

Absence of ferromagnetic order in ultrathin Rh deposits grown under various conditions on gold

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(Received 17 July 2000; revised manuscript received 13 February 2001; published 7 August 2001)

Growth and magnetism of Rh films in the thickness range between 0 and 6 monolayers (ML) on Au(111) have been investigated over a wide range of coverages and deposition temperatures by means of variable temperature UHV-STM, Auger spectroscopy, and *in situ* Kerr effect measurements. Contrary to theoretical predictions, no ferromagnetism has been detected by the Kerr effect, irrespective of the film thickness and the growth conditions. This disagreement may be due to invalid theoretical predictions, however it is most probably due to the experimental impossibility to grow a perfectly uniform film: surface intermixing in the first stage of growth is observed. Even upon low temperature deposition (at 30 K and above), a Rh-Au surface alloy forms, followed by a Rh layer-by-layer growth.

DOI: 10.1103/PhysRevB.64.094410

PACS number(s): 75.70.Ak, 61.46.+w, 78.20.Ls, 61.72.Cc

I. INTRODUCTION

One of the most fascinating results in the field of magnetism of low dimensional systems is the discovery that magnetic entities can be built out of materials such as transition metals from the end of $4d$ and $5d$ series that are not magnetic in the bulk state.¹ For these metals, magnetism with a sizeable magnetic moment per atom has been predicted by several theoretical studies, either for isolated clusters,² for deposited small clusters on silver,^{3,4} in epitaxial ultrathin layers deposited on noble metal,^{5,6} or on Rh(001) and Pd(001) surfaces.⁷ These calculations either use *ab initio* approaches based on the local spin density approximation (LSDA) or other methods of electronic structure calculations as for example the self-consistent tight-binding methods. Experimentally, the most striking result has been obtained from molecular beam experiments on free clusters in which Rh clusters containing between 9 and 30 atoms have been found magnetic.⁸ From weak localization and anomalous Hall effect measurements,⁹ it is anticipated that very small Rh clusters (atom pairs) on Au, corresponding to a coverage of only a few percents of a monolayer, might bear a finite magnetic moment (about $0.1 \mu_B$). Recently, magnetic dichroism has been measured at the Rh(100) surface,¹⁰ while Rh clusters on graphite have been found nonmagnetic by the same technique.¹¹

In this paper we deliberately focus on supported Rh deposits and on their topographic characterization. Among the theoretical studies cited above, some have predicted magnetic ordering for one monolayer (1 ML) of Rh on Au(100) and Ag(100) with a magnetic moment per Rh atom of about $1.0 \mu_B$ and $0.6 \mu_B$, respectively.^{5,6} Despite many efforts, ferromagnetic order was never observed experimentally for the Rh monolayer.^{9,12} While the former experimental results have been obtained by MOKE (Ref. 12) without detecting any ferromagnetism, a somewhat different approach was proposed later. Li *et al.*¹³ attributed the splitting of the $4s$ level in their UPS spectra to the presence of a magnetic moment. However, many nonmagnetic effects, such as charge transfers, could explain this splitting.¹⁴ The reason for the negative results was attributed to the inability of experimental

techniques to produce the ideal monolayer configuration. As a matter of fact, Volmer-Weber growth has been observed at room temperature (RT) on Rh/Au(111) by STM.¹⁵ One also often advocates that interface mixing could be at the origin of the absence of ferromagnetism. Therefore some theoretical studies have been done to characterize magnetism in various stages of diffuse interfaces. They show that for bilayer ordered surface alloys and diffuse interfaces for Rh/Ag(001), the magnetic moment vanishes.^{4,16} For a Ag/1MLRh/Ag(001) sandwich, the magnetic moment is reduced by a factor of two with respect to the uncovered perfect Rh monolayer on the Ag(001) surface ($1.09 \mu_B$).^{4,6} Turek *et al.* showed that, for Rh and Ru on silver, interfacial diffusion strongly reduces the local magnetic moments.¹⁷

