicating that much of the Cu is alloying into the top layers of the surface rather than staying on top of the surface, (b) the Cu island size is significantly larger at comparable coverages, and (c) much higher (XPS) coverage of Cu is needed to lift the Au(100) reconstruction. When Cu coverage is high enough to lift the reconstruction in local regions of the surface (1.2 ML), the Cu islands are much larger than they were for the other metals (compare Figs. 1, 3, and 6). Based on the discussion above about the relative strain of the reconstruction vs. local unreconstruction and in combination with the XPS signal indicating much higher coverage than STM, this indicates that the Cu content of these islands may be low at the initial stages of growth and that the coverage

may need to reach this 1.2 ML point for these islands to contain enough Cu atoms to lift the reconstruction. The reconstruction is not fully lifted until a coverage of 3.3 ML of Cu, much higher than the 0.5-0.6 ML needed for Pt, Cr, and Fe. If Cu alloying or bulk diffusion in Au is relatively facile, it may be possible for the Au atoms to mix into the islands observed on the surface, which would also be consistent with the large island size as the Au self-diffusion rate could be high compared to the other metals. High Au content in the islands would also account for the higher Cu coverage required to lift the surface reconstruction: if the top layer is still largely Au atoms, the reconstruction would persist. (Note that it is not possible in the STM images to distinguish whether we are imaging the reconstruction rows through an island sitting on top of them or whether we are imaging reconstruction rows within the island itself.)

Each of the metals studied has a higher surface energy than the Au(100) surface itself (Table S2) [43], so the flat morphology of the nanoislands (wetting) indicates a favorable interfacial interaction between the ad-metal and the Au surface [44], which may be related to the relief of the surface reconstruction.

Table 1. Nearest neighbor distances, d , for (100) faces of the metals used in this study [45]. For BCC metals (Cr, Fe), this is the lattice constant. For FCC metals (Au, Pt, Cu), this is the lattice constant / $\sqrt{2}$. The right column of the table shows the epitaxial match to Au(100).

Metal	d (Å)	d / d_{Au}
Au	2.884	
Cr	2.885	1.000
Fe	2.867	0.994
Pt	2.774	0.962
Cu	2.556	0.886

The relative sizes of the adsorbate metal atoms and the surface atoms could also influence their growth, as has been seen in the growth of metal nanoparticles [14, 46]. The nearest neighbor distances for the metals discussed in this paper are shown in Table 1. Au, Cr, and Fe are nearly identical in (100) nearest-neighbor distance. Pt shows only a 4% mismatch, while Cu has a 12% mismatch to Au, likely a contributing effect in Cu growth being so different from the other metals. Cu growth on unreconstructed Au(100) has previously been reported to form epitaxial layers with an excellent lattice match in a BCC structure [24]. Growth of a similar fashion was also seen on the Ag(100) surface [47].

Conclusion

Using real-space STM measurements, our results indicate that Pt, Fe, Cr, and Cu metals grow in a flat, layer-by-layer fashion almost up to completion of the first layer. Initial growth of Pt, Fe, and Cr on Au(100) are very similar in forming rectangular, flat nanoislands. Cu also forms flat, rectangular islands, but these are much larger than for the other metals and require a higher coverage to lift the reconstruction, likely due to mixing of the Cu into the Au surface. The rectangular growth along the reconstruction rows is due to the anisotropic nature of the reconstructed Au(100) surface. The gradual lifting of the Au(100) surface reconstruction with increasing coverage of any of these four metals was observed by STM imaging. The comparison of multiple metals to one another in this fashion, while not commonly done, is an effective way to learn how different metals behave on the same surface. This information provides valuable insight into metal on

metal growth to aid our understanding of such systems in bimetallic nanoparticles or heterogeneous catalysis. In future studies, it may be helpful to conduct low-energy electron diffraction (LEED) experiments, if they could be done with sufficient sensitivity to resolve the atomic packing structure within the islands at low coverage. This could provide integral information complementary to the local STM structural characterization presented here.

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Graphical abstract

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