Cobalt growth on two related close-packed noble metal surfaces

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Received 13 July 2006; accepted for publication 14 February 2007
Available online 24 February 2007

Abstract

We report on scanning tunneling microscopy (STM) studies of submonolayer growth of cobalt on the close-packed (111) surfaces of Au and Ag. Both substrates belong to the category of noble metals, and they both exhibit a lattice misfit of ∼13% with respect to the (0001) plane of Co. However, whereas the Au(111) surface reconstructs into the rather complex herringbone structure that disperses the cobalt into nanoclusters, the Ag(111) surface does not reconstruct in its clean state, and the surface dispersion of Co on this surface is therefore different. For Ag(111) at temperatures ranging from 160 to 200 K and for Au(111) at room temperature, the Co growth is three-dimensional starting with double layer islands followed by additional single layers. For both the Co/Au(111) and the Co/Ag(111) system, a Moiré pattern develops in the first bilayer of the Co islands, indicating an epitaxial but not commensurate growth. For Co islands with more than two layers, the subsequent layers are commensurate with the lower Co layers in the islands, but exhibit a decreasing corrugation of the Moiré pattern as observed in STM images. Despite a difference in the Moiré lattice constant and rotational angle, we show that the cobalt lattice constant is the same on both surfaces. We furthermore relate defect nucleation on the herringbone reconstruction on Au(111) to defect nucleation on steps on Ag(111).

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Keywords: Scanning tunneling spectroscopies; Growth; Nucleation; Cobalt; Gold; Silver; Low index single crystal surfaces

1. Introduction

The studies of Co nanostructures formed on weakly interacting substrates are attracting special attention owing to the potential use of Co in high-density, magnetism-based data storage media [1]. A key issue in this application is the development of highly disperse and well-controlled Co nanocluster arrays, which should be stable under the harsh conditions offered by the ambient atmosphere and the elevated temperatures to which they are exposed in electronic applications. Co/Au(111) is of particular interest in this context because of its role in the study of perpendicular magnetization in thin magnetic films, which makes it a promising candidate for magneto-optical technology [2,3]. Since the first scanning tunneling microscopy (STM) investigation on the growth of Co on Au(111) in 1991 [4], interest has not diminished. For instance, it has been shown that the 2 ML high islands are super-paramagnetic above 30 K [5], and for Co films grown at 30 K an in-plane magnetic anisotropy has been observed, even for a thickness as low as 1.7 ML [6].

Here we study the growth of Co islands on two close-packed noble metal substrates, the Au(111) and Ag(111) surface, by means of STM. We characterize arrays of Co islands grown on the reconstructed Au(111) surface at room temperature and at different coverages, and then characterize the growth of cobalt islands on Ag(111) terraces and at step edges. Thermal and hyper thermal Co growth on Ag(001) has previously been investigated by STM [8–10], but no study of Co/Ag(111) with STM has been published so far. Previous studies have shown that deposition of cobalt on one monolayer Ag islands on
Ru(0001) at 343 K leads to alloyed Co–Ag monolayer islands [11]. We find that the same surface alloy mechanism is present for Co growth on the Ag(111) system at room temperature. The interfacial intermixing reaction [12] can be reduced or even suppressed by depositing cobalt at low temperature as reported for cobalt on Cu(111) [13]. To compare with the Co/Au(111) system for which no similar surface alloying occurs, we therefore deposit cobalt on Ag(111) at a temperature between 160 K and 200 K, and at this substrate temperature we detect no alloy formation.

2. Experimental section

The experiments were performed in a standard ultrahigh vacuum (UHV) chamber with a base pressure below $10^{-10}$ mbar. The UHV system is equipped with a home-built high-resolution Aarhus-type scanning tunneling microscope [14] as well as equipment for Auger electron spectroscopy (AES) for chemical analysis and a quadrupole mass spectrometer (QMS) for residual gas analysis. The Au and Ag single crystals were prepared by sputter cleaning cycles using 1.5 kV Ar$^+$-ion bombardment followed by annealing to 900 K for 10 min.

Submonolayer amounts of Co were deposited by use of an e-beam evaporator (Oxford Applied Research, EGCO4) capable of evaporating refractory materials with a high degree of precision in the flux. Prior to the experiments, the evaporator was loaded with cobalt (purity 99.99%) supplied in the form of rods with a diameter of 2 mm. The source material was thoroughly outgassed until evaporation under UHV conditions resulted in only a minute increase in background pressure to about $4 \times 10^{-10}$ mbar. The desired evaporation rate was reached by heating the target material by 2 kV electron bombardment. Between 0.05 ML and 0.15 ML cobalt was evaporated at a fixedand reproducible rate below 5 monolayer/min.