One way of growing very thin structures is to exploit the low temperature growth kinetics which allows us to grow very small, monolayer-thick clusters with a high surface density, even on systems that potentially like to grow 3D. As a matter of fact, low temperature growth has been shown to be quite successful for growing small particles of Co ($N < 20$ atoms) on Au(111) by MBE at a substrate temperature of 30 K.¹⁸ These small Co clusters are coupled magnetically and show long-range magnetic order. In this work, we explore the low temperature growth conditions and the magnetism of Rh on Au(111). Our results, however, show that, contrary to cobalt, Rh atoms undergo exchanges with the substrate even for temperatures as low as 70 K, forming a surface alloy. In the following, we first report on the MOKE results for 300 K and 30 K deposition. Then we discuss the STM images recorded for the same temperatures. For the low temperature deposited films, we analyze the effect of annealing up to RT. In any cases, no ferromagnetism has been detected.

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) chamber at a base pressure of 1.10^{-10} mbar. It contains a variable temperature scanning tunneling microscope (STM), a low energy electron diffraction (LEED) optics, also used as a retarding field analyzer for chemical characterization, and an *in situ* electromagnet (maximum field 65 mT) for magneto-optical Kerr effect (MOKE) measurements. The sample is coupled to a helium flux cryostat working at tem-

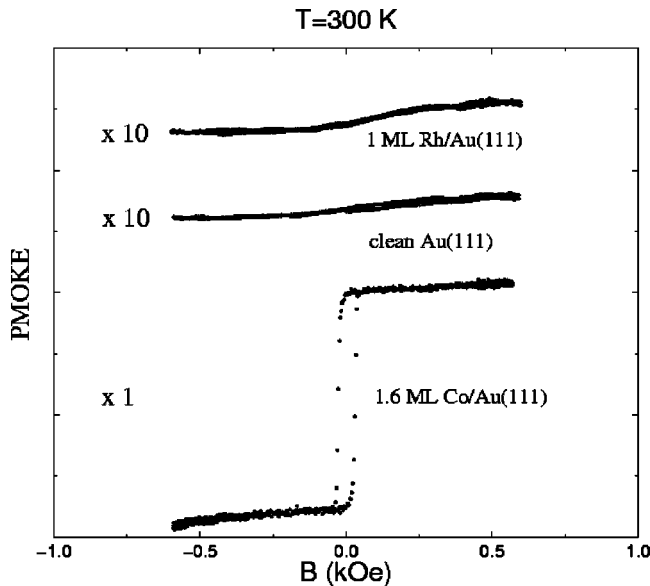


FIG. 1. Polar Kerr signal for 1 ML Rh/Au(111) grown and measured at 300 K. The polar Kerr signals of clean gold and 1.6 ML Co/Au(111) at 300 K are shown for comparison. The signal averaging of Rh and bare Au(111) was 10 times higher than for Co. The Rh and bare gold signals have been magnified by a factor of 10 to evidence the absence of hysteresis.

peratures down to 30 K. The experiments are performed on a gold single-crystal substrate previously cleaned by Ar^+ ion bombardments (1 keV) and annealed at 1000 K for a few seconds. These operations are repeated before each run in order to remove the previous rhodium adlayers. The cleanliness of the surface is checked by both Auger electron spectroscopy (AES) and STM. Atomically flat terraces, about 200 nm wide, separated by monoatomic step edges, are currently obtained. The elbows of the $(22 \times \sqrt{3})$ reconstruction of Au(111) are very sensitive to adsorbates, that are revealed by STM. In our experiment, no signs of contamination could be observed after cycling to low temperature. Rhodium is evaporated from a high-purity rod by electron bombardment and deposited onto the gold (111) surface at a rate of 0.18 ML min^{-1} . The rhodium evaporation cell is equipped with a flux monitor calibrated by STM and cross-checked by AES. MOKE measurements, in both polar and longitudinal geometries, are performed on Rh films between 0 and 6 ML, deposited either at room temperature, or 30 K and analyzed between 30 K and 300 K.

III. RESULTS AND DISCUSSION

A. MOKE measurements

For all films deposited at RT, in the thickness range between 1 and 4 ML, no magnetic Kerr signal is observed, neither in the longitudinal, nor in the polar geometries. In the longitudinal configuration, only one arbitrary in plane direction was tested since a threefold symmetry of the anisotropy is expected due to the formation of cluster rows (see Sec. III B). Figure 1 shows the Rh signal for 1 ML Rh deposited on Au(111) at 300 K. As shown in the same figure, the signal from the bare Au(111) surface is not significantly different

from the one of the Rh films. For comparison, Fig. 1 also shows a hysteresis loop taken at RT, in the polar configuration for 1.6 ML of Co on Au(111). Signal averaging in the case of Rh is 10 times higher than for Co. In addition, the Rh signal has been amplified by a factor 10 in Fig. 1, to show the absence of hysteresis. As a consequence we conclude that the RT deposited Rh films are not ferromagnetic.

Rh films deposited at 30 K were analyzed in two ways. First, the Kerr signal was monitored continuously in the longitudinal and polar geometries during the growth at low temperature for films between 0 and 2 ML. Second, Rh films deposited at 30 K of a given thickness (up to 6 ML) have been followed during annealing to RT. The Kerr signal is measured as a function of the annealing temperature in the polar and longitudinal geometries. No magnetic Kerr signal versus applied magnetic field has been measured within the detection limit, whatever the coverage of Rh. Consequently, no ferromagnetic order is obtained for Rh on Au(111) at low temperature. Our results are consistent with all other experimental data on Rh deposited on a gold surface, showing a lack of ferromagnetic order.^{9,12}

It must be emphasized that the Kerr technique should easily allow the detection of a signal 10 to 20 times smaller than the one obtained for 1.6 ML Co in Fig. 1. Since the Kerr sensitivity depends on the spin-orbit coupling, Rh is expected to be even more favorable than Co. Therefore magnetic moments in the order of 0.1 to $0.2 \mu_B$ per atom should be detectable, provided the film is magnetically saturated. Calculated magnetic moments per atom are predicted to be in the range $0.6\text{--}1.0 \mu_B$ (Refs. 5 and 6) for a Rh monolayer on Ag or Au substrates. Therefore the lack of hysteresis in our MOKE measurement confirms that the Rh monolayer on Au is not ferromagnetic over a wide range of growth parameters. We cannot exclude, however, the presence of superparamagnetic clusters at low Rh coverages. Such clusters would be saturated only by magnetic fields in the tesla range, inaccessible for our electromagnet. Ferromagnetism with a high coercive field (H_c) is less probable, since upon the superparamagnetic-ferromagnetic transition, the hysteresis loops first appear with a vanishingly small H_c . Also, it is reasonable to assume that 30 K is a low enough temperature to see ferromagnetism, if it is there. From known values on ultrathin films of ferromagnetic materials, a Curie temperature of a few 100 K is expected.¹⁹

B. Growth mechanism

In this section, we try to further our understanding of the negative magnetic results by studying in detail the growth process of Rh on Au(111) surfaces with STM at 300 K and 30 K. First, we recall briefly the peculiarity of the Au(111) surface reconstruction because of its influence on the growth of Rh at RT. Second, we study low temperature growth and the influence of annealing.

STM measurements at 300 K

The clean surface of a Au(111) single crystal is a close-packed surface and shows a particular $(22 \times \sqrt{3})$ reconstruction.²⁰ It presents zigzag patterns which separate alternately hcp and fcc (wider) domains. The domain walls