3. Clean Au(111) and Ag(111) surfaces

Both noble metals, Au and Ag, belong to the class of face centered cubic metals with a fully occupied $d$ band and have near-equal lattice constants with values of 0.288 nm for the nearest-neighbor distance on Au(111) and 0.289 nm for Ag(111), respectively. However, whereas the Ag(111) surface terminates by an ideal (111) face, the Au(111) surface reconstructs into the characteristic “herringbone” pattern [7]. Fig. 1a shows a large-scale STM image of the reconstructed Au(111) surface. In brief, the reconstruction is characterized by a $(2 \times \sqrt{3})$ unit cell in which the gold atoms in the topmost surface layer are compressed gradually up to $\sim$4.2% along the [110] direction. Due to this contraction, 23 surface gold atoms are distributed among 22 bulk sites in the unit cell, resulting in alternating fcc and hcp stacking regions which run parallel along the [112] direction. Brighter dislocation lines of Au atoms located near bridge positions are separating the fcc and hcp areas, as shown in the atom-resolved image in Fig. 1b. Long-range elastic interactions introduce domain boundaries, approximately every 14 nm [15]. At these boundary lines, the domains bend by alternating $\pm 120^\circ$, and a zig–zag pattern often referred to as the “herringbone” reconstruction forms. On a length scale even larger than the image size of Fig. 1a, three rotational co-existing domains appear to relieve the surface stress isotropically.

At the domain walls, where two ridges join, two types of elbows are observed, called $x$ and $y$ (see Fig. 1a). The elbows, which are associated with a surface dislocation, act as the preferential nucleation site for the epitaxial growth of a number of different metals or molecules on the Au(111) surface [16–18]. The surface thus provides a well-ordered periodic network of nucleation sites. It is noted that the average misfit is approximately 10% for the Co(0001) ($a = 0.251$ nm) on the gold surface, but locally it is smaller than 10% near the domain boundaries separating the fcc- and hcp-domains. In the following sections we will present the experimental results for the growth scenarios of Co on Au(111) and Ag(111) separately and then later discuss similarities and differences.

4. Cobalt growth on Au(111)

To investigate the growth of Co on the Au(111) we have systematically varied the deposition rate and total coverage of Co and studied the surface morphology by STM. Within a range in the deposition flux corresponding to 0.5 ML/min to 5 ML/min, no significant differences are found for the Co island morphology for the used rates of deposition, and we therefore conclude that the surface mobility is sufficiently high at room temperature to reach an equilibrium situation at all investigated coverages in this study. The panels in Fig. 2a–d show STM images representing the
growth of Co on Au(111) at four different coverages corresponding to 4%, 12%, 28% and 70% of a ML, respectively. In all these cases we observed that Co nucleates at the elbows of the Au(111) reconstruction [4,17], resulting in the formation of very regular arrays of islands (Fig. 2), the location and spacing of which are determined by the herringbone structure. In general, we observed that nucleation starts later on $x$-elbows as opposed to the $y$-elbows (see also Fig. 1b). It was previously shown that nucleation and growth of Co at the defect sites are initiated by an exchange process of Au at the elbow sites with the Co adatoms [4]. The observation that nucleation starts at $y$-elbows suggests that different energies are associated with the exchange process of Co at the two different ($x$ and $y$) elbow dislocation sites. The images also show that the original double-ridge Au reconstruction remains unperturbed even at high Co coverages (Fig. 2c).

In addition, we also observed in the STM images that the Co growth does not start simultaneously for all islands. Specifically, the image in Fig. 2a recorded at a coverage of 4% shows that a number of islands have already reached a volume of about 1 nm$^3$ corresponding to the average size of islands at much higher Co coverages (i.e. 28% in Fig. 2c), whereas some nucleation sites do not even have a Co nucleus. The bimodal distribution is reminiscent of a bimodal distribution found in Monte Carlo simulations for nucleation on regularly spaced impurities [19]. This growth scenario was shown to occur for a flux to diffusion ratio that would lead to a lower nucleation density on a defect free surface than the one forced by the defect density. We thus conclude that for the particle flux used here, the homogeneous island density would be smaller than induced by the elbows of the reconstruction.