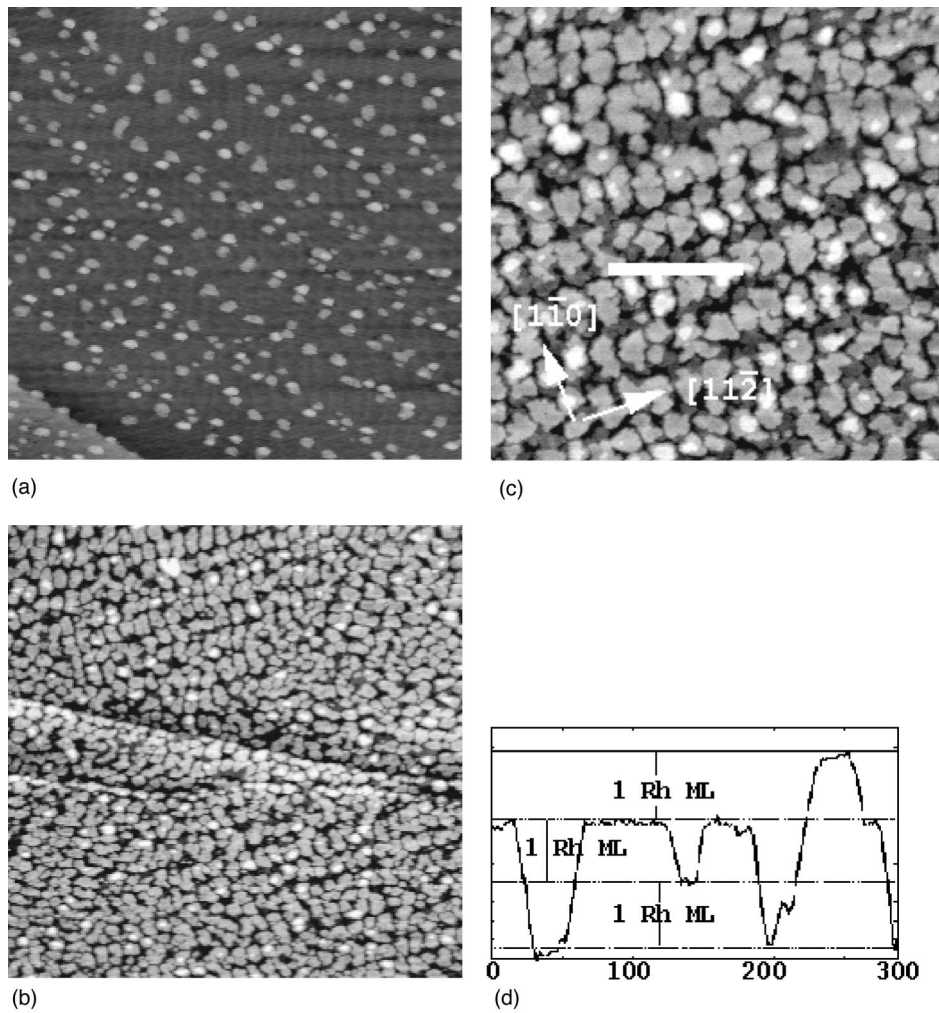


FIG. 2. STM images for Rh on Au(111) deposited at 300 K (a) 0.1 ML (100 nm \times 100 nm); (b) 0.8 ML (200 nm \times 200 nm); (c) 2.25 ML (100 nm \times 100 nm). (d) Line scan, drawn on (c) which confirms the presence of single, double, and third layer Rh islands (2.0 Å, 4.0 Å, and 6.0 Å, respectively).

correspond to Au atoms relocated from hollow sites. This configuration allows the release of surface stress and leads to point dislocations localized at the elbows of the zigzags. A rectangular network (75 Å \times 150 Å) of point dislocations is formed.

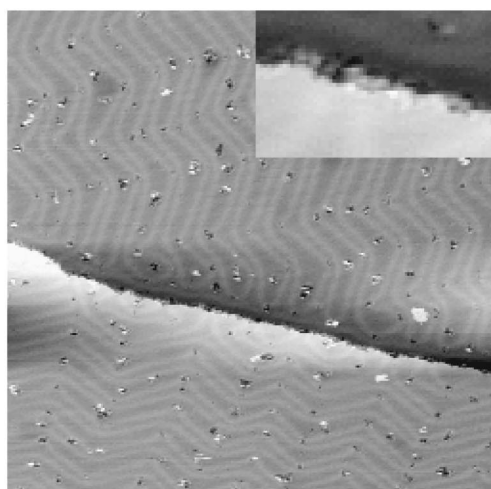
It is known that at RT, Rh atoms preferentially nucleate at the elbows of the Au(111) reconstruction to form clusters aligned in rows along the $[11\bar{2}]$ direction.¹⁵ This particular nucleation mode has been seen with many metal adsorbates such as Fe, Co, and Ni.^{21,22} It has been attributed to site-selective place exchange of incoming adatoms with gold surface atoms, followed by nucleation of clusters at the elbows.²² For RT growth, Altman *et al.*¹⁵ observed that Rh atoms have a tendency to form island pairs at the elbows. In the early growth stage (0.1 ML), some Rh clusters are monolayer high (2.20 Å) while others are bilayer high (4.40 Å) [see Fig. 2(a)]. Upon increasing the Rh coverage to 0.8 ML [Fig. 2(b)], Rh islands increase in size and some cluster pairs coalesce to form bigger clusters, all along the $[11\bar{2}]$ direction. Clusters which have grown between elbows begin to connect. Figure 2(c) shows the surface after deposition of 2.25 ML of Rh. The morphology at this coverage is similar to the 0.8 ML situation except that the third layer has started to grow while the first and second layers have not completely

coalesced. The line scan in Fig. 2(d), drawn in Fig. 2(c), clearly shows the situation since three levels of layers can be seen. The fact that RT grown Rh films are far from the perfectly flat continuous film considered in theoretical calculations^{5,6} may easily explain the lack of ferromagnetic order. As shown in Fig. 2(b), the 0.8 ML film consists in an assembly of large Rh clusters, containing more than 200 atoms, which is far too big for Rh clusters to be magnetic: only very small Rh clusters (10 to 30 atoms) have been predicted to be magnetic.²⁻⁴

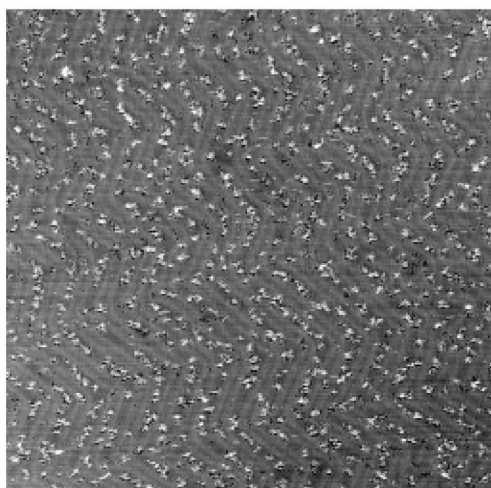
Since it is not possible to grow continuous Rh films at RT, we therefore considered low temperature deposition. As we have shown for Co on Au(111), the Co growth at low temperature (30 K) is not dictated by the gold reconstruction, but rather by the growth kinetics.¹⁸ Indeed, contrary to RT growth where Co forms bilayer clusters, the film is monolayer high at 30 K. Because of a similar self-organization of Co and Rh on Au(111) at RT, and their high surface energy compared to gold, one could expect the same behavior at low temperature for Rh.

STM measurements at 30 K and annealing to room temperature

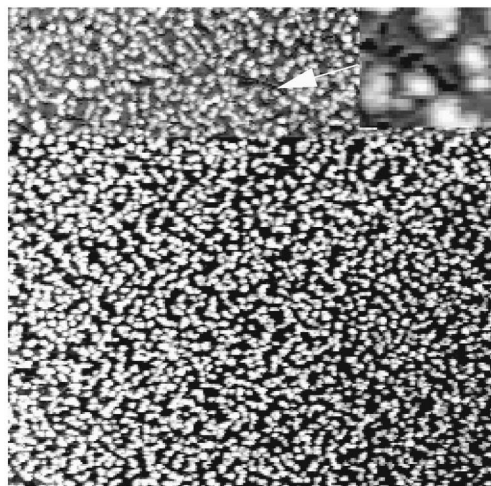
Figures 3–5 show the evolution of the morphology of different Rh coverages on Au(111) deposited at 30 K and



(a)

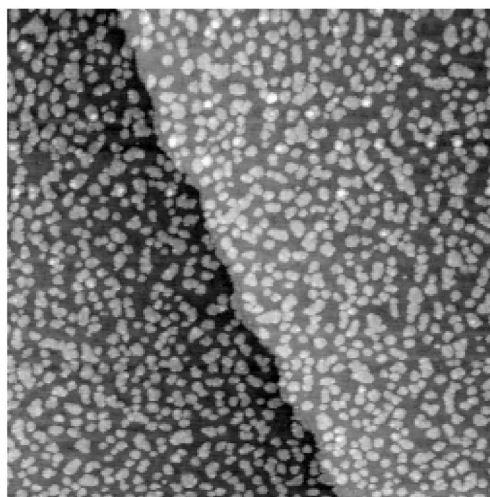


(b)