However, despite the time-dependent nucleation probability, the islands grow at higher coverages into polygonal islands with a narrow size distribution. This result is expected from calculations for defect nucleation sites in a regular array [20]. At 28% coverage more than 90% of the islands in the elbows have a volume of between 1.3 and 1.9 nm$^3$. The low fraction of smaller islands that do not belong in this category are typically nucleated outside the elbow regions.

At the higher coverages of 28% and 70% (Fig. 2c and d) the islands have adopted a clear equilibrium shape exhibiting a hexagonal morphology with straight edges oriented along the six main (110) crystallographic directions. We note that the islands prefer to grow in the direction of the reconstruction lines over coalescing (Fig. 2d). The islands predominantly show a threefold symmetry consisting of long and short edge segments belonging to different facets aligned opposite to each other. The preferred stacking and uniform orientations of the Co islands are clear indicatives of epitaxial growth on the gold surface [4]. In addition, the Co islands shown in the STM image in Figs. 2c and d are clearly seen to be oriented with two preferential orientations on the substrate rotated by 180$^\circ$ relative to each other. The orientation is seen to depend on the type of elbow dislocation site from which the nucleation started, and in a row with $y$-elbows the triangles are placed on the fcc-domains pointing predominantly towards the reconstruction line with higher curvature. In a row with $x$-elbows, the triangles are placed on the hcp-domain and point in the opposite direction. Table

![Fig. 2. Four STM images of the nucleation and growth of Co on Au(111). All STM images were recorded under similar conditions and tunneling parameters ($V_t = 1.3–1.8$ V, $I_t = 0.4–0.6$ nA). The Co coverages are: (a) 4% ML: The STM image shows an early stage of nucleation of Co at elbows of reconstruction. Rows with $x$ and $y$ elbows, respectively, are indicated at the right-hand side of the image. The histogram shows the volume distribution of Co islands; islands with $V < 1$ nm$^3$ are those not nucleated at elbows. (d) 70% ML: No coalescence between Co islands are seen even at very high Co coverages. The inset is a zoom-in showing a Moiré pattern on Co islands. The histogram to the right shows the height distribution, revealing two, three, and four layer Co islands.](image-url)
orated with three-dimensional Co islands with a density of 5% of a ML of Co deposited at 160–200 K. The STM images show that pre-existing atomic silver steps have become dec- 

5. Co growth on Ag(111)

Table 1
Percentage of islands in different stacking deduced from the orientation of the triangle at the two types of elbows on Au(111)

<table>
<thead>
<tr>
<th>Elbow-type</th>
<th>x (%)</th>
<th>y (%)</th>
</tr>
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<tbody>
<tr>
<td>Major orientation</td>
<td>66</td>
<td>55</td>
</tr>
<tr>
<td>Minor orientation</td>
<td>11</td>
<td>23</td>
</tr>
<tr>
<td>Unidentified</td>
<td>23</td>
<td>26</td>
</tr>
</tbody>
</table>

1 shows the percentage of stacking deduced from the orientation of the triangular islands. Non-identified stackings result from perfectly hexagonal shaped islands. Thus, the same stacking with respect to the first surface layer is preferred in both domains and on both elbow types. This scenario resembles the growth of Ir islands on Ir(111), which was previously studied by STM at different temperatures. For the Ir islands, the stacking fault probability was successfully described by a kinetic model for stacking fault nucleation [21]. For Ir/Ir(111) the stacking fault energy of 80 meV leads to a comparable ratio between the different orientations as found for Co on Au(111) here. This finding suggests a stacking fault energy of comparable magnitude for Co/Au(111).

The height of the Co islands is estimated in STM images for the experiments performed at the highest coverage (70% ML), and a histogram is shown in Fig. 2d. The histogram reveals three peaks located approximately at 0.43 nm, 0.62 nm and 0.82 nm. Co(0001) has a monolayer height of 0.205 nm, and therefore we conclude that the first peak at 0.43 nm, which contains the majority of the clusters, corresponds to bilayer Co clusters. The subsequent peaks reflect three-layer high islands at 0.62 nm and four-layer high islands at 0.82 nm.