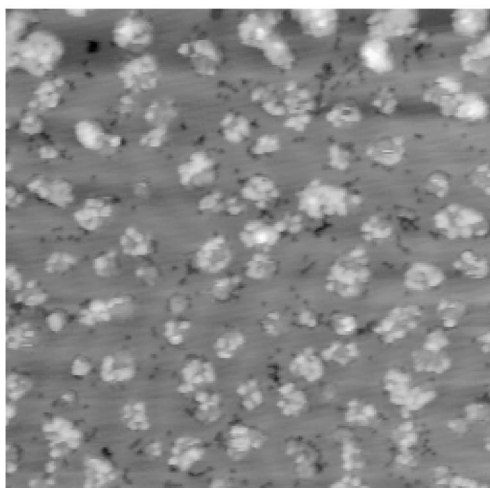


(c)

FIG. 3. STM images recorded at 200 K after deposition of Rh/Au(111) at 30 K (a) 0.006 ML [inset: zoom on the step edge (10 nm \times 6 nm)]; (b) 0.06 ML; (c) 0.2 ML [inset: zoom (6 nm \times 6 nm)]. All pictures are 100 nm \times 100 nm.



(a)



(b)

FIG. 4. STM images recorded at 300 K after annealing of 0.2 ML Rh/Au(111) previously deposited at 30 K. (a) (100 nm \times 100 nm); (b) zoom (30 nm \times 30 nm).

recorded for different annealing temperatures. Because of thermal drifts in the scan below 70 K, it was not possible to follow the evolution of the morphology of Rh films between the deposition temperature (30 K) and 70 K with the STM. However, from the Auger analysis, we do not observe drastic changes upon annealing from 30 K to 70 K. Moreover, between 100 K and 200 K, STM images show that the morphology of the surface has not changed for a given Rh coverage. Small changes are only noticed between 200 K and 300 K.

Figure 3(a) shows a STM picture for 0.006 ML Rh/Au(111) deposited at 30 K, recorded at 200 K. Small islands and depressions on the Au(111) surface are seen. Depressions appear at the elbows of the reconstruction, on the fcc and hcp domains and also at the Au step edges [Fig. 3(a)]. Notice that, contrary to the straight Au step edges observed on the bare Au(111) surface, or to the steps with Rh nucleation at RT [see Fig. 2(a)], the Au steps after Rh deposition at

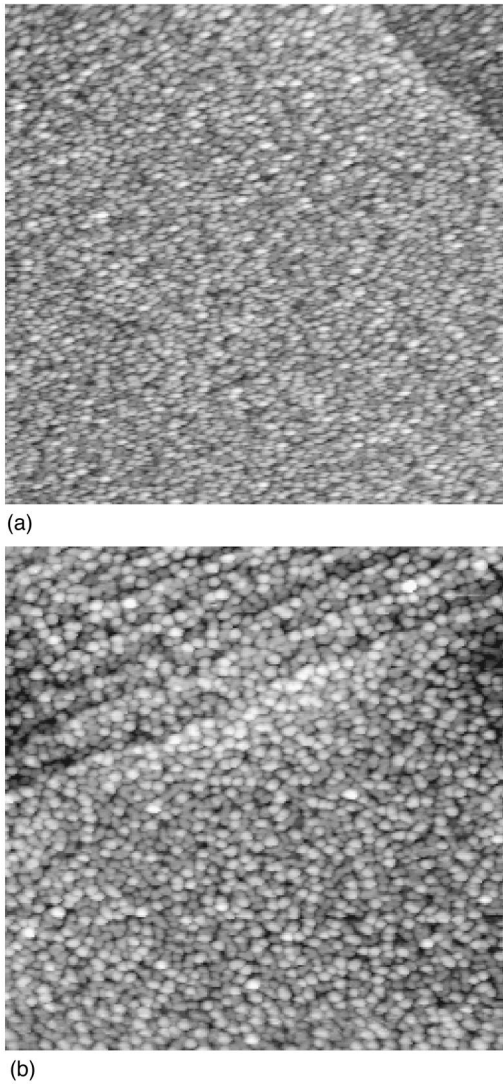


FIG. 5. STM images of 2.25 ML Rh/Au(111) at 30 K after annealing at (a) 200 K and (b) 300 K (100 nm \times 100 nm).

low temperature show rough edges [Fig. 3(a)]. Among the depressions and associated islands located far from the elbows, 54% and 20% of them are, respectively, localized in the fcc and hcp domains and 26% appear close to the domain walls of the reconstruction. These proportions remain unchanged for a Rh coverage ten times larger [Fig. 3(b)]. Since the 54/20 ratio corresponds roughly to the ratio of the surfaces of fcc and hcp domains, we conclude that there is no preferential nucleation on one particular domain type.

The analysis of the STM pictures for Rh submonolayer coverages shows that the height of the islands is $2.63 \pm 0.33 \text{ \AA}$ or $1.66 \pm 0.22 \text{ \AA}$. These values neither correspond to pure Rh(111) nor to Au(111) atomic steps (respectively 2.19 \AA and 2.35 \AA). This is in contrast with islands grown at RT where pure Rh clusters with the expected heights can clearly be identified. The depth of depressions varies from 0.91 \AA to 0.32 \AA . From the tests described in the experimental section it is unlikely that the depressions are a result of contamination. Because of the nonmonoatomic height of depressions and islands, we associate the contrast

within the islands and the depressions on the gold surface to changes in the local density of states due to, respectively, alloyed Rh-Au islands and substituted Rh atoms in the gold surface. Recent, first-principles simulations of the tunneling current, based on the perturbation approach, show that the chemical contrast in the STM images can be obtained on a surface alloy and is generally due to interplay between tip and sample.²³ Indeed, such electronic effects have already been noticed on several surface alloy systems, among them Rh/Au(111) (annealed at 400°C),¹⁵ Rh/Ag(100),²⁴ Ni/Ag(111),²⁵ Au/Ni(110),²⁶ and Co/Cu(100).²⁷

For a Rh coverage of 0.2 ML, recorded at 200 K [Fig. 3(c)], the Au surface is covered with a high density of randomly distributed islands about 1.2 nm in diameter. It must be stressed that for such small islands, an analysis of the STM images overestimates the coverage by as much as a factor two due to the convolution of tip and island shape.²⁸ The parts of the surface that are not covered with islands show small depressions [see inset in Fig. 3(c)]. Upon annealing to RT [Fig. 4(a)], the islands have slightly coalesced. On a smaller scale [Fig. 4(b)], it can be clearly seen that the gold reconstruction has partially disappeared and that clusters which appear on the surface are surrounded by depressions. For 2.25 ML, STM pictures taken, at 200 K show a nearly percolated Rh film [Fig. 5(a)]. Annealing at 300 K [Fig. 5(b)] produces a coalescence of the islands which have now a diameter of about 25 \AA . No further alloying has been observed, indicating that the Rh-Au surface alloy is confined at the interface between the Rh film and the Au substrate, in agreement with the AES results. Indeed, there is no evolution of the AES spectra upon annealing from 100 K to 300 K, for thicknesses between 0.2 and 4.25 ML (Fig. 6), except for a small carbon contamination (at 272 eV) due to electron beam exposure.

While exchanges can usually be activated at 300 K, it is quite surprising to see that these processes occur at low temperatures. This excludes a purely thermal origin of the phenomenon. As a matter of fact, site exchanges are possible in some systems when the transfer of energy from the heat of adsorption is important, in our case typically 4.5 eV, and the activation barrier for an exchange E_{act} is low. Such exchange processes are termed as nonthermal or “transient exchanges” in the literature.^{29–31} They have been observed previously on (100) fcc metal surfaces. Rhodium on Au(111) seems to show a quite high probability for such an effect; we estimate it to be of the order of 20–30% from the low temperature STM images. Adatoms undergo an exchange within a few picoseconds upon adsorption.³¹ If they miss this opportunity, they have no chance to do it again during their diffusion on the surface, since after thermalization with the substrate $kT \ll E_{\text{act}}$ ($kT = 0.0025 \text{ eV}$ at 30 K).