A zoom-in on the top facets of the Co islands reveal a clear Moiré pattern (Fig. 2d, inset). The corrugation of the Moiré pattern is measured to be ~70 pm on the bilayer, ~50 pm on the third layer, and still visible on the fourth layer. The decreasing corrugation at same Moiré lattice constant suggests that the subsequent layers have the same lattice constant as the first bilayer. The periodicity of the Moiré pattern is estimated in line scans on a number of islands and measured to be (2.6 ± 0.15) nm. The STM images furthermore reveal that the step edges of the Co islands and the close-packed directions of the Moiré pattern are both oriented along a closed-packed ((110)) direction of the Au(111) surface. We determined the island orientation to be 2° ± 3° with respect to the (110) direction. Using the Moiré formula for a rotated hexagonal overlayer (\(d_{\text{Moiré}} = a_1 \cdot a_2 / \sqrt{(a_1^2 + a_2^2) - 2a_1a_2\cos \alpha} \)) [22] for this range of angles, we determine possible lattice constants of the cobalt of \(a_{\text{Co}}^x = (0.32 \pm 0.01) \) nm or \(a_{\text{Co}}^y = (0.26 \pm 0.01) \) nm.

5. Co growth on Ag(111)

Fig. 3a shows STM images of the Ag(111) surface with 5% of a ML of Co deposited at 160–200 K. The STM images show that pre-existing atomic silver steps have become decorated with three-dimensional Co islands with a density of 0.2 cluster/nm. In addition, on larger terraces small Co islands are observed with a height corresponding to two or more Co layers. The growth continues from these nucleation centers onto the terrace (Fig. 3b and c). Thus, a quasi-one-dimensional finger-like growth seems to be preferred over coalescing. The growth rate at the step edges and the size of the islands on the terraces depend on terrace width (Fig. 3d), showing that the steps act as impermeable sinks of the Co adatoms. This points to a very different behavior of the Co adatoms, when reaching a cobalt or a silver step, because some transport over a Co step edge is necessary in order to form the observed three-dimensional islands.

The Co islands on the terraces have a wide size distribution ranging from a few nm\(^3\) up to ~400 nm\(^3\) at 0.5 ML with no particular size preference (Fig. 4a). The largest islands are thus estimated to contain ~30000 atoms,\(^1\) indicating a substantial mobility of cobalt even at the low deposition temperature. The heights of the individual layers of the Co islands are 0.38 nm, 0.58 nm, and 0.80 nm (Fig. 4b) corresponding to a bilayer of Co(0001) followed by either one or two single close-packed Co layers. The same height distribution is found for the islands grown from the step edges.

\(^1\) The number of atoms in the islands were estimated by multiplying the average area by the packing density of hexagonal Co in the basal plane. The number represents an upper limit, due to the convolution with the tip.
The STM images in Figs. 4c and d show a clear superstructure associated with a Moiré pattern. The individual Co layers are all observed to exhibit the same Moiré pattern corresponding to a lateral periodicity of \((2.3 \pm 0.10)\, \text{nm}\). While the Moiré pattern shows no measurable difference in lateral periodicity as a function of the height, the corrugation decreases in the 3rd and 4th layer compared to the first bilayer (see STM image in Fig. 4c). The corrugation of the Moiré pattern in the layers was measured to be 50 pm, 40 pm, and 25 pm, successively. Interestingly, we also find a difference in the apparent height between the neighboring hollow sites in the Moiré pattern (20 pm in the example shown in Fig. 4d). This finding is reminiscent of different apparent heights of hcp and fcc sites in atomic resolution images [23].

On some islands a rotation of the Moiré pattern is observed in different parts of the islands (see e.g. Fig. 4d) indicating the coalescence of nuclei with different orientation. The different domains in the Moiré pattern of the Co islands on Ag(111) are found to be rotated by \(14^\circ \pm 2^\circ\) against each other, which points to a rotation of the Co lattice with respect to Ag(111) by \(\approx 7^\circ\). With this rotation, possible lattice constants of Co of \(a_{\text{Co}}^+ = (0.32 \pm 0.01)\, \text{nm}\) or \(a_{\text{Co}}^- = (0.27 \pm 0.01)\, \text{nm}\) are calculated with the Moiré formula.

The islands at the step edges are similar in size to the islands on the Au(111) surface. To increase the monodispersity of the island distribution, the silver step density can be enhanced artificially by sputtering the surface at elevated temperature prior to the Co deposition (Fig. 3e) [24]. This process leads to vacancy islands and thus to an enhanced step density, which helps to disperse the cobalt mimicking a catalyst for future gas interaction. Cobalt island growth on the artificially created steps is observed to be equivalent to the one at the natural steps with a 10% difference in nucleation density between A-type and B-type step edges (Fig. 3e). The length of the fingers growing within the vacancy island depend on island size, i.e. the material that is deposited within the island.