While site exchanges are possible, both at low and high substrate temperatures, the outcome of the experiment will be quite different. At low temperature (30 K), the mean free path of an atom is small so that an exchanged atom may act as a nucleation center for Rh or Au atoms diffusing nearby: a high density of small alloyed islands are formed on the surface [see Figs. 3(b) or 3(c)]. At room temperature (300 K) exchanges occur as well with approximately the same prob-

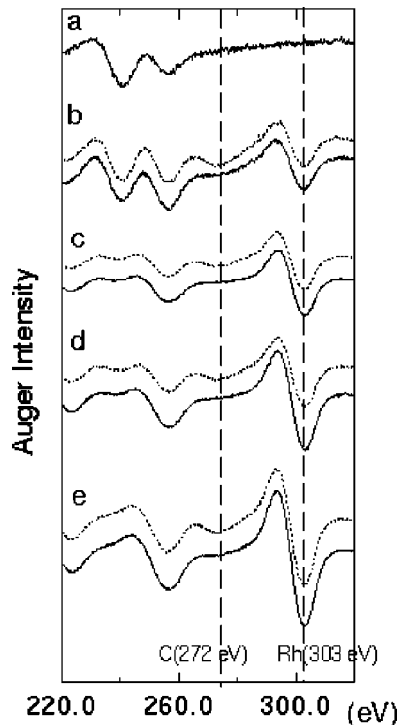


FIG. 6. Auger spectra (a) for clean Au(111) and Rh deposited at 30 K for (b) 0.2 ML, (c) 0.8 ML, (d) 2.25 ML, and (e) 4.25 ML. Solid and dotted lines show respectively spectra recorded at 100 K and 300 K.

ability. However, atoms that did not undergo an exchange continue diffusing, and travel a long distance in a short time (a few 10 ns) before they meet another atom or a defect. Therefore, diffusing Rh atoms mainly nucleate at the point dislocation of the zigzag reconstruction [Fig. 2(a)] since these sites are much more efficient for a room temperature activated exchange ($kT=0.025$ eV). The presence of few very small, randomly distributed, islands [Fig. 2(a)] confirms that some exchanged atoms may also occasionally act as nucleation centers.

The formation of a mixed first Rh-Au layer easily explains the absence of ferromagnetic order. Turek *et al.*¹⁷ have shown, by means of *ab initio* calculations on the example of Rh/Ag(100), that the formation of a surface-confined alloy of

Rh-Ag dramatically reduces the magnetism of Rh. The atomic disorder within the alloy induces a smearing and broadening of the local density of states which, in turn, produces an extinction of the ferromagnetic state. Since Ag and Au are isoelectronic, the same result should hold in the case of the Rh/Au system.

IV. CONCLUSION

The magnetism and the growth of Rh films (up to 6 ML) have been studied at 300 K and 30 K and after annealing to 300 K. Upon deposition of Rh on Au(111) at 300 K, STM images show that Rh self-organizes at the elbows of the gold reconstruction. By increasing the Rh coverage up to 0.8 ML, big Rh clusters are formed by coalescence along a $[11\bar{2}]$ direction and a three-dimensional growth starts. At 30 K, in the early stages of growth (0.006 ML), we observe the formation of depressions and protrusions attributed to a mixed Rh-Au interface layer, although these metals are known to be immiscible below 650 °C in the bulk.³² The mixing is confined to the very first monolayer. To our knowledge, the formation of a mixed interface at very low deposition temperature has not been observed before. Above 2 ML of Rh, a nearly layer by layer growth is observed. Annealing to RT does not significantly change the morphology of the films. This has been confirmed by AES. No ferromagnetism has been observed by Kerr effect measurements, irrespective of film thickness and growth conditions. This result disagrees with previous theoretical predictions, which is not to say that the predictions are wrong. We suggest that the Rh-Au intermixing is at the origin of the lack of the ferromagnetism of Rh films. Upon RT growth, Rh does not form a continuous and flat film, but more or less connected 3D clusters which are too big to be magnetic. However a superparamagnetic behavior cannot be excluded for very low coverages, where Rh clusters are composed of only several ten atoms.

ACKNOWLEDGMENTS

We would like to thank C. Demangeat, W. Hergert, V.S. Stepanyuk, and C. Massobrio for fruitful discussions. This work has been supported by the Centre National de la Recherche Scientifique (CNRS-ULTIMATECH program).

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