6. Similarities and differences between Co growth on Au(111) and Ag(111) surfaces

The initial nucleation scenarios are very different for the two close-packed surfaces. On Au(111) it is well established that the nucleation is heterogeneous and initiated by an atom exchange process at the elbow sites. On a perfect Ag(111) the nucleation is homogeneous, resulting in a much smaller nucleation density even at much lower temperature. Despite of the different nucleation scenarios, the Co islands grow qualitatively in a similar way in the submonolayer regime on the two surfaces: First, Co bilayer islands grow with an orientation of the Co(0001) facet in parallel to the surface. The islands are incommensurate with respect to the surface, which is revealed by the existence of a Moiré pattern. This initial growth process is followed by a commensurate homo-epitaxial Co growth in subsequent layers of the islands.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison of Co islands on the two surfaces</th>
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<tbody>
<tr>
<td></td>
<td>Au(111)</td>
</tr>
<tr>
<td>Bilayer height (nm)</td>
<td>0.43</td>
</tr>
<tr>
<td>Trilayer height (nm)</td>
<td>0.62</td>
</tr>
<tr>
<td>Four layer height (nm)</td>
<td>0.82</td>
</tr>
<tr>
<td>Moiré lattice constant (nm)</td>
<td>2.6</td>
</tr>
<tr>
<td>Moiré angle (°)</td>
<td>2</td>
</tr>
<tr>
<td>Moiré corrugation bilayer (pm)</td>
<td>70</td>
</tr>
<tr>
<td>Moiré corrugation trilayer (pm)</td>
<td>50</td>
</tr>
<tr>
<td>Moiré corrugation four layer (pm)</td>
<td>–</td>
</tr>
<tr>
<td>Deduced lattice constants of Co (nm)</td>
<td>0.32</td>
</tr>
<tr>
<td></td>
<td>0.26</td>
</tr>
</tbody>
</table>

For clarity error bars are not repeated here.
Also quantitatively, the results are very similar (see Table 2). Despite a difference in Moiré constant and a (slightly) different rotation angle, the two possible lattice constants of the Co islands are identical within the error bar. It is not immediately clear whether the Co lattices distances are given by the plus or minus solutions from the Moiré formula (\(a_{\text{Co}}^+\) and \(a_{\text{Co}}^-\), respectively). However, we tentatively suggest that the lowest values are correct, since they represent a Co lattice with a low strain.

The absolute heights of the islands are different from that expected for a bulk Co lattice, indicating a vertical relaxation. In absolute heights, the Co islands are slightly different on the two surfaces being by 50, 40, and 20 pm smaller on Ag(111) than on Au(111) for the bilayer, the third, and the fourth layer, respectively. The difference in apparent height is especially pronounced for the bilayer with more than 10% difference between Au(0.43 nm) and Ag(0.38 nm). Calculations are needed to shed new light on this difference, but for the moment we suggest that the reason lies in the different orientations of the Co islands with respect to the close-packed directions of the substrate lattice. This difference might also be responsible for the less straight island edges on Ag(111) as compared to the ones on Au(111).

7. Conclusion

In conclusion we have found a hexagonal growth of Co on both Au(111) and Ag(111) with a lattice mismatch resulting in a Moiré pattern. Furthermore, we have shown that on both surfaces a high surface-to-volume ratio of the deposited material is easily achieved. The attraction of depositing Cobalt on Au(111) lies in the fact that monodispersed islands, which, as we have shown, do not or hardly coalesce to larger islands, can be produced. The growth from defect nucleation at the step edges of Ag(111) shows a similar behavior, in that the islands avoid coalescence at a comparable size (5 nm as opposed to 7 nm). This avoidance may be explained by the tensile strain induced by the strained growing island into the substrate as has been calculated for Co on Cu(111) and shown there to enhance the adatom diffusion barrier towards the island considerably [25]. On an adequately sputtered or a vicinal surface it is thus possible to induce cobalt islands of similar size and of high-density, which could be used in future for magnetic measurements similar to the measurements on Au(111).

Acknowledgements

The work was financed in part by the Danish Research Councils through a Grant to iNANO, the Velux Foundation, and the Danish National Research Foundation. J.V.L. acknowledges financial support from the Carlsberg Foundation.

